Exploring the nature of the interactions between the molecules of the sodium dodecyl sulfate and water in crystal phases and in the water/vacuum interface

Yosslen Araya, José G. Parra, Ricardo Paredes, Luis Javier Álvarez, Antonio Diaz-Barrios

1. Introduction

Studies on the molecular arrangement of surfactants at the vacuum-water interfaces [1, 2] have found the formation of molecular aggregates of surfactants at the interfacial region when they have relatively high concentrations of surfactants. Recently, molecular dynamic simulations of 8-phenyl hexadecane sulfonate, located at the n-tetradecane/water interface, have reported similar aggregation of surfactants at low concentration [2]. In that work, Paredes et al. concluded that the interface equilibrium time (several microseconds) is orders of magnitude greater than the obtained in other systems simulated. In fact, there was convincing indication that this slow equilibration process is due to surfactant aggregation at the interfacial region [2]. Therefore, the understanding of the nature of the aggregation in this type of molecules is fundamental and would have strong consequences on their simulation times. Specially, in the case of anionic surfactants, it is imperative to understand the influence of the characteristics of the head group on the molecular structure of these surfactants [1, 3]. Sodium Dodecyl Sulfate (SDS) is one of the most relevant anionic surfactants and it is widely used, as a model substance, in experimental studies and theoretical simulations...
in order to explain different surface and colloidal phenomena [4]. Many of these theoretical simulations have used SDS in monolayers, bilayers and micelles, where this surfactant is considered to be an ideal structural model [5, 6, 7, 8, 9, 10, 11, 12]. SDS surfactant have well-defined and characterized four crystal forms [13], an anhydrous form and three hydrates having the composition SDS.nH2O (n = 1/8, 1/2, 1), these systems crystallize with lamellar structures that present distinctive polar and nonpolar regions [13, 14, 15, 16, 17]. The SDS crystalline phases offer a unique opportunity to perform a detailed study of the interactions between the individual SDS molecules in the crystals using quantum mechanical calculations.

The Quantum Theory of Atoms in Molecules, QTAIM, in combination with Density Functional Theory, DFT, is a widely used tool to describe the nature of the chemical bonds [18, 19, 20, 21, 22, 23]. With the DFT methods is possible to determine the exact electron density $\rho(r)$ of molecular systems such as crystals, ions and molecules at their ground states. In contrast, the QTAIM tool allows to do a topological analysis of the electron density $\rho(r)$ in order to study the nature of the chemical bonds. In this case, with QTAIM is possible to determine the bond critical points, BCPs, locate the bond path that is formed between atomic nucleus and make a quantification of the bond strength [18, 21, 22, 23].

Recently, a localized-electrons detector (LED) function, which complement the QTAIM analysis has been presented [24, 25]. This function can be determined using the quantum mechanics local momentum representation as function of the electron density $\rho(r)$ [24, 26]. LED function allows to do a representation in three dimensions of the space in where electrons are localized [24, 26]. This LED function can display, in 3D, the various types of bonding interactions present in molecules and crystals, that can be obtained with the topological analysis of the QTAIM: the shared and the closed shell interactions [25, 27]. Generally, LED contour forms are used as detectors of the bonding interactions present and their values are a measure of the electron localization in a given volume [25, 26, 27].

QTAIM has been used to evaluate the crystals packing of organic molecules that have hydrocarbon chains. In fact, Matta et al. [28] demonstrated, by means of this theory, the existence of hydrogen-hydrogen interactions between the hydrogen atoms present in hydrocarbon chains, which can lead to a specific crystal packing. Generally, hydrogen-hydrogen interactions between the hydrogen pairs linked to carbon atoms are weak (homopolar interaction type). Matta et al [29] suggested that these interactions fall into the category of van der Waals interactions and this type of interactions occurs in hydrogen atoms linked to carbon atoms in both saturated and unsaturated hydrocarbon compounds.

In the present work, to further understand the nature of the interaction between the SDS surfactant molecules; the two crystal phases of SDS, anhydrous and with n = 1, have been studied in detail using the QTAIM and the LED function. It has been found that for the anhydrous crystal, the headgroups of the SDS molecules are linked in a head-to-head pattern, through a network of Na-O ionic bonds, where each Na atom is bonded to four SO4 groups. Each of this SO4 group occupies a volume of 66.864 Å³. For the hydrated crystal, the Na atoms are additionally linked to two H2O molecules by mean of Na-O ionic bonds. Each water molecule is in turn bonded to two SO4 groups via hydrobond bonds producing a general volume increase of 11 Å³ on the SO4 groups. These results corroborate that as consequence of hydration [13], the head group volume increases, which results in a growth of the polar interface that produces the separation of the hydrocarbon chains. The hydrogen-hydrogen interactions of the pairs of hydrogen linked to carbon atoms of the hydrocarbon chains were not considered in this work. Finally, the phenomenon of the aggregation of the SDS molecule at the liquid water/vacuum interface has been explored using a molecular dynamics simulation. It has been found that, like the crystalline phases, the surfactant molecules tend to form a head-to-head network pattern of ionic Na-O bonds linking their heads. The present results indicate that the clustering of anionic surfactant at the water/vacuum interface is a consequence of the electrostatic alignment of the cationic and anionic groups as it occurs in the crystalline phases of sodium dodecyl sulfate.

2. Quantum theory of atoms in molecules

The quantum theory of atoms in molecules, QTAIM [18, 19, 20, 21, 22, 23, 30], establishes a quantitative relation between the electron density function $\rho(r)$ (irrespective of how it attained, either from experiments or calculations) and the electronic properties of molecules or crystals. One of the main advantageous features of QTAIM is the provision of a rigorous quantum mechanics and topological definition of atoms [18, 19, 30]. In molecules and crystals, the topology of electron density function $\rho(r)$ is determined from the critical points (CPs) and gradient vector field, $\nabla\rho(r)$ [18, 30]. These CPs are defined by the behavior of gradient vector field, $\nabla\rho(r)$ (the collection of gradient paths vanishes) and are classified by the curvatures in the electron density function $\rho(r)$. For this, three eigenvalues $\lambda_i$ are necessary, which are associated to the Hessian matrix $(H_{ij} = \partial^2\rho(r)/\partial x_i\partial x_j)$. Based on these eigenvalues, the CPs in the electron density function $\rho(r)$ are of four types: minima, maxima and two types of saddle point. Here, the maxima $(3, -3)$ CP has eigenvalues $\lambda_1, \lambda_2$ and $\lambda_3 < 0$, the minima $(3, +3)$ CP corresponds to eigenvalues $\lambda_1, \lambda_2$ and $\lambda_3 > 0$. Finally, saddle points $(3, +1)$ CP and $(3, -1)$ CP have eigenvalues $\lambda_1 > 0, \lambda_2 > 0$ and $\lambda_3 < 0$ and $\lambda_1 < 0, \lambda_2 < 0$ and $\lambda_3 > 0$, respectively. Every CP has a collection of trajectories or gradient paths associated to the electron density function $\rho(r)$. These trajectories have their origin and end at critical points. The $(3, -3)$ CPs correspond to the maxima of the density function $\rho(r)$. In general, these maxima CPs are present at the nuclear positions. Here, each nucleus is an attractor for a collection of gradient paths in the $\nabla\rho(r)$. The region generated by the gradient paths which terminate at a given attractor, defines the basin of the nuclear positions [18]. At the same time, the critical link point, BCP, lies between two adjoining nuclei. This BCP corresponds to a saddle point called $(3, -1)$ CP. This $(3, -1)$ CP is a saddle point of the electron density function $\rho(r)$ that have the maxima in two directions and minimum in the other [18]. This saddle point is a 2D-attractor and 1D-source in the respective directions. Furthermore, the QTAIM analysis generates the interatomic surfaces, IAS, which are defined by the gradient paths involved with the negative eigenvalue of the $(3, -1)$ CP. These IAS divide the molecules in the volume region called atomic basins. The negative eigenvalues (negative curvatures) of density function $\rho(r)$ in a $(3, -1)$ CP, $\rho_{ib}$, are associated with the perpendicular contraction of electron density function $\rho(r)$, that produces a contraction of charge toward $(3, -1)$ CP [18]. Additionally, there is a unique pair of trajectories involved with the positive eigenvalue of $(3, -1)$ CP that originates at this point and ends at the two nucleus attractors. These two gradient routes characterize a line connecting the nuclei, which are called bond paths. Along this bond path, the charge density is a minimum at $(3, -1)$ CP. Therefore, the charge is completely reduced at $(3, -1)$ CP with respect to neighboring nuclei points on the bond path. In addition, the rest of CPs are associated to the geometrical arrangements of bond paths [18], which describe rings and cages elements present in the structure of molecules and crystals. The $(3, +1)$ CP is present in the interior of the ring when the bond paths are linked forming a ring of bonded atoms. Finally, the $(3, +3)$ CPs are called cage critical points. This type of CPs located in the interior of a cage nuclear arrangement. In a $(3, +3)$ CP, the charge density is a local minimum [20, 27] and in crystals, trajectories of $\nabla\rho(r)$ have its origin at such CPs and terminate at nuclei, bond or ring CPs.

3. The localized electrons detector, LED, function

In quantum theory an observable $A$ can be separated into two fundamental terms: a real portion $A(r)$ (the local value) and an imagi-
The real part is associated with the classical approximation of the observable \( A \), while the imaginary part describes the quantum variation of this observable \( A \):

\[
A(r) = i \lambda A'(r) + i \hbar \frac{\partial}{\partial r}
\]

[1]

For the momentum operator \( \hat{P} = i \hbar \nabla \), the term representing the local momentum \( P(r) \) [24] is defined by the Eq. (2):

\[
P(r) = \hat{P}(r) = \hat{P}(r) - i \hbar \frac{\nabla}{\partial r}
\]

[2]

Therefore, the term \( \hat{P} \) called quantum variation is proportional to the relation \( \nabla \rho(r)/\rho(r) \). The term \( P \) is a direct spatial representation of the volume of the orbital-free of localized electron pairs in atoms and molecules [25, 26]. The density of the kinetic energy of the particle is used to determine the localization of the electron pairs in molecular systems, and hence their momentum \( P \) is an ideal localized electron pair detector [24], which is defined in terms of the electron density and its gradient in Eq. (3) [24, 25, 26].

\[
\text{LED} = \left[ \nabla \rho(r)/\rho(r) \right] = -\hbar \frac{\nabla}{\partial r} \rho(r) / \rho(r)
\]

[3]

The values of \( \hat{P} \) represent the regions where electron pairs are spatially localized, producing bonding regions and regions with atomic shells [24, 25]. Furthermore, with the term \( \hat{P} \) is possible to make a direct spatial representation of bonding interactions in the molecules. The isosurfaces obtained with LED show the same type of symmetries around the BCPs that the given by the Laplacian of \( \rho(r) \) [24, 25]. In this sense, LED shows the diverse types of bonding interactions (closed shell and shared interactions) that are obtained with the analysis of the topology of electron density function \( \rho(r) \). This LED determines the local amounts of electrons in spatial regions around the \( \rho(r) \) critical points [26, 27]. For the (3,3) CPs that are nuclear attractors (three negative curvatures) of the \( \rho(r) \) gradient field, the LED isosurfaces indicate a high local charge concentration of \( \rho(r) \) on the inner core shells electrons. In contrast, for the (3, -1) CP that have 2D attractor (two negative curvatures that are perpendicular to the bond of \( \nabla \rho(r) \)), the LED isosurface represents the local charge concentration in the bonding zones around the BCPs. The spatial forms of LED contours around these critical points are related to the \( \rho(r) \) curvatures [24, 25, 26]. Therefore, for a chemical bond of covalent type formed between two atoms, \( |\lambda_3| < |\lambda_1| \cong |\lambda_2| \), the LED isosurfaces have a cylindrical spatial form, where the main axis is aligned with the bond path. In contrast, a chemical bond with closed shell, where the ionic contribution is the most important, \( |\lambda_3| > |\lambda_1| \cong |\lambda_2| \), the LED isosurfaces are disks shaped perpendicular to the bond paths [24]. In general, the spatial forms of the LED isosurfaces are used to evaluate the type of interaction and their values represent a measure of the electron localization in a spatial region of the molecule [24, 26].

4. Method of calculations

Anhydrous SDS (Na\(^+\).C\(_{12}\)H\(_{25}\)O\(_4\)S) have a monoclinic crystal structure with space group P2\(_1\)/c [14]. The unit cell dimensions are \( a = 38.915\text{Å} \); \( b = 4.709\text{Å} \); \( c = 8.198\text{Å} \) and \( \beta = 93.29^\circ \) and the asymmetric unit is formed by a single SDS molecule (See Figure 1a). The crystal packing consists of double layers of molecules (Fig. 1b). On the other hand, Na\(^+\).C\(_{12}\)H\(_{25}\)O\(_4\)S .H\(_2\)O, is triclinic, space group \( \text{P1} \); \( a = 10.423\text{Å} \); \( b = 5.662\text{Å} \); \( c = 28.913\text{Å} \); \( \alpha = 86.70^\circ \); \( \beta = 93.44^\circ \); \( \gamma = 89.55^\circ \) [16]. Each asymmetric unit is built with two waters and two sodium dodecyl sulfate (SDS) molecules with different spatial conformations (See Figure 2a). The SDS molecules have a lamellar array with alternately polar and nonpolar regions. The adjacent polar heads of the same monolayer are displaced in a zigzag fashion along an axis forming a rippled structure (See Figure 2b) [16].

The optimization of the geometries that are present in the cell units was carried out with the DFT methods contained in ADF software [31, 32, 35]. For each system the electron density function \( \rho(r) \) was determined using the Kohn-Sham method with the gradient-corrected Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [34]. The ADF software calculates variational self-consistent solutions for the DFT methods using a highly optimized numerical integration scheme for the estimation of matrix elements associated to the Fock operator [31, 32]. The Coulomb potential is determined using the charge density by means of an accurate fitting [31]. In this paper, the triple-zeta plus polarization basis set (TZP) [35] was used in all calculations. These simulations

![Figure 1](image-url)

**Figure 1.** (a) Unit cell of the anhydrous SDS crystal. The white, gray, yellow, red and purple spheres denote the H, C, S, O and Na atoms, respectively. (b) Lamellar structure defined for the anhydrous SDS bulk. The distance tail-tail between the layers measured as the H...H distance is 2.016 Å. Three lamellas are shown in the picture.
determine the molecular electron densities, which are used to carry out the QTAIM analysis and the evaluation of the LED functions of the studied systems [27]. The topology of the electron density function \( \rho(r) \) for QTAIM analysis was performed with the method described in the reference 36, using the AIM-UC software [36]. The LED function and the LED isosurfaces were determined with a modified version of the MC33 software, which is described in the references 37 and 38 [37, 38].

5. Results

5.1. SDS molecule

An isolated SDS molecule was built from the Anhydrous SDS unit cell and subsequently optimized using standard ADF methods. For this geometry, all the CPs were located and the topological properties (electron density, \( \rho_b \), the curvatures \( \lambda_i \) and the Laplacian, \( \nabla^2 \rho_b \)) that characterize the head bond critical points are shown in Table 1. The bond paths network (the molecular graph) [18] defining this geometry are shown in Figure 3. Gray, red, yellow and pink denote the C, O, S, and Na atoms, respectively.

The data provided in Table 1, shows that, the C–C BCPs have characteristics associated with covalent type interactions: large \( \rho_b \) value, absolute value of \( \lambda_1 = \lambda_3 > 1 \) and \( \nabla^2 \rho_b < 0 \). All the molecule head bonds show the usual characteristic of polar type interactions, i.e., \( \lambda_1 / \lambda_3 < 1 \). The C–O and S–O bonds show covalent-polar features: \( \lambda_1 / \lambda_3 < 1 \) and \( \nabla^2 \rho_b < 0 \) while the S=O bonds show characteristics of very covalent-polar interactions: large \( \rho_b \) value, of \( \lambda_1 / \lambda_3 < 1 \) and \( \nabla^2 \rho_b > 0 \). The Na–O bonds present close-shell type interactions, with are typical characteristics of ionic bonds such as Na–Cl (\( \rho_b = 0.242 \text{ e}/\text{Å}^3 \)) [20]: very small

| Bond | \( \rho_b \) e/Å\(^3\) | \( \lambda_1 \) | \( \lambda_2 \) | \( \lambda_3 \) | \( |\lambda_1| / |\lambda_3| \) | \( \nabla^2 \rho_b \) e/Å\(^5\) |
|------|-----------------|------------|------------|------------|----------------|----------------|
| C–C  | 1.658           | -11.422    | -10.840    | 9.173      | 1.245          | -13.089        |
| C–O  | 1.486           | -9.159     | -9.107     | 9.493      | 0.965          | -8.773         |
| S–O  | 2.076           | -12.947    | -12.428    | 36.370     | 0.356          | 10.995         |
| S–O  | 2.132           | -14.457    | -14.024    | 41.463     | 0.355          | 12.482         |
| Na–O | 0.169           | -0.747     | -0.634     | 4.816      | 0.155          | 3.435          |
| Na–O | 0.117           | -0.450     | -0.193     | 2.950      | 0.153          | 2.307          |

Figure 2. (a) Unit cell of the SDS.1H2O crystal. The white, gray, yellow, red and purple spheres denote the H, C, S, O and Na atoms, respectively. (b) Lamellar structure defined for the hydrated SDS bulk. Three lamellae are shown in the picture. A higher lamellae separation than the case of the anhydrous lamellar structure can be observed (compare with Figure 1b).

Table 1. Bond Critical points properties of \( \rho(r) \) for the SDS molecule: electron density, \( \rho_b \), curvatures \( \lambda_i \) I=1,2 and \( j = 3 \) are the negative and positive curvatures perpendiculars and parallel to the bonds, respectively; and the Laplacian, \( \nabla^2 \rho_b \) at the BCP.
Figure 3. Molecular graph of the SDS isolated molecule. The gray, white, red, yellow and purple spheres denote the C, H, O, S and Na atoms, respectively. Small gray spheres indicate the bond critical points.

Figure 4. LED isosurfaces for the SDS molecule. (a) LED value of 1.5 au (yellow), containing the core electrons of the C, S and Na atoms while the blue isosurfaces correspond to LED = 0.5 au. These blue areas mainly involve the electron density around the BCPs. The red and white balls represent the O and H atoms, respectively. (b) LED = 1.5 au isosurfaces which encloses the inner core of the heavy atoms. (c) LED = 1.2 au isosurfaces showing that for each oxygen atoms a bell-shaped form around the lone pair electrons appeared. (d) LED = 1.0 au and (e) LED = 0.6 au shows the depicted isosurfaces for the C–H bonds. (f) LED = 0.5 isosurfaces let anyone to visualize and explore the nature of all bonds.
$\rho_b$ value and the $\lambda_3$ curvature dominates ($\lambda_1/\lambda_3 < 1$), consequently $\nabla^2\rho_b > 0$. In general, the $\lambda_1/\lambda_3$ value gives the bond nature trends: the ionic character of a bond increases as the $\lambda_1/\lambda_3$ value decreases. Thus, the ionic trend for the SDS molecule bonds is $C–C$ (1.245) $<$ $C–O$ (0.965) $<$ $S–O$ (0.559) $<$ $S–O$ (0.324) $<$ Na–O (0.153).

The nature of these bonds can be easily and directly visualized using the LED function [25, 27]. Thus, Figure 4 shows several LED isosurfaces for SDS. Figure 4a shows regions enclosed by yellow spherical isosurfaces with a LED value of 1.5 au and blue zones corresponding to LED = 0.5 au. The yellow zones that contain the core electrons of the C, S, O and Na...
atoms. The blue areas mainly involve the electron density around the BCPs. The shape of the LED contours around the bond critical points are closely related to the $\rho(r)$ curvatures [25]. For the C–C bonds of the tail, which are typical covalent bond, $|\lambda_3| < |\lambda_1| \approx |\lambda_2|$ and the associated LED isosurface has a perfect cylindrical shape filling the bond zones [25]. For the covalent-polar type bond, C–O, S–O and S–O, $|\lambda_3| > |\lambda_1| \approx |\lambda_2|$ and the LED isosurface corresponds to bent disks perpendicular to the bond paths. These disks are curved towards the least electronegativity atom and fill only part of the bond area. For the Na–O bonds which are pure closed-shell interaction, the LED isosurface around the BCP appears as a very thin region (See Figure 4f) leaving the bond area almost empty.

To better understand the LED function, in Figs. 4b to 4f are shown the different depicted spatial regions of interest for the SDS molecule in the range of 1.5 to 0.5 au. Thus, Figure 4b displays the LED $\rho_e = 1.5$ au isosurfaces which enclose the inner core of the heavy atoms. These zones contain inside all the electron density corresponding the Na, S, C and O core. Spherical contours of LED $\rho_e = 1.2, 1.6, 6$ and 8 au values (equal to the atomic number and not shown in Figure) denote the limiting regions of the respective atom core. At LED $\rho_e = 1.2$ (See Figure 4c) appears, at the non-bonded zones of each oxygen atoms, a bell-shaped form around the lone pair electrons. These O lone-pair zones persist in the range of $1.0 < \rho_e < 1.5$ au. A curved banana-shape forms that characterize the C–H covalent regions appear at LED $\rho_e = 1.0$ au (Figure 4d) and change to a bell-shaped form (Figure 4e) with the top of the bell toward the hydrogen nucleus as the LED value decreases. These forms persist fused to the C atom in the range of $0.6 < \rho_e < 1.0$ au. At LED $\rho_e = 0.6$ au (Figure 4e) the oxygen lone pairs have disappeared and bonded areas around the bonds between the S and O atoms appeared. In addition, the thin disk around...
the Na–O bond can be equally visualized. Finally, at LED = 0.5 au (Figure 4f) all the areas around the BCPs are depicting. Therefore, these LED = 0.5 isosurfaces provide an appropriate tool to explore the nature of the molecule bonds.

6. Anhydrous SDS crystal

For the optimized cell unit geometry of the anhydrous SDS crystal, all the CPs were also located and the topological properties that characterize the head bond critical points are listed in Table 2. Comparison of Tables 2 and 1 show that, in general, the topological properties and nature of the bonds of the individual molecules, that make up the crystal, are similar to the isolated molecules. Interestingly, for each Na atoms, three of the Na–O bonds exhibit topological values (0.188–0.137 e/Å³) like the isolated molecules (0.169–0.117 e/Å³). One of these bonds shows a much lower value (0.086), which is almost half of the other Na–O bonds. Each Na atom has three nearest SO₄ groups and another one farther away. Overall, the ionic character of the bonds increases as the λ₁/λ₃ value decreases. The crystal graph (bond paths network) defining the anhydrous SDS geometry is shown in Figure 5. This graph shows that each Na atoms is bonded to four O atoms by BCPs (black spheres in Figure 5a), forming a bond paths network (yellow lines in Figure 5b) of ionic bonds (Na–O) that link the SO₄ groups (green lines in Figure 5b). Each Na atom is bonded to four O atoms, one by SO₄ group.

The basin of the Na atoms (purple zones) are shown in Figure 6. The atomic properties in QTAIM are determined by integration of the corresponding property over these basins; where each basin is defined by the set of IASs (Interatomic surfaces) that define the atom [18]. In the present work, the atomic charge and volume for the SDS-head atoms were calculated using the method proposed by Yu et al. [39], implemented and improved in AIMUC-1.5. The obtained results are listed in Table 3 and show that each Na atoms has a charge of +0.895e and a volume of 8.544 Å³; while the SO₄ shows a charge of -1.375 e and a volume of 66.864 Å³. Additionally, Figure 6 also shows the isosurfaces depicted by the LED = 0.5 au value. Same to the SDS molecule, for the covalent C–C bonds of the tail, the LED contour has a perfect cylindrical shape filling the bond values.

Figure 7. Crystal graph for the unit cell of a layer of the H₂₅C₁₂–SO₄ Na.1H₂O system. (a) Side-view on the unit cell. Gray, white, yellow and pink balls denote the C, H, S, and Na atoms, respectively. Red and orange spheres denote the oxygen atoms of the SO₄ groups and the water molecules, respectively. Green lines denote the S–O bonds. White arrows highlight the H₂O molecules. Light blue lines denote the H–O water bonds. Pink lines denote the hydrogen bonds between the water molecules and the O atoms of the SO₄ groups. A white ellipse highlights the fact the water molecules form a kind of casing around the surfactant head. (b) Top-view showing the basin of the Na (pink area) and the O atoms (orange area) of the water molecules surrounding the Na atoms.
zones. For the covalent-polar C–O, S–O and S=O bonds, the LED contours
correspond to bent disks, that only fill up part of the bond area; while for
the ionic Na–O bonds, the LED isosurfaces around the BCP appear as a
very thin region leaving almost empty the bond area.

The topological properties that characterize the head bond critical
points of the hydrated crystal with one water molecule by unit cell, are
listed in Table 4. In general, the values of \( \rho(\rho) \) at the Na–O bonds, even for
the Na–\( \text{H}_2\text{O} \) bonds, are in a range of 0.096–0.154 au; while the SIO–H\( _2\)O
hydrogen bonds show a much higher value (0.320 au). This \( \rho_b \) and \( \lambda_1/\lambda_3 \) values show that those hydrogen bonds have a higher covalent character
than the Na–O bonds. Generally, same to the ionic bonds, the hydrogen
bonds exhibit closed shell character [18]. The molecular graph
defining this geometry is shown in Figure 7. Gray, white, yellow and
purple balls denote the C, H, S, and Na atoms, respectively. The red and
orange spheres denote the oxygen atoms of the SO\( _4 \) groups and the water
molecules, respectively. This graph shows that each Na atoms is bonded
to four O atoms on the SO\( _4 \) groups and two O on the water molecules,
forming a bond paths network (yellow lines) of ionic bonds (Na–O) that
link the Na atoms with the H\( _2\)C\( 12 \)-SO\( _4 \) chains and the H\( _2\)O molecules.

The water molecules (light blue lines) are bonded by mean of hydrogen
bonds (pink lines) to SO\( _4 \) groups. Table 5 displays the atomic charge and
volume of the atoms that make up the SDS head. Comparing with Table 4,
it is evident that the water molecules induce a volume increase in the
SO\( _4 \) groups from 66.864 \AA\(^3\) in the anhydrous crystal to 77.898 \AA\(^3\), when
just one molecule is inserted in that crystal unit cell. When adding the
volume of two water molecules, the resulting SO\( _4 \)-2H\( _2\)O groups volume
is about 131.898 \AA\(^3\). It is clear that H\( _2\)O molecules contribute to separate
the surfactant layers. Summarizing, the present quantum calculations
show that the SDS molecules are linked in a head-to-head pattern by a
bond path network of Na–O ionic bonds. For the anhydrous crystal, each
Na atom is bonded to four SO\( _4 \) group, occupying a volume of 66.864 \AA\(^3\).
For the hydrated crystal, each H\( _2\)O molecule is bonded to two SO\( _4 \) groups
via hydrogen bonds producing a general volume increase of 11 \AA\(^3\) in the
SO\( _4 \) groups. These results corroborate that, as consequence of hydration,
the head group volume (the sulfate group and associated sodium ions and
water) increases, which results in an expansion of the polar interface that
produces the separation of the hydrocarbon chains.

Table 5. \( \text{H}_2\text{C}_{12}-\text{SO}_4 \) Na.H\( _2\)O crystal atomic charges and volume (\AA\(^3\)).

| Atom | Group | Atomic Charge | Atomic Volume |
|------|-------|---------------|---------------|
| Na   |       | +0.896        | 8.865         |
| Na   |       | +0.887        | 8.742         |
| Na   |       | +0.886        | 8.742         |
| Na   |       | +0.894        | 8.865         |
| S    |       | +3.564        | 5.444         |
| O    |       | -1.369        | 17.950        |
| O    |       | -1.285        | 18.031        |
| O    |       | -1.298        | 20.250        |
| O    |       | -1.046        | 16.223        |
| SO\( _4 \) | | -1.358 | 77.898 |
| S    |       | +3.532        | 5.391         |
| O    |       | -1.311        | 16.699        |
| O    |       | -1.300        | 17.473        |
| O    |       | -1.283        | 17.644        |
| O    |       | -1.044        | 13.461        |
| SO\( _4 \) | | -1.103 | 20.587 |
| H    |       | +0.593        | 2.495         |
| H    |       | +0.472        | 3.918         |
| H    |       | +0.540        | 4.485         |
| H\( _2\)O | | -0.014 | 27.581 |

7. Molecular dynamics simulations of the SDS molecules
adsorption at the water/vacuum interface

Finally, we have explored the phenomenon of aggregation of the SDS
molecules at the water/vacuum interface using Molecular-Dynamics, MD,
the Compass force field and a NVT (composition, volume and tempera-
ture constants) ensemble. The Forcite software [40] with the Compass
force field [41] for the MD simulations was used. Initially, an ortho-
rhombic simulation box with dimension of 24 \AA\( \times 24 \AA \times 110 \AA \) con-
taining the water/vacuum interfaces with 900 water molecules was
build. The water phase was prepared separately using the Amorphous
Builder software [42] to create an initial random and 1.0 g/cm\(^3\) density
sample using a suitable Monte Carlo procedure, to achieve a right dis-
tribution of the conformational states. After that, this phase was inte-
grated into the simulation box. Then, a monolayer of 14 SDS molecules in
a hexagonal arrangement with the hydrophilic head pointing toward
water was placed in the simulation box (Figure 8 shows the initial
conformation). Two sets, one for the water phase and one for the SDS
molecules were defined. The next step was an energy minimization to
relax the system. Finally, an NVT simulation of 8 ns at 300K was carried
out. The Trajectory analysis gives a final average of the binding energy,
BE, between the water phase and the SDS monolayer of -3358.797
Kcal/mol with electrostatic and vdW contributions of -3306.616 and
48.501 kcal/mol, respectively.

Figures 9a and 9b show a snapshot of the final configuration. Figure 9a
shows the cross-sectional view perpendicular to the plane of the
interface. This picture clearly illustrates the formation of SDS

Figure 8. Simulation box showing the initial conformation of the water phase and the SDS monolayer. Red, white, gray, yellow and pink spheres denote the O, H, C, S, and Na atoms, respectively.
aggregates at the water/vacuum interface. Figures 9b and 9d show the top-view for just the SDS-aggregates heads at the monolayer formed at the water/vacuum interface.

Interestingly, these top-view shows that these SDS aggregates tend to form a kind of structures that resemble those of the crystalline states, where the water molecules and, the Na$^+$ atoms and SO$_3$/C$_{10}$ groups of the SDS heads are electrostatically bonded (See Figure 7). Comparable results, where the formed clusters at the water/vacuum interface tend to be linear, aligning phenyl-SO$_3$ groups and Na$^+$ atoms, were reported in ref. 2.

To better understand the nature of this aggregation, Figure 10 shows the bond path network of the hydrated crystal and the last configuration snapshot for the 14 SDS molecules adsorbed at the water/vacuum interface. Figure 10a shows the side-view of the bond paths graph of the surfactant heads of a 2 $\times$ 1 unit cell of this crystal. For clarity, the tails are removed and only the bond pattern of the SDS heads is shown.

![Image](a) Snapshot of the side-view of the simulation box showing the last configuration of the SDS molecules at the water/vacuum interface. A white circle highlights just one formed aggregate. (b) Snapshot showing the top-view of the simulation box. A white oval highlights the fact that the SDS heads show the tendency to organize themselves along a line. (c) Top-view of the monolayer formed by 14 SDS molecules heads at the water/vacuum interface at 2 ns and (d) at 8 ns of NVT simulation. For clarity in (c) and (d) the aliphatic chains have been removed. A white square highlights the fact that the Na-SO$_4$ groups tend to form linear structures.

Figure 9.
this graph, each Na⁺ atom (purple spheres) is bonded to four SO₄ groups (yellow lines) and two molecules of H₂O (white lines). Note that for one SO₄ group (top-right of the picture), the O atom (highlighted with a yellow arrow), coordinated to the C₁₂ tail, is linked by hydrogen bonds (green lines) to two H₂O molecules, while that of the other three O atoms, no coordinated to the surfactant tail, is shared with its nearest two Na atoms. This SO₄ group is linked to four Na⁺ atoms. For the other SO₄ group (locate at the left-top of the picture), only one O atom is shared with two Na atoms, while two other O ones are linked by H-bonds to two H₂O molecules. This SO₄ group is linked to two Na⁺ atoms. This obtained pattern is repeated along the network of Na-O-S bonds.

A similar view of the bond pattern for the aggregates highlighted in Figure 9b (inside the white oval) forming the surfactant monolayer at the water/vacuum interface, is shown in Figure 10b. Dark blue spheres denote the O atom of the SO₄ groups where the surfactant tails are bonded. These hydrocarbon chains are just at the vacuum and above the picture plane. Using the Material Studio software [43], the 14 SDS molecules inside the simulation box were selected and then the water molecules located around the Na atoms (underlined with light blue spheres) in a radius less than 2.3 Å were additionally selected. The electronic density and QTAIM analysis of the final cluster were calculated using the methodology described in the Method of Calculations Section. It can be seen the Na⁺ ions are linked to a maximum of three SO₄ groups by mean of ionic Na-O bonds (highlighted with yellow lines) and three water molecules. Contrary to the hydrated crystal, each of the O atoms forming these Na-O bonds is linked just only to one Na⁺ ion. Despite these differences, like the crystal phases, the surfactant molecules tend to form a head-to-head network pattern of ionic Na-O bonds linking their heads. Therefore, the present results suggest that the clustering of anionic surfactant at the water/vacuum interface is a consequence of the electrostatic alignment of the cationic and anionic groups such as it happens in the crystalline phases of SDS.

8. Summary and conclusions

The nature of the interaction between the SDS surfactant chains of the two crystal phases of SDS, anhydrous: NaC₁₂H₂₅O₄S and hydrated: NaC₁₂H₂₀O₄S·H₂O, with one water molecule for unit cell, have been studied in detail using the quantum theory of atoms in molecules and the LED function. It was found that for the anhydrous crystal, the head groups of the SDS molecules are linked into a head-to-head pattern, through a bond path network of Na-O ionic bonds, where each Na⁺ atom is bonded to four SO₄ groups. The nature of the bond between the SDS molecules was analyzed using the LED function. This analysis has shown that for the covalent C-C bonds of the tail, the LED isosurfaces have a perfect cylindrical shape that fills the bond zones. For the covalent-polar C-O, S-O and S=O bonds, the LED surfaces correspond to bent disks that only fill up part of the bond area; while for the ionic Na-O bonds, the LED isosurfaces around the BCP appear as a very thin region that leaves the bond area almost empty. For the hydrated crystal, each Na atoms is bonded to four O atoms and two O on the water molecules, forming a bond path network of ionic Na-O bonds that link the Na atom with the H₂₅C₁₂-SO₄ groups and the H₂O molecules. Each H₂O molecule is bonded to two SO₄ groups through hydrogen bonds producing a general volume increase of 11 Å³ in the SO₄ groups. These results corroborate that, as consequence of hydration, the volume of the head group increases, which results in an expansion of the polar interface that produces the separation of the hydrophobic chains.

The phenomenon of aggregation of the SDS molecule at the water/vacuum interface was also studied using NVT molecular dynamics simulations. We have found that the clustering of anionic surfactant at the water/vacuum interface is a consequence of the electrostatic alignment of the cationic and anionic groups such as those formed in the SDS crystal phases.

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