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Exploring the effect of the \(O-(1\text{-heptylnonyl})\) benzene sulfonate surfactant on the nature of the linear hydrocarbons/water interface by means of an atomistic molecular dynamics simulation

Yosslen Aray\textsuperscript{a,b,d,*,} José Gregorio Parra\textsuperscript{c}, Doris Marianela Jiménez\textsuperscript{a}, Ricardo Paredes\textsuperscript{e}, Alejandro Martíz\textsuperscript{d}, Samantha Samaniego\textsuperscript{f}, Mauricio Conejo\textsuperscript{g}, Eduardo V. Ludena\textsuperscript{c,d} and Cecilia Paredes\textsuperscript{d}

\textsuperscript{a}Laboratorio de Físicoquímica Teórica de Materiales, Centro de Química, Instituto Venezolano de Investigaciones Científicas, IVIC, Caracas, Venezuela

\textsuperscript{b}Facultad de Ciencias, Universidad de Ciencias Aplicadas y Ambientales, UDCA, Campus Universitario Norte, Bogotá, Colombia

\textsuperscript{c}Laboratorio de Química Computacional, Dpto. de Química, Facultad Experimental de Ciencias y Tecnología, Universidad de Carabobo, Edo. Carabobo, Venezuela

\textsuperscript{d}Facultad de Ingeniería Mecánica y Ciencias de la Producción, Escuela Superior Politécnica del Litoral, ESPOL, Guayaquil, Ecuador

\textsuperscript{e}Facultad de Ingeniería en Ciencias de la Tierra, ESPOL, Campus Gustavo Galindo, Guayaquil, Ecuador

\textsuperscript{f}Departamento de Física, Facultad de Ciencias Naturales y Matemática, ESPOL, Campus Gustavo Galindo, Guayaquil, Ecuador

\textbf{Abstract}. Using molecular dynamics simulations a systematic study of the binding energy per cross sectional area for the water/n-alkane (hexane, octane, decane, dodecane and tetradecane) interfaces was performed. The effect of the Sodium p-(1-heptylnonyl) benzene sulfonate surfactant, on the adhesion forces of the water/n-hydrocarbon (decane, undecane, dodecane, and tetradecane) interfaces was studied. Scanning of the binding energy per area against n-alkanes shows that the magnitude of this parameter for the surfactant tail-alkane interactions at the interface systematically increases with the chain length of the alkane, whereas it shows a maximum at undecane for the water-surfactant head interactions at the interface. This maximum of head adhesion forces thus agrees with the reported minimum value of the interfacial tension at undecane for the p-(1-heptylnonyl) benzene sulfonate, suggests that for the water/alkane interface it is this trend in surfactant head adhesion at the interface that defines that interfacial tension minimum value.

Keywords: Linear alkyl benzene sulfonates, molecular dynamics, hydrocarbon water interface, binding energies per area

\* Corresponding author: Yosslen Aray, Facultad de Ciencias, Universidad de Ciencias Aplicadas y Ambientales, UDCA, Campus Universitario Norte, Calle 222 No 55-37, Bogotá, Colombia. Tel.: +571 6684700; E-mail: yaray@udca.edu.co

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1. Introduction

The interfacial properties of the adsorption film formed by surfactant molecules at oil/water interface play a crucial role on many scientific technological processes such as oil recovery [1–3]. In order to obtain the maximum benefit from surfactants used in this process, a good knowledge of their interfacial behavior is demanded [3]. Additionally, in designing new types of the most efficient oil-displacing surfactants, the key question is how to gain an insight into the structure/function relationship of these materials [1]. In this sense, many studies have been reported from both experimental [1–16] and theoretical points of view [17–24]. A considerable number of experimental research works have been reported concerning interface properties such as the behavior of interfacial tension (IFT), area per surfactant molecule (A), density profile, etc., between oil and water for alkyl benzene sulfonates [2–4,8,11], alkyl methyl napthalene sulfonates [9], Gemini surfactants [7], other quite complicated surfactant system such as sorbitan [5] and also at the air-water interface [12–16]. Molecular dynamics simulation of similar properties, namely, surface tensions, density profiles and several radial distribution functions of surfactant monolayers at the air/water [17–22] and hydrocarbons/water [23,24] interfaces, have also been reported. Molecular simulations have become an important tool for the study of the complex interface systems, as they are capable of providing quite accurate estimates of the dynamical, thermodynamical and structural properties of the interface system at the molecular level [24].

Sodium linear alkyl benzene sulfonates (LAS) belong to the kind of very popular surfactants which are widely used in industry and daily life. In fact, linear alkyl benzene sulfonates form the most important synthetic surfactant family in the world [20]. This compound has a sulfonate group and a linear alkyl chain which is usually attached to the para positions of a benzene ring (Fig. 1). The alkyl chain may have \( m + n \) carbons atoms with the benzene ring attached to the \((m + 1)\) carbon \((m < n)\) [20]. The specific example in Fig. 1 has a chain of 16 carbons atoms, and the benzene ring is attached to the 8th carbon. This is the \( O\)-(1-heptylnonyl) benzene sulfonate, more briefly denoted as 8-phenyl hexadecane sulfonate, 8-C16. These surfactants may be regarded as \( Ch \) alkyl benzene sulfonates with a substituted \( Cm \) alkyl chain. Previous works [4,24] have clearly indicated that the nearer to the end of the chain the benzene ring is attached, the lower the molecular weight is of the alkane which yields the lowest IFT. In general, when the total number of carbons atoms in the alkyl chain of the surfactant is increased, the minimum in IFT appears at a higher alkane carbon number [4]. Scanning of interfacial tensions against all or part of the homologous series of \( n \)-alkanes is a useful method [4,8,11] of characterizing the low tension behavior of surfactants and oil at the water/oil interface. Each surfactant shows a minimum tension at a particular \( n \)-alkane carbon number. In this way, a key concept is the alkane carbon number, \( n_{\text{min}} \).
corresponding to the minimum IFT when measured against an n-alkane series. For the 8-C16 case the optimum n_{min} at undecane was experimentally determined [4]. Deep insights into the nature of the interaction at the molecular level between the immiscible phases and the surfactant at the interface can be gained by studying the adhesive forces operating at that interface. In the present paper, to get a better understanding of the behavior of surfactants, we have performed a systematic study of those forces calculated as the interaction energy or binding energy per area for the water/n-alkane (hexane, octane, dodecane and tetradecane) interface, for the 8-C16 monolayer at the water/vacuum interface and for this monolayer at the n-alkane (decane, undecane, dodecane and tetradecane)/water interface. As a result, through the use of the concept of adhesive forces we have been able to explain in greater detail the origin of the minimum of the IFT for 8-C16 at C11 and have gained a more adequate understanding of the nature of the interface interactions.

2. Methods

2.1. Adhesion and interfacial tension.

The work of adhesion, W_{ij}, is the free energy change, or reversible work per unit area done to separate to infinity two different media initially in contact, a process that results in the creation of two new surfaces [25]. W_{ij} it is related to the intermolecular forces that operate at the interface between the two media. When the media are liquids W_{ij} is defined by the equation of Dupre as [25],

\[ W_{ij} = \gamma_i + \gamma_j - \gamma_{ij} \]  

(1)

Where \( \gamma_i \) and \( \gamma_j \) are the surface tensions of the two individual liquids and \( \gamma_{ij} \) is the IFT between the two liquids in contact. For two identical media, the work of cohesion, \( W_i \) for the liquid \( i \) is given by

\[ W_i = 2\gamma_i \]  

(2)

From Eqs (1) and (2), the relationship between the work of adhesion and IFT can be written as,

\[ \gamma_{ij} = \frac{1}{2}(W_i + W_j) - W_{ij} \]  

(3)

This equation suggests that the interfacial tension results from the competition between the cohesion forces holding molecules together in the separate liquids and the adhesive forces at the interface [25]. Experimental reports [26–28] of measured IFT for the n-hydrocarbon water interface, hyd/wat, with the n-hydrocarbon going from C_\text{6} to C_{16}, have clearly shown that there is a linear relationship with the number of carbon, \( n_{C_i} \) of the chain length: IFT systematically increases as \( n_{C_i} \) increases.

Equation (3) has very important implications for enhanced oil recovery (EOR). In EOR, surfactant formulations are injected into the reservoirs to reduce the interfacial tension to very low values between the aqueous chemical solution and the crude oil, with the purpose of mobilizing the oil and thus producing more oil than by conventional methods. Equation (3) shows that by increasing \( W_{ij} \) it is possible to obtain very low values of \( \gamma_{\text{Hyd/Wat}} \). This is just the role [29] of the surfactant: to produce an appreciable increase of the adhesive forces between the interfaces involved in the water/surfactant/oil systems.

The energy change for separating two media \( i \) and \( j \) in a medium \( k \) [29], such as a surfactant monolayer (medium \( k \)) between hydrocarbon/water interfaces is given by

\[ W_{ikj} = (W_k + W_{ij}) - (W_{ik} + W_{jk}) \]  

(4)

Where \( W_k \) is the work of cohesion between the surfactant molecules, while \( W_{ij} \) is the corresponding work of adhesion water/hydrocarbon. In the case when the surfactant forms an entire monolayer, \( W_{ij} \) will be negligible (there is no direct contact water-hydrocarbon) and adhesion only involves forces between the surfactant and the water and hydrocarbon phases.
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Fig. 2. (a) Simulation box of the water/n-hydrocarbon interfaces. Red and yellow spheres denote the oxygen and hydrogen atoms of the water molecules while gray and white spheres denote the carbon and hydrogen atoms of the Cn molecules. (b) Density profile along the z-axis normal to the interface at the left for the water molecules (red line) and C14 molecules (blue line). The perpendicular axis corresponds to the density in g/cm$^3$ and the horizontal one to the position (Å) along the z-axis. Heavy black lines define the interface zone.

2.2. Calculations

The hydrocarbons/water interface was determined by running a combination of NVT (constant volume and temperature) and NPT (constant pressure and temperature) molecular dynamics simulations for a cell under periodic boundary conditions [22]. An orthorhombic simulation box with dimension of 34 Å × 34 Å × 110 Å containing two water-hydrocarbon interfaces (Fig. 2a) with 900 water molecules and 1080/$n_{Ci}$ hydrocarbon molecules (1080 carbon atoms per molecule) was initially constructed. These simulation boxes have similar dimensions as those used in previous molecular dynamic studies of the water/n-alkane interface [24]. First the hydrocarbon and water phases were prepared separately using the Amorphous Builder software [30] to create an initial random and low density sample using a suitable Monte Carlo procedure to achieve a right distribution of conformational states. After that, the two phases were integrated into the simulation box. The next step was an energy minimization to relax the system. Finally, NVT and NPT simulations were sequentially carried out to equilibrate the system. First, a NVT
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Table 1

<table>
<thead>
<tr>
<th>nCi</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Calculated density (g/cm³)</th>
<th>Hydrocarbon Experimental density [33]</th>
<th>IT calc</th>
<th>IT Exp [34]</th>
<th>IT Estimated [34]</th>
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</thead>
<tbody>
<tr>
<td>6</td>
<td>25.545</td>
<td>25.545</td>
<td>75.132</td>
<td>0.754 ± 0.006</td>
<td>0.659</td>
<td>3.76</td>
<td>3.5 ± 0.2</td>
<td>3.99</td>
</tr>
<tr>
<td>8</td>
<td>25.242</td>
<td>25.242</td>
<td>74.240</td>
<td>0.780 ± 0.006</td>
<td>0.703</td>
<td>4.02</td>
<td>5.5 ± 0.2</td>
<td>4.28</td>
</tr>
<tr>
<td>10</td>
<td>25.000</td>
<td>25.000</td>
<td>73.529</td>
<td>0.802 ± 0.0062</td>
<td>0.730</td>
<td>4.41</td>
<td>4.6 ± 0.2</td>
<td>4.58</td>
</tr>
<tr>
<td>12</td>
<td>26.045</td>
<td>26.045</td>
<td>76.603</td>
<td>0.804 ± 0.0056</td>
<td>0.749</td>
<td>4.60</td>
<td>5.0 ± 0.2</td>
<td>4.89</td>
</tr>
<tr>
<td>14</td>
<td>27.384</td>
<td>27.384</td>
<td>80.540</td>
<td>0.839 ± 0.0056</td>
<td>0.763</td>
<td>4.83</td>
<td>4.8 ± 0.2</td>
<td>5.20</td>
</tr>
</tbody>
</table>

A simulation was performed for 4 ns at 300K to thermalize and equilibrate the system. Then, a NPT simulation for 4ns at 300K was done to adjust the system to the right density. To obtain a good statistic at constant volume, a final equilibration was performed by means of a NVT simulation for 4ns. Forcite software [31] with Compass force field [32] for the MD simulations was used.

Forcite [31] allows the possibility to extract potential energy contribution between pre-specified groups defined as sets. The work of adhesion, taken as the binding energy (\(\Delta E = E_{AB} - (E_A + E_B)\)) per cross sectional area for each pair of sets can be calculated along the trajectory, taking a final averaging of the calculated values. A script in Perl program language was written for that purpose.

3. Results and discussion

3.1. Water/n-alkanes interfaces

The cell parameters of the simulation box resulting from the equilibration process are collected in Table 1. The obtained density in g/cm³ is also summarized in Table 1. Density fluctuations less than 1% of the average values for subsequent NPT steps were observed. Note that the density of the total system shows an intermediate value between that of the pure bulk phase, 0.997 g/cm³ for water and those of the linear hydrocarbons [33] (also reported in Table 1). The present result for C10 is in good agreement with the value calculated in ref. [23] (0.81 ± 0.01 g/cm³). In general, the density of the hydrocarbon/water system increases with the density of the hydrocarbons and shows a systematic increase with the hydrocarbon chain length. Density profiles of each system along the Z-axis direction of the simulation box were also calculated by dividing the system into Z/100 thick slabs parallel to the xy plane. Figure 2(b) shows the density profile for water/C14 box. Two well-defined interfaces can be observed. The alkane densities show significant fluctuations with peaks of about 5Å from one another. In a previous report [24] a similar effect was observed and it has suggested that these peaks correspond to the position of minimum energy for the carbon Lennard-Jones potential. This means that alkane density fluctuations do not dissipate until far from the alkane/water interface and that small potential system size effects may be present in the alkane phase.

The interfacial thickness, IT, between the hydrocarbons and water phases was determined using the “90-90” criteria which is the distance between two positions where the densities of hydrocarbon and water are 90% of their own bulk densities [23]. The calculated IT values are in good agreement with the measured thickness (see Table 1) observed from the synchrotron X-ray reflectivity experiment [34], except for octane where an anomalous experimental high value was reported. Additionally, in that work, an estimation combining the capillary-wave prediction, \(\sigma_{gap}\), with a contribution from the intrinsic structure was reported. The intrinsic contribution was chosen to be the radius of gyration, \(R_g\), of the alkane. These
estimated values are shown in the last column of Table 1. It can be seen that our calculated IT values show the same trend as the estimated IT values and a good linear relationship \( \text{IT}_{\text{calc}} = 1.098 \text{IT}_{\text{estimat}} - 0.158 \) with \( R^2 = 0.98 \) was found. Note also that the interfacial thickness grows monotonically with the length of the \( n \)-alkane chain, i.e., it increases with the number of carbon atoms. The following linear relation with the carbon number, \( \text{IT}_{\text{calc}} = 0.136 n_{C_i} + 2.964; R^2 = 0.99 \) was determined. Thus the present results corroborate the linear variation of the interfacial width for the water/\( n \)-alkane interface with the alkane length chain.

Finally, to estimate the work of adhesion at the interface we have calculated the binding energy per cross sectional area, \( \text{BE/area} \), and the results are collected in Table 2. The experimental values for the work of adhesion for the studied interfaces are shown, as well, in this Table. The agreement with the experiment is good and validates our adhesion calculations. The calculated \( \text{BE/area} \) values indicate that the adhesion at the interface shows the same behavior as that evinced by the density and IT with respect to the hydrocarbon chain length, namely, a linear increase of \( \text{BE/area} \) with \( n_{C_i} \): \( \text{BE/area} = 0.706 n_{C_i} + 43.080; R^2 = 0.97 \).

\( \text{BE/area} \) is a measurement of the adhesive forces between the water and hydrocarbon molecules at the interface and depends on the intrinsic structure of this interface. Experimental measurements of the nonlinear susceptibility using optical second harmonic generation [35] have suggested the presence of highly ordered \( n \)-alkanes molecules at the interface; similarly, molecular simulation studies [36] have shown a preferred parallel orientation of the \( n \)-alkanes molecules close to the interface. We have checked our simulation boxes for the studied interfaces and for all these cases we have corroborated the favored parallel orientation of the hydrocarbon molecules at the interface. For example, Fig. 3 shows the snapshot (4000 ps of the last simulation step) at the interface (depth \( \Delta Z = 4.83 \) Å) for the water/C14 cases where the H atoms were deleted. Red spheres denote the water oxygen atoms and the yellow ones the C14 molecules inside the interface in parallel orientation (see Fig. 3a); the blue and green molecules only have their end parts inside the interface. Thus, the present results support the parallel orientation of the \( n \)-alkane molecules at the water/alkane interface. This orientation will produce the best packing of the molecules favored by the \( \text{H}_2\text{O-CH}_2 \) interaction. At the interface the structures of both water and \( n \)-alkane are different from those in the bulk: there occurs a decrease in the density of the water molecules at the interface due to a local expansion of the structure of these molecules (this can be seen in Fig. 2), whereas there is an increase in the local density of alkanes due to their local concentration at the interface (see Table 1 and Fig. 2). The alkane molecules are laterally oriented with respect to the interface in order to be in close contact with water. Hence, because the alkane molecules lay somewhat flat against the water surface in order to maximize surface contact they minimize penetration into the water phase. The combination of the water expansion and a more marked inclination of the alkane molecules as the chain gets larger could be at the origin of the IT increase. The increase in the alkane density should produce an increase in the number of water molecules having their hydrogens pointing towards the carbons of the alkane phase and thus showing greater orientation preference. All these factors contribute toward increasing the number of water molecules having greater contact with the alkane molecules, which, in

<table>
<thead>
<tr>
<th>( n_{C_i} )</th>
<th>( \text{BE/area} ) (dyn/cm)</th>
<th>( \text{Wij exp} ) (dyn/cm) [26]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>43.693</td>
<td>40.9</td>
</tr>
<tr>
<td>8</td>
<td>45.370</td>
<td>43.3</td>
</tr>
<tr>
<td>10</td>
<td>46.850</td>
<td>44.9</td>
</tr>
<tr>
<td>12</td>
<td>47.905</td>
<td>45.8</td>
</tr>
<tr>
<td>14</td>
<td>49.104</td>
<td>46.6</td>
</tr>
</tbody>
</table>
Fig. 3. Snapshot of the C14 molecules at the water/C14 interface. (a) Interface side-view and (b) top-view (perpendicular to the z-axis). For visual clarity the hydrogen atoms have been removed. Red spheres denote the water oxygen atoms while yellow sticks denote the C14 molecules closest to the interface. Note in (a) that the yellow molecules are parallel to the interface.

...turn produce an adhesion increase at the interface. However, additional studies about the inclination degree of the alkane molecules at the interface as their chain length increases should be done.

At this point, we would like to emphasize that the above results suggest that the COMPASS force field provides an acceptable accuracy for describing the interfacial n-hydrocarbon/water system in which we are interested.

3.2. 8-C16 monolayers at the air/water interface

At the air/water interface, water molecules are subjected to unequal short-range attraction forces and produce a net inward pull into the bulk phase [29]. Minimization of the contact area with the gas phase is therefore a spontaneous process. Depending on the surfactant molecular structure, adsorption takes place over various concentration ranges and rates. Above a well-defined concentration (the critical micelle concentration – CMC) micellization or aggregation takes place. At the CMC, the interface is at its maximum coverage forming an adsorbed surfactant monolayer. Above the CMC value, molecules begin to aggregate in the bulk phase [29]. Understanding the structure and properties of the adsorbed monolayer is of considerable interest not only because of their scientific significance but also because of their importance in a number of industrial and technological processes. In order to obtain information about the microscopic nature of the monolayer of amphiphilic molecules at the water/air interface, different experimental techniques including fluorescence, resonance Raman scattering, neutron reflection, second harmonic generation, Brewster angle microscopy, atomic force microscopy, calorimetry, X-ray, etc, have been performed [15,19]. Special attention has been given to the study of the monolayer structure, its dynamic properties (extension of the chains, thickness of the monolayer, etc.) [19,39,40] and its interfacial properties (surface excess concentration at surface saturation, \( \text{minimal} \) area per molecule at the air-water interface, \( A_\text{ad} \), and standard free energy of adsorption, \( \Delta G_\text{ad} \), etc.). Information related to the degree of packing and the orientation of the adsorbed surfactant molecules at the interface is provided by the area...
Table 3
Reported experimental $\cal A$ values for head group positional isomers of sodium para-dodecyl benzene sulfonate and sodium hexadecyl o-xylene sulfonates

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\cal A$ ($\text{Å}^2$) at 25°C</th>
</tr>
</thead>
</table>
| 2-C12BS [41] | $\begin{array}{c}
\text{H}_2\text{C} \\
\text{CH}_{2} \text{C}_9
\end{array}$ | 43 |
| 3-C12BS [41] | $\begin{array}{c}
\text{CH}_3\text{CH}_2 \\
\text{H}_2\text{C}(\text{H}_2\text{C})_8
\end{array}$ | 54 |
| 4-C12BS [41] | $\begin{array}{c}
\text{H}_2\text{C}(\text{H}_2\text{C})_2 \\
\text{H}_2\text{C}(\text{H}_2\text{C})_7
\end{array}$ | 61 |
| 5-C12BS [41] | $\begin{array}{c}
\text{H}_2\text{C}(\text{H}_2\text{C})_3 \\
\text{H}_2\text{COH}_6
\end{array}$ | 65 |
| 6-C12BS [41] | $\begin{array}{c}
\text{H}_2\text{COH}_5 \\
\text{H}_2\text{COH}_4
\end{array}$ | 65 |
| 3-C16-o-XS [14] | $\begin{array}{c}
\text{H}_3\text{CH}_2\text{C} \\
\text{CH}_{12}\text{C}_6
\end{array}$ | 47.38 |
| 5-C16-o-XS [14] | $\begin{array}{c}
\text{H}_3\text{CH}_2\text{C}_3 \\
\text{H}_3\text{C}(\text{H}_2\text{C})_{10}
\end{array}$ | 79.67 |
| 7-C16-o-XS [14] | $\begin{array}{c}
\text{H}_3\text{CH}_2\text{C}_5 \\
\text{H}_3\text{C}(\text{H}_2\text{C})_8
\end{array}$ | 88.83 |
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<table>
<thead>
<tr>
<th>$A$ (Å$^2$)</th>
<th>Interfacial thickness Å</th>
<th>$-BE$/area (Wat/8-C16) (dyn/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>96.000</td>
<td>6.50</td>
</tr>
<tr>
<td>7</td>
<td>82.29</td>
<td>6.63</td>
</tr>
<tr>
<td>8</td>
<td>72.000</td>
<td>6.70</td>
</tr>
<tr>
<td>10</td>
<td>57.600</td>
<td>6.75</td>
</tr>
<tr>
<td>12</td>
<td>48.000</td>
<td>6.80</td>
</tr>
</tbody>
</table>

The per molecule parameter, which is a measurement of the interface coverage density. Experimental $A$ values for six monodispersed head group positional isomers (see Table 3) of sodium para-dodecyl benzene sulfonate (C12BS) have been recently reported (43 Å$^2$ to 65 Å$^2$) at CMC [41]; for sodium hexadecyl o-xylene sulfonates [14] the values lie between 47.38 and 88.83 Å$^2$ (see Table 3). We have not found experimental values for the corresponding parameter for 8-C16.

In the present work, in order to calculate $A$, we have constructed simulation boxes of 24 Å $\times$ 24 Å in the $x$ and $y$ directions and 100 Å in the $z$ direction (see Fig. 4) and have placed inside the box 900 water molecules to form an initial 40 Å thick slab with a density of 1.0 g/cm$^3$. Then, 8-C16 molecules were placed with the hydrocarbon chains extending perpendicularly with respect to the $xy$ plane in all-trans conformation, distributed averagely in that plane, and with the hydrophilic head pointing into the water and the alkyl tails pointing out to the vacuum space. Four boxes with 6, 8, 10 and 12 surfactant molecules with given area/molecules ($A$) values of 96.0, 72.0, 57.6 and 48.0 Å$^2$, respectively, were constructed. Each system was simulated for 8 ns using an NVT ensemble; the trajectories for the last 2 ns were used for data analysis. Table 4 collects the calculated $A$ values averaged along the last 2 ns of the trajectory. Simple inspection of this table shows that the larger adhesion at the interface corresponds to the 8-surfactant-molecule case ($BE$/area $=$ 1502.462 dyn/cm). By means of a polynomial regression, the values of $A$ were fitted against the $BE$/area and a minimum $A$ value of 74.0 Å$^2$ was calculated.

Unfortunately, we have not found the exact data for 8-C16 in the literature; however, our results suggest that, as one might expect, this value is larger than the corresponding one for 6-C12 (62 Å$^2$) [41] and smaller than that for sodium hexadecyl o-xylene sulfonates (88.83 Å$^2$) [14] where the benzene ring point of attachment is located at the seventh carbon of the hexadecyl tail.

Figure 4a shows a snapshot of the cross-sectional view perpendicular to the plane of the interface for the 8-molecule case at the end of the simulation. Detailed structural properties can be obtained by studying the density profile of the components of the system along the $Z$ direction. The different components of the surfactant molecule were computed separately each one as a set, including the carbon chain, the benzene ring group, the head group – $SO_3^-$ and the sodium atoms. The corresponding density profiles are shown in Fig. 4b. It can be seen that the $SO_3^-$ groups are hydrated and localized in the water phase. The benzene ring groups are also almost hydrated while the carbon chains are very nearly excluded from the interface. The degree of hydration gradually decreases along the carbon chain. Only a very small fraction of the water molecules penetrates into the hydrocarbon tails. Most of the head, the benzene ring and the sodium atoms are inside the interface.

Table 4

<table>
<thead>
<tr>
<th>$A$ (Å$^2$)</th>
<th>Interfacial thickness Å</th>
<th>$-BE$/area (Wat/8-C16) (dyn/cm)</th>
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<tr>
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<td>6.80</td>
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In summary, the performed simulations for the 8-C16/water interface yield the values of $A$ = 74.0 Å$^2$, $IT$ = 6.7 Å and $BE$/area = 1502.462 dyn/cm. It is interesting to notice that we have found very much stronger interactions between the surfactant polar head group with sodium and water molecules than those occurring at the water/hydrocarbons interface (see Table 2). Additionally we have also found...
Fig. 4. (a) Interface side-view. Red, purple, yellow, blue and whites spheres denote the sodium, oxygen, sulfur, carbon and hydrogen atoms of 8-C16. Light pink and green sticks denote the hydrogen and oxygen atoms of the water molecules. (b) Density profile along the z-axis normal to the 8-C16/water interface. The sodium atoms, benzene rings, sulfonate, carbon chain and water molecules have been defined as separated sets. The perpendicular axis corresponds to the density in g/cm$^3$ and the horizontal one to the position (Å) along the z-axis. Heavy broken black lines define the interface zone.
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Simulation boxes similar to those of Fig. 2(a) with two interfaces were constructed (Fig. 5(a)). Two opposite 8-C16 monolayers at the alkane phase were built with the monolayer normal pointing in the z-direction. The monolayer/alkane/monolayer system was placed in the middle of the box. Then, the water molecules with experimental density were placed on both sides of the monolayers. The density of the alkane phase in the initial model corresponds to the experimental values. The number of water and alkane molecules was exactly the same as in the above simulations. An initial periodic box with a size of 32 Å × 32 Å × 140 Å was used and NVT and NPT MD simulations similar to those described above.
were sequentially carried out to equilibrate the system. First, a NVT simulation was performed for 4 ns at 300K to thermalize and equilibrate the system. Then, a NPT simulation for 4 ns was done to adjust the system to the right density. A final equilibration was performed by means of a NVT simulation for 4 ns and the trajectories for these last NVT 2 ns were used for data analysis.

For C14, boxes with 1, 2, 4, 6, 8, 10 and 12 surfactant molecules in each interface were constructed. The resulting cell parameters of the simulation box, density and the area/molecule, $A$ are collected in Table 5, while the $BE/area$ between the different phase components are reported in Table 6. Comparison of $A$ with $BE/area$ and a polynomial regression have shown that the optimum value for the area/molecule corresponds to the case when there are eight surfactant molecules at the interface leading in this case to $A = 79.44 \text{ Å}^2$. In agreement with experimental results [42] for mixtures of linear alkyl benzene sulfonate, for which sodium dodecyl benzene sulfonate is the primary component, the area/molecule at hydrocarbon/water interfaces is larger than the respective area at air/water interface. However, this value is only 5.44 units bigger to that obtained in the above section for the water/8-C16 interface, while the experimental reported valued at ref. [42] is significantly larger at the oil (soybean oil)/water interface (106 \text{ Å}^2) than the air/water interface (83 \text{ Å}^2). This last value is significantly bigger than the reported experimental range (43 to 65 \text{ Å}^2) [41] for pure dodecyl benzene sulfonate.

For this surfactant molecule coverage, Fig. 5(b) shows the density profile along the z-axis direction. The original $IT$ of 4.83 \text{ Å} for the water/C14 interface increases to 18.77 \text{ Å}. In this case, due to the presence of surfactant molecules, the interfacial thickness consists of three components: $IT$ of the water interface, $IT$ of the surfactant and $IT$ of the C14 interface. Interestingly, the broadening of the interface

<table>
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<tr>
<th>$n_{surf}$</th>
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<th>$b$</th>
<th>$c$</th>
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<th>$BE$(C14/8-C16)</th>
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Table 5  
Equilibrated Cell parameters of the orthorhombic simulation box, area per molecule, $A$ and calculated density of the water/surfactant/Cn system for 1 to 12 molecules of 8-C16 surfactant at each interface

Table 6  
Calculated $BE/area$ for the water/8-C16/Cn interface, $n = 14, 12, 11$ and $10$. For C14 the number of surfactant molecules, $n_{surf}$, is changed from 1 to 12.
mainly occurs in the hydrocarbon side. Note that the sulfonate and benzene ring are mainly inside the
water interface while the nonpolar tail groups tend to avoid the water molecules. Note (see Fig. 5a) that
when the 8-C16 molecules substitute water and C14 molecules at the original water/C14 interface, the
interaction across the interface occurs between the surfactant hydrophilic head and water molecules on
one side of the interface and between the alkyl tail and C14 molecules on the other side of the interface.

It is well known [29] that these interactions have to be much stronger than the original ones between
immiscible phases such as C14 and water. Our results (see Table 6) suggest that the BE/area of the 8-
C16/C14 and the water/8-C16 interfaces are about 3 and 29 times larger, respectively, than that of the
water/C14 (49.10 dyn/cm) interface. It is clear that the hydrophilic groups provide very strong interac-
tions between the surfactant molecules adsorbed at the water interface and the molecules of the solvent.

These results are coherent with reported values for the free energies of solvation, $\Delta G_S$, of alkanes in
water [43], alkanes in alkanes [44] and ionic molecules in water [45]. For example, for octane in water
and octane in decane the values of $\Delta G_S$ are 12.09 and $-21.92$ KJ/mol, respectively, while the reported
solvation free energy for 90 anions [44] ranges from $-57.80$ for $[\text{NO}_2\text{C}_6\text{H}_4\text{O}^-]$ to $-437.48$ KJ/mol for
$[\text{HO}^-]$. As one would expect, the interactions between phases formed by polar and ionic molecules are
much more favorable than the interactions between phases where dispersive forces are the main ones.

This is the origin of the surfactant effect: it changes unfavorable interactions between molecules hav-
ing different natures (polar/non polar) by allowing the generation of very favorable interactions at the
interface between molecules with similar character (polar/ionic or non-polar/non-polar).

Finally we have studied the effect of the alkane scanning on the calculated BE/area parameter for
the 8-C16 surfactant, water interfaces with C10, C11 and C12 hydrocarbons were additionally studied
and the results are also collected in Table 6. It is well known [11] that $n_{\text{min}}$ in alkane interfacial ten-
sion scanning curve can represent the hydrophilic-lipophilic ability of surfactant, the lower the $n_{\text{min}}$
value is, the more hydrophilic the surfactant is. Reduction of IFT depends directly on the replacement
of solvent at the interface by molecules of surfactant. The tension across the interface is significantly
reduced by the adsorption of surfactant molecules because these interactions are much stronger than the
original interaction between the hydrocarbon and water molecules. In general, the higher the interfacial
surfactant concentration is, the lower the IFT is. From Table 6 it can be seen that the BE/area absolute
value of the water-head of 8C16 shows a maximum just at C11. The obtained trend for this interaction
is C10 (1203.351 dyn/cm) < C11 (1608.277 dyn/cm) > C12 (1482.277 dyn/cm) > C14 (1445.803 dyn/cm).

while for the tail-alkane interaction the BE/area systematically increases as the chain length of Cn in-
creases, C10 (142.44) < C11 (148.015) < C12 (150.02) < C14 (162.25). This result shows that for the
water/8-C16/Cn interface it is this trend in adhesion of the surfactant in the water phase that defines the
$n_{\text{min}}$ value of IFT and not the interaction between surfactant molecules. In this manner we are able to
rationalize the observed facts by resorting to the concept of binding energy per area as a measure of the
adhesion forces.

4. Conclusions

This work reports on a systematic study using molecular dynamics simulations of the density pro-
files and the adhesion forces (binding energy per cross sectional area, BE/area) for the water/n-alkane
(hexane, octane, decane, dodecane and tetradecane) interfaces. The calculated interfacial thickness, IT,
and BE/area are in good agreement with reported experimental values and both of these quantities grow
monotonically with the atom carbon number. Excellent linear correlations with the carbon number were
obtained ($IT_{\text{calc}} = 0.136 \, nC_1 + 2.964$; $R^2 = 0.99$). Values of $BE/area$ ranging from 46.69 for $C_6$ to 49.10 for $C_{14}$ were calculated.

Similar studies for the vacuum/sodium $O$-$(1$-heptylnonyl) benzene sulfonate ($8$-$C_{16}$)/water interface were carried out. The optimum minimal area per molecule at the interface, $A$, the $BE/area$ and profiles densities were determined. These are: $A = 74.0 \, Å^2$, $IT = 6.7 \, Å$ and $BE/area = 1502.462 \, \text{dyn/cm}$. This study shows the presence of strong interactions between the surfactant polar head group with sodium and water molecules. The density profile suggests that the surfactant head ($\text{NaSO}_3$-benzene) is almost entirely hydrated and that it is located inside the interface while the carbon tails are almost excluded from the water/$8$-$C_{16}$ interface.

The effect of $8$-$C_{16}$ on the interfaces $n$-hydrocarbon/$8$-$C_{16}$/water were also explored. For $C_{14}$, an optimum value of around eight surfactant molecules forming the monolayer at the interface was found; this corresponds to a value of $A = 79.44 \, Å^2$. The calculated $BE/area$ values of $-162.25$ and $-1445.80 \, \text{dyn/cm}$ for the $8$-$C_{14}$/$C_{14}$ and water/$8$-$C_{14}$ interface sides, respectively, were found. It is clear that the hydrophilic surfactant-head provides very strong adhesive interaction and miscibility with the water phase. Scanning of $BE/area$ against $C_n$ ($C_{10}$, $C_{11}$, $C_{12}$ and $C_{14}$) have shown that the magnitude of the binding per area of the tail-$C_n$ interaction at the interface systematically increases as the chain length of $C_n$ increases, whereas, in agreement with the experimental $IFT$ values, the $BE/area$ at the interface for the water-head interaction shows a maximum at $C_{11}$. These results suggest that for the water/$8$-$C_{16}$/$C_{14}$ interface, the $n_{\text{min}}$, of $IFT$ is mainly determined by the trends of adhesion of the surfactant head with the water molecules at the interface.

Acknowledgements

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