



Desorption of decane molecules from a graphite surface produced by sodium alpha olefin sulphate/betaine surfactant mixtures: A computer simulation study



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ABSTRACT

Molecular dynamics simulations of decane molecules adsorbed on a graphite substrate were carried out to study removal of alkanes from the solid surface by using two surfactants. Three different systems were prepared to understand, from the molecular point of view, the removal process. The first system was constructed with sodium alpha olefin sulphate surfactants (AOS), the second system with betaine surfactants and the third system with a mixture of both surfactants. In each case different features were observed. Studies of density profiles show how the decane molecules were adsorbed on the solid surface in a layer structure. Although both surfactants promoted the formation of an additional decane layer, indicating separation or removal from the graphite surface, it was observed that the AOS surfactant had less influence than betaine. Studies of adsorption and orientation of decane molecules were also analysed on the graphite surface, with the different surfactants and the mixture, and it was observed that those molecules present more structure on the surface with the AOS surfactant than with the betaine surfactant. However, the best removal of decane molecules was obtained with the surfactant mixture. In this case it was observed that the first layer close to the surface was modified while an extra layer of decane molecules emerged suggesting decane separation from the surface. Moreover, the maximum removal was found at AOS/betaine ratio concentration of 0.24/0.76.

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1. Introduction

For several years investigations of surfactant molecules at liquid/vapour, liquid/liquid and liquid/solid interfaces have been the subject of extensive studies not only for their scientific interest but also for their industrial applications. For instance, Rosen [1], showed that attractions between the hydrophilic head groups in surfactants are mainly dominated by electrostatic interactions. Nyuta et al. [2], by conducting different experiments (small-angle neutron scattering (SANS), dynamic light scattering (DLS), cryogenic transmission, electron microscopy (cryo-TEM)) studied zwitterionic surfactant aggregation, with nonidentical headgroups, in aqueous solution and they found that aggregation strongly depended on the hydrocarbon chain length and the surfactant concentration. They observed a change in the structure from spherical to rod-like shapes to vesicle by increasing surfactant concentration.

Several studies have been carried out on single surfactants by using different experimental techniques including fluorescence, Raman scattering, vibrational sum-frequency spectroscopy, Brewster angle

microscopy and atomic force microscopy [3–6], however, most of the actual problems, such as commercial products, consist of a mixture of surfactants that have more interesting properties, such as the reduction of the interfacial tension, than individual ones. For instance, anionic surfactants are generally used with zwitterionic surfactants as active ingredients for distinct industrial applications such as shampoo, washing powders and in petroleum industry to remove oil from rocks. Therefore, studies of surfactant mixtures have also been conducted using different experimental techniques such as calorimetry, X-ray, neutron scattering, and surface tension measurements among others [7–14]. One of those interesting works was conducted by Christov et al. [15] who observed, through dynamic light scattering experiments, the phase transition of micellar aggregates from spheres to rods for pure surfactants and for binary mixtures of betaine/SDS in water. They found that formation of rod micelles from spheres was more stable for a betaine/SDS fraction ratio of 0.8/0.2. They related the phenomenon to a loss of entropy (due to a decrease number in the micelle concentration) that should be compensated by a gain in the interaction energy between the molecules. On the other hand, Danov et al. [16] performed surface tension measurements of SDS and betaine in water and they found lower critical micelle concentration (cmc) for a betaine/SDS fraction of 0.75/0.25, suggesting that only a small amount of SDS in the mixture helps to reduce the contact area at the interface. In fact, several works have reported the

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effectiveness of mixtures of anionic surfactants with zwitterionics [17–19] such as the work of Basheva et al. [19] who found that foaming and foam stability decrease may be impaired by the presence of surfactants.

The study of surfactants on solid surfaces has also been a subject of a lot interest, in particular to understand adsorption (desorption) processes. In fact, several of those investigations have been conducted using computer simulations which have proved to be a powerful tool to investigate such complex systems. For instance, Hu et al. [20] conducted molecular dynamics simulations to study adsorption of zwitterionic surfactants (dodecyl sulfobetaine) and divalent cations (calcium and magnesium) on a surface of silica. Liu et al. [21] investigated dodecane desorption on a silica surface in an aqueous dilution of cetyltrimethylammonium bromide (CTAB) by showing that the formation of a water–oil channel is needed for detachment. However, due to the water and oil nature, the formation of that channel is not possible without the presence of a surfactant. Wettability has also been investigated and it was found how it is modified by the presence of surfactants [22,23].

In previous works we carried out simulations of SDS and mixtures of SDS/dodecanol to obtain more insights about aggregation and adsorption of those molecules on different substrates [24–26]. In the present paper we are interested to investigate, from a molecular point of view, how surfactants help desorption of alkane phases from a substrate. In particular we focus on zwitterionic and anionic surfactants with decane molecules deposited on a graphite surface.

2. Computational model

Simulations of three systems were conducted using two surfactants on a graphite substrate with a layer of decane molecules; system 1 with an anionic sodium alpha olefin sulphate (AOS), system 2 with a non-ionic cocoamidopropyl betaine (see Fig. 1 of Supplementary data) and system 3 with mixtures of AOS/betaine. The initial configuration started with 2416 water molecules in a bulk phase on a graphite wall where 40 decane molecules were previously deposited. Then, the system was run until decane was adsorbed on the substrate by forming a layer structure (Fig. 1a). It was used a graphite surface due to the good affinity with alkane molecules, therefore, a strong adsorption of decane molecules on the surface was expected. The dimensions of the simulation cell were $X = Y = 40.249 \text{ \AA}$ and $Z = 150 \text{ \AA}$, i.e. the Z-length was large enough

to have a liquid/vapour interface at one end of the simulation box to prevent the formation of a second water/solid interface due to the periodicity of the system.

Then, systems with individual surfactants at 7 different number concentrations; 0.0021, 0.0041, 0.0062, 0.0082, 0.0102, 0.0123 and 0.0143, (5, 10, 15, 20, 25, 30, 35 surfactant molecules) of AOS or betaine molecules were prepared. The concentration was calculated as the number of surfactants divided by the total number of water molecules. For the systems with anionic surfactants a sodium anion (Na^+) per each AOS molecule was included. For the mixtures (AOS/betaine) the total number of molecules was constant (19 total surfactant molecules) and the results were given in terms of the betaine concentration (number of betaines/number of water molecules) 0.0033, 0.0045, 0.0062 and 0.0078. Due to the affinity between surfactant tails and alkane groups the surfactants were initially placed with their tails close to the alkane layer to save computer time. Simulations with heads close to alkanes and tails next to water were also tested, however, the main results did not change significantly.

The AOS and the betaine force fields consisted of intra and inter molecular interactions. The intra-molecular interactions included harmonic bonds, harmonic angles and dihedral potentials whereas the intermolecular interactions consisted of Lennard Jones and coulombic potentials. The parameters for the AOS headgroup were taken from Yan et al. [27] whereas the parameters for the tail were taken from the tails of SDS reported in the literature (due to the similarity in both tails) [24–26]. The parameters for the betaine molecule were taken from references [28,29]. The charges for both AOS and betaine were obtained from quantum chemistry calculations using the GAUSSIAN software (Fig. 1 of Supplementary data). The parameters, used in the work, for both surfactants are given in Tables 1–3 of the Supplementary data. Decane molecules were simulated with the force field proposed by Nath et al. [30] whereas water was simulated using the SPC model. The water model has been used in similar systems (of SDS/water/solid interfaces, [24–26]) and good tendencies with experimental results have been observed. The graphite plate was simulated using an atomistic model constructed with four layers (2706 atoms) [24,25] where all the atoms were frozen to have a rigid wall.

All simulations were carried out in the NVT ensemble with a time step of 0.002 ps using the DL_POLY package [31]. As mentioned above there is a vapour–liquid interface at one edge of the simulation box which should allow the systems to have appropriate thermodynamic

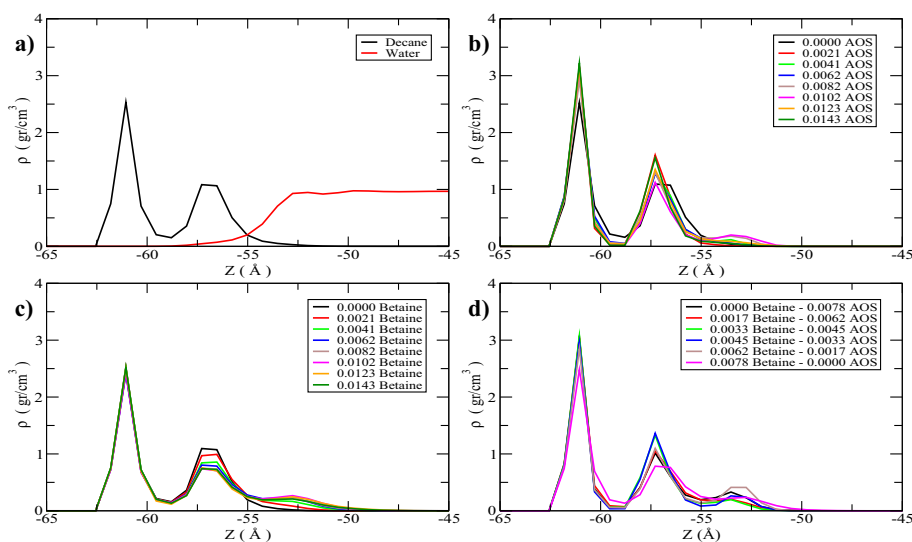


Fig. 1. Density profiles for a) the decane/water system b) decane with AOS surfactant c) decane with betaine surfactant and d) decane with the AOS/betaine mixture. The surfactant concentration in each system is given in colours as indicated in the inset tables. The graphite surface is located on the left of the plot.

conditions, such as the correct density value for water (see Fig. 1a). Periodic boundary conditions were imposed and the temperature was controlled with the Hoover–Nosé thermostat with a relaxation time of 0.1 ps at a temperature of $T = 300$ K. The electrostatic interactions were handled with the particle mesh Ewald (PME) method and the Van der Waals interactions were cut off at 10 Å. Finally, all systems were run up to 15 ns after 2 ns of equilibration and the last 3 ns were taken for data analysis.

3. Results and discussion

Several simulations were conducted to study the behaviour of adsorbed decanes on the graphite surface as a function of pure and mixtures of two surfactants (AOS and betaine).

3.1. Density profiles

The first simulations were carried out for the system decane/water to observe adsorption of the alkane molecules on the graphite surface. In Fig. 1 plots of density profiles are shown where it is possible to observe two layers of decane molecules adsorbed on the surface. The density profiles were constructed by considering all the CH_n unit atoms of the decane molecules. Then, subsequent simulations were conducted by introducing AOS or betaine molecules at different concentrations to study the effects on alkane adsorption.

In Fig. 1b and c the density profiles of the decane molecules for different AOS and betaine concentrations are shown, respectively. As stated before, it is possible to observe two well adsorbed layers of decanes on the surface in the absence of surfactant molecules in the system. However, when AOS molecules were added, the first peak in the decane

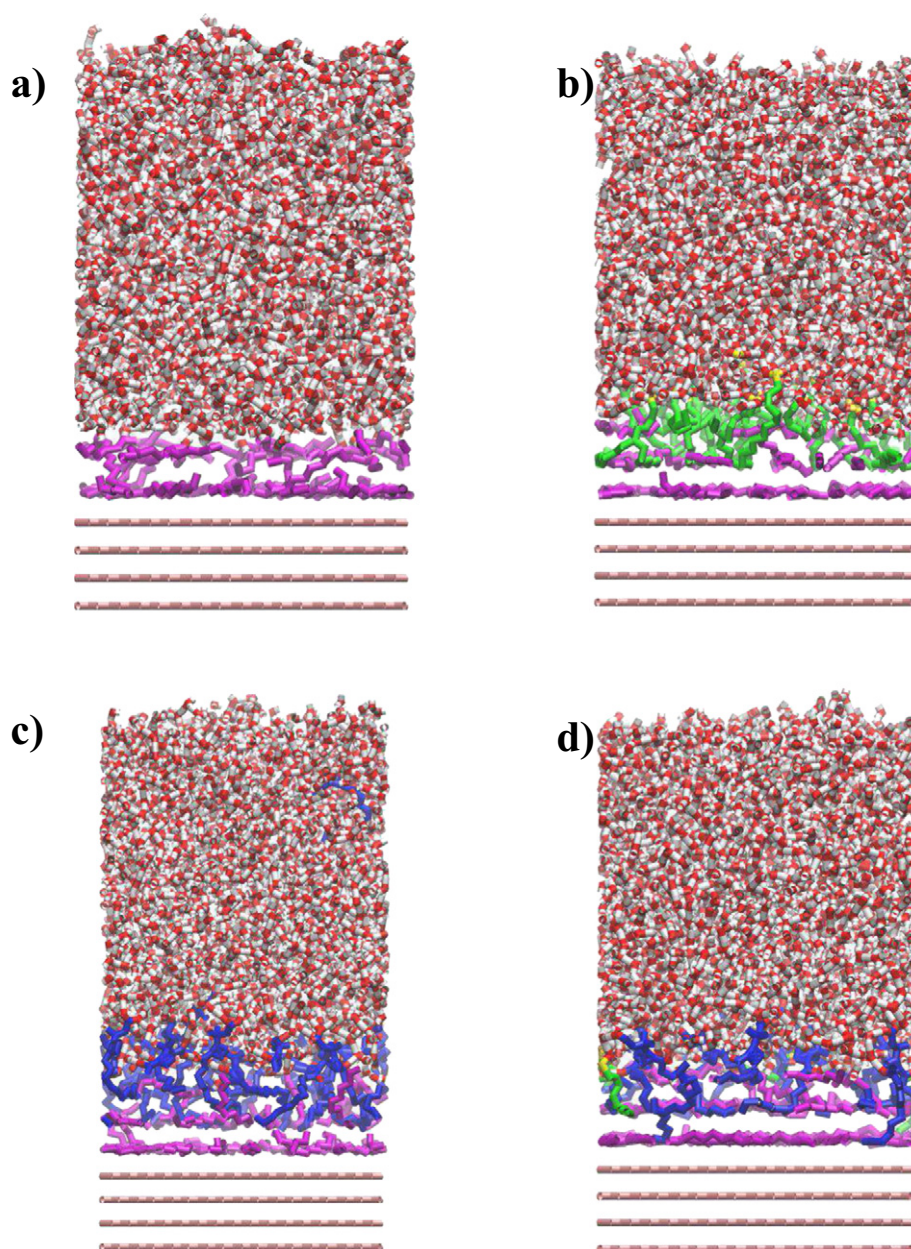


Fig. 2. Snapshots of the decane–water interface on the solid graphite surface a) without any surfactant b) with the AOS surfactant c) with the betaine surfactant and d) with the AOS/betaine mixture. Water is represented in red, decane molecules in purple, AOS in green, betaine in blue and graphite substrate in pink.

density profile became higher (Fig. 1b) suggesting adsorption on the surface. The second layer peaks decreased when AOS concentration increased and a third layer was created indicating desorption of decane. In Fig. 2b a snapshot of the last configuration is shown. When betaine molecules were used, different issues were observed (Fig. 1c). The peak of the first adsorbed layer did not change with concentration. The second layer decreased with surfactant concentration and at the same time a small third layer started developing. The last results indicated that some decane molecules began to separate from the surface as noted in the snapshots of Fig. 2c.

As it was mentioned in the Introduction, it has been observed that surfactant mixtures might enhance and help some properties, such as stability of rods [15,16]. Therefore, in the present work we also conducted simulations of AOS/betaine mixtures to investigate the difference with pure surfactants. The mixtures were constructed with a total of 19 (AOS + betaine) surfactants. In this case, it was observed that the first peak in the density profiles became smaller and at the same time a third layer of decane molecules appeared (Fig. 1d). These results suggested separation of few decane molecules from the surface (Fig. 2d).

3.2. Adsorption of decane on the surface

In order to have more information about decane attachment on the surface we conducted a more detailed analysis of the molecules in three different regions in the density profiles of Fig. 1. Region 1 is defined from the graphite surface to the first minimum of the first layer, region 2 is defined to the end of the second layer and region 3 starts from the end of the second layer. In Fig. 3 the ratio of decane molecules in each region is calculated as a function of surfactant concentration (AOS and betaine) where the ratio was calculated by the number of CH_n groups in each region divided by the total number of CH_n groups of all decane molecules.

In Fig. 3a the number of CH_n groups are plotted where it is observed that the number of those groups increased more than 10% in the first region, once AOS was added in the system. On the other hand, as the AOS concentration increased the number of CH_n groups in the second region decreased up to 30% from concentration 0.010. In fact, it seems that few CH_n groups of the second region moved to the first region whereas others moved away to region three. It is worthy to mention that error bars were calculated for the data, however, they are of the size of the symbols.

In Fig. 3b the results for the betaine surfactant are shown. In the first region the number of CH_n groups did not change for any betaine concentration whereas in the second region the ratio decreased up to rarely 30–40% from concentration 0.0062. In region 3 an increment of decane molecules of $\approx 30\%$ from concentration 0.0062 was observed. In fact the increment of decane molecules in that region came from molecules in region 2 suggesting desorption of decane from the surface.

It was observed that the first surfactant (AOS) produced attachment of some molecules to the surface and at the same time it made a reduction of decanes in the second layer. On the other hand, the second surfactant (betaine) also made a reduction of decane molecules in the second region, however, in that case decane moved towards the water phase as suggested by the presence of a third layer.

In Fig. 3c plots of the variation of decane molecules in the three different regions, as a function of the betaine concentration, are shown for the AOS/betaine mixture. Here, in region 1 the amount of decane molecules slightly decreased up to concentration of 0.033, then reduction in the number of CH_n groups was depicted. In region 2, an increment of CH_n groups (probably due to the CH_n groups which moved from region 1) up to concentration 0.033 was observed. In region 3 different features were observed, i.e., a slight reduction, up to concentration of 0.0045, in the amount of CH_n groups with betaine concentrations, then a significant increment of CH_n groups was noted. The reduction in the first layer and the increment in the third one, at betaine concentration of 0.0062, indicated that decane was removed from the surface. It is

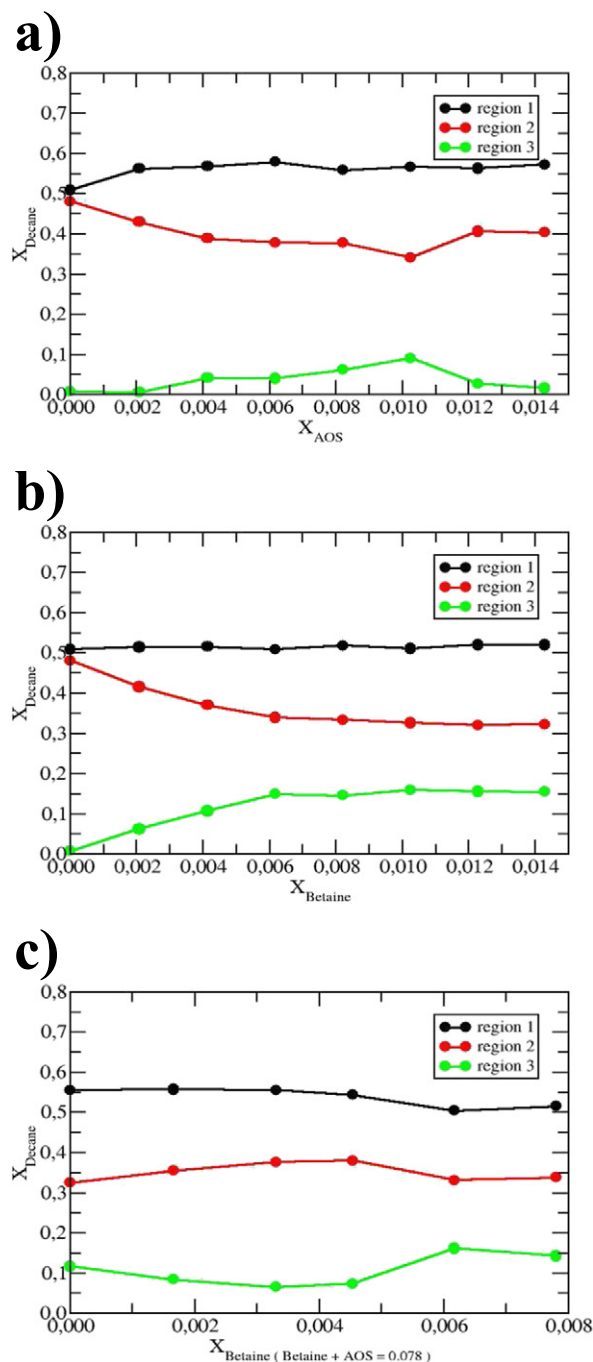


Fig. 3. Concentration of decane molecules in three regions (defined in the text) for different surfactant concentrations. a) AOS, b) betaine and c) AOS/betaine mixture in terms of the betaine concentration.

worthy to mention that the increment of decanes at the concentrations 0.0062 (betaine)–0.0017 (AOS) corresponded to a fraction ratio (AOS/betaine) of 0.24/0.76.

3.3. Structure of surfactants at the interface

To better understand adsorption of decane on the surface we also analysed the surfactants behaviour at the oil–water interface. In Figs. 4 and 5 the CH_n group (for betaine even those in the backbone) and headgroup density profiles of AOS, betaine and the mixture are shown. As it was expected the surfactant tails were deposited close to

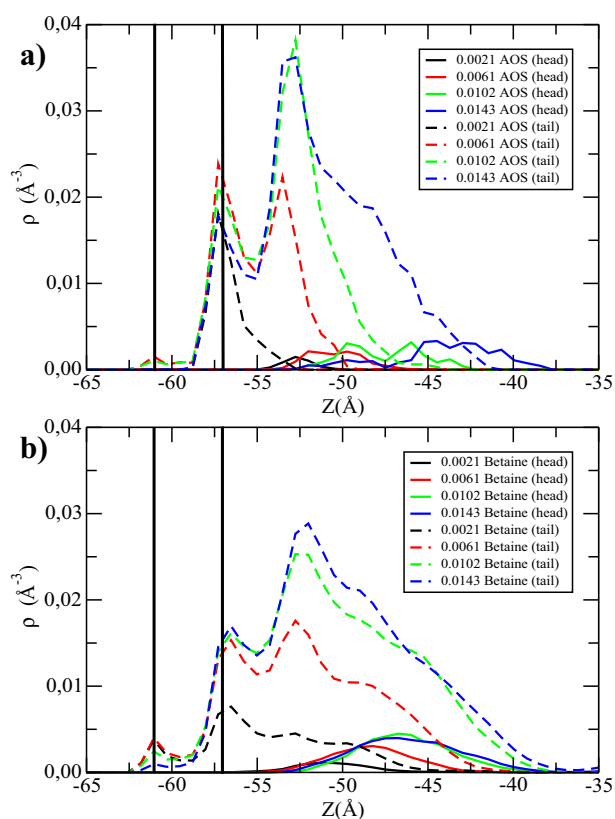


Fig. 4. Density profiles for the heads and CH_n groups for the different surfactants. a) AOS (S atom for the headgroup) and b) betaine (N atoms for the headgroup) surfactants. The dashed colour lines are the CH_n groups and the solid colour lines the headgroups. The Black solid lines represent the positions of the first and second adsorbed decane layers as indicated in Fig. 1.

the decane molecules whereas the headgroups were immersed into the water phase. From Fig. 4a it is possible to observe that surfactant tails (CH_n groups) stratified at the interface. Moreover, due to the affinity of the hydrocarbon tails with alkane molecules, some surfactant CH_n groups were located at the same positions of the first and second decane layers (only few in the first layer).

For the simulations with the betaine surfactant we also noted the formation of layers at the interface (Fig. 4b). However, the peaks of the surfactant CH_n profiles were smaller and the layer at the interface was significantly broader which could explain the presence of decane molecules far from the surface. In fact, the effect was more pronounced at higher surfactant concentrations.

Similar features were observed for the AOS and the betaine density profiles in the mixtures (Fig. 5), i.e. it was observed broader betaine profiles as the betaine concentration increased (Fig. 5b). At low concentrations the two main peaks in the profiles were asymmetric (for both surfactants), however, those peaks became alike as the concentration increased. When the mixture ratio concentration was 0.24/0.76 the two main peaks became symmetric (in betaine profiles) and an additional small peak appeared. It is worthy to mention that at this ratio concentration it was observed the maximum desorption of decane molecules from the surface (see Fig. 3c).

3.4. Structure of the adsorbed decane molecules on the Surface

In Figs. 6–8 configurations and orientation probabilities of decane molecules in region 1, i.e. deposited on the first adsorbed layer, are

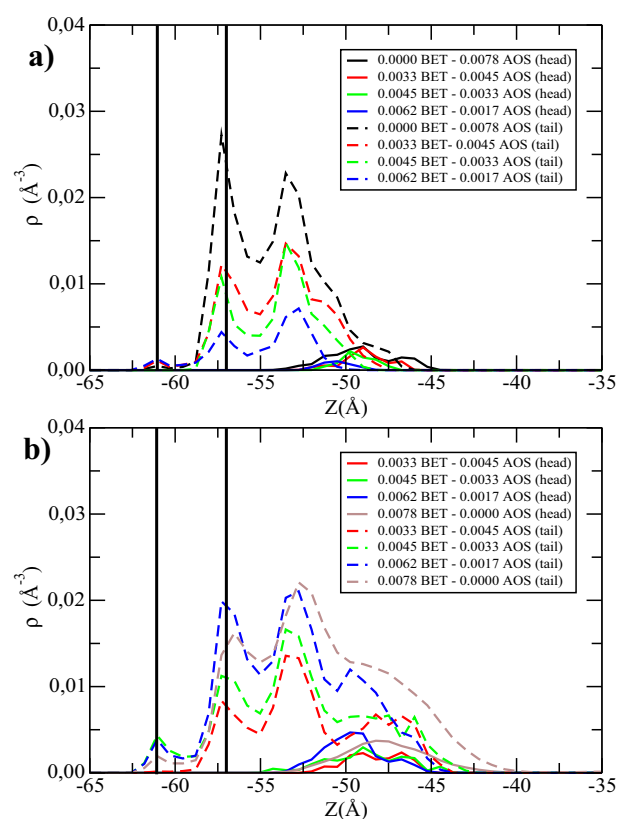


Fig. 5. Density profiles for the heads and CH_n groups for the different surfactants. Top and bottom panels are for the AOS and betaine profiles, respectively. a) AOS (S atom for the headgroup) and b) betaine (N atoms for the headgroup) surfactants. The notation is the same as Fig. 4.

shown. The orientation was measured as the angle of the horizontal axis with the molecular orientation vector, defined from the first to the last CH_n groups in the chains. Figures with AOS, betaine and mixtures are given in Figs. 6, 7 and 8, respectively. At low and high AOS concentration it was possible to observe some preferred orientation of decane molecules (Figs. 6a and 7a). Those images suggested good affinity and strong interaction of decane molecules with the graphite surface which could explain the raise of the first peak in the density profiles (Fig. 1b).

In the case of the systems with betaine molecules different features were observed. At low betaine concentration it was not observed any preferred orientation (Fig. 6b), the molecules were more disordered than those molecules interacting with AOS at the same surfactant concentration. As the surfactant concentration increased the same tendency was observed in the adsorbed decanes, i.e. without any preferred orientation even at the highest concentration (Fig. 7b). These results were in agreement with those given in the density profiles of Fig. 1c where it was observed that the first adsorbed layers looked alike each other at all surfactant concentrations. Moreover, the results suggested that, due to the betaine surfactant, the alkane–graphite interactions were reduced helping removal of decane from the surface.

The orientation of decane molecules on the graphite surface with the surfactant mixture is shown in Fig. 8. At low betaine concentration it was observed some orientation of the decane molecules (see e.g. Fig. 8a) similar to that observed in Fig. 6a. As the betaine concentration increased it was not possible to define a preferred orientation and, when the mixture is rich in betaine molecules the decane molecules on the surface present more uniform orientations (e.g. see Fig. 8b). Those results suggest that the attraction of decane with the graphite substrate

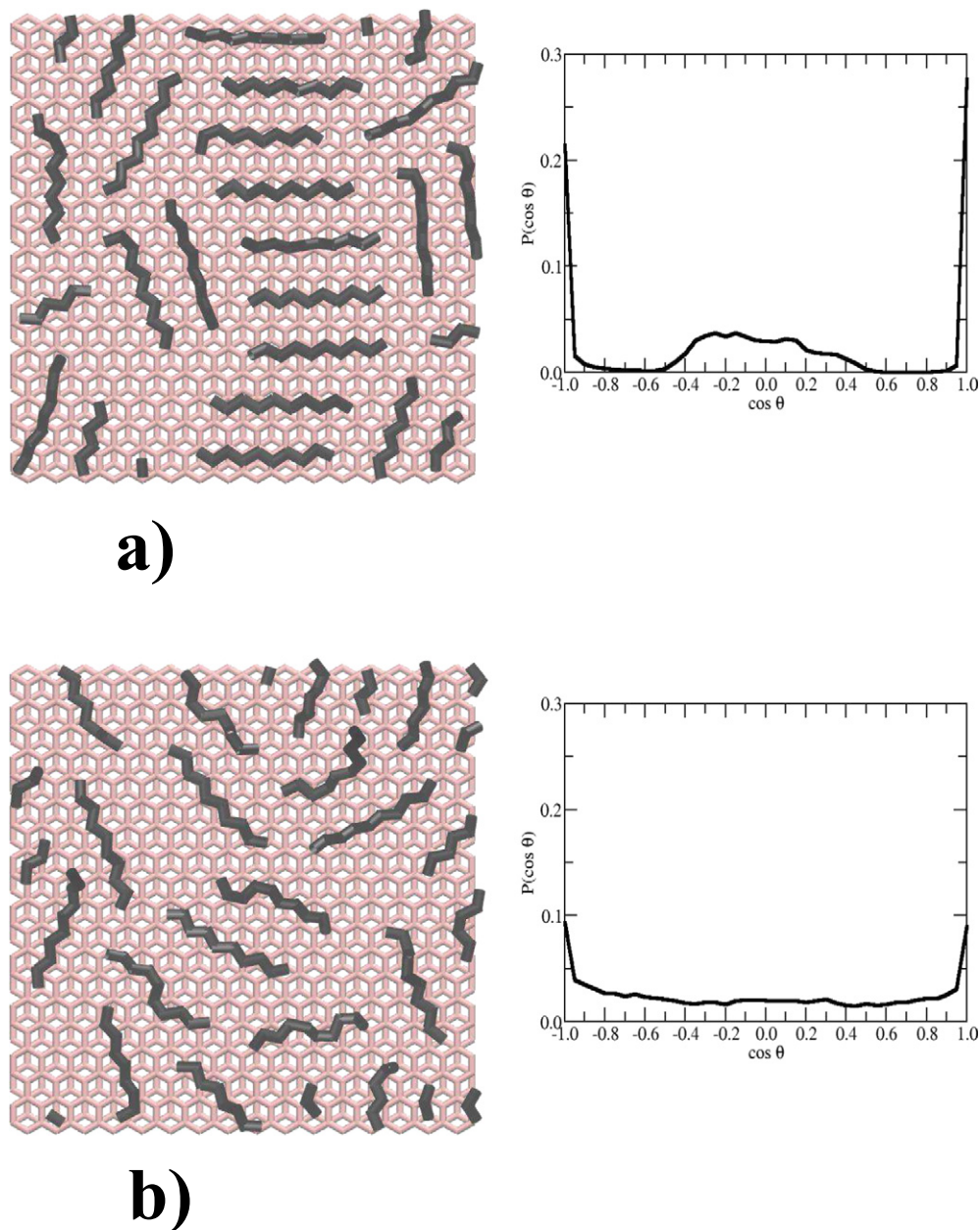


Fig. 6. Snapshots (left) and orientation probability (right) of decane molecules on the first adsorbed layer at surfactant concentration of 0.0021 for a) AOS and b) betaine. Decane molecules are given in grey and graphite substrate in pink.

changed as the betaine concentration increased by modifying adsorption of decane molecules from the surface.

4. Conclusions

A set of computer simulations were carried out to study the removal of decane molecules on a graphite surface interacting with AOS and betaine molecules and a mixture of both surfactants. From all the above results it was observed that both surfactants break water–hydrocarbon interface, however, they did it in different ways. In each layer distinct features were depicted which lead to a different behaviour of the decane phase. Molecular dynamics simulations for several surfactant concentrations were conducted and different effects on the alkane desorption for each surfactant was depicted. The anionic AOS molecules had less

effect on the decanes whereas the zwitterionic surfactants (betaines) had more influence on the removal of the alkane molecules. Since the betaine backbone likes water (due to the electrostatic interactions) the surfactant chains did not move deep into the oil phase and they stayed on the interface. As the surfactant concentration increased the betaine–water attraction also increased and betaine moved away from the solid surface with attached decanes in the surfactant tails which could explain the appearance of an additional alkane layer. However, the best removal was obtained for the AOS/betaine mixture with maximum desorption ratio at a 0.76/0.24. Despite the works on solid surfaces using surfactants (e.g. [22–24]), as far as we know, there are not reports of a specific concentration to enhance adsorption (desorption). Here, we observed a competition between the interactions of surfactants with water and with decane until an optimal ratio concentration was

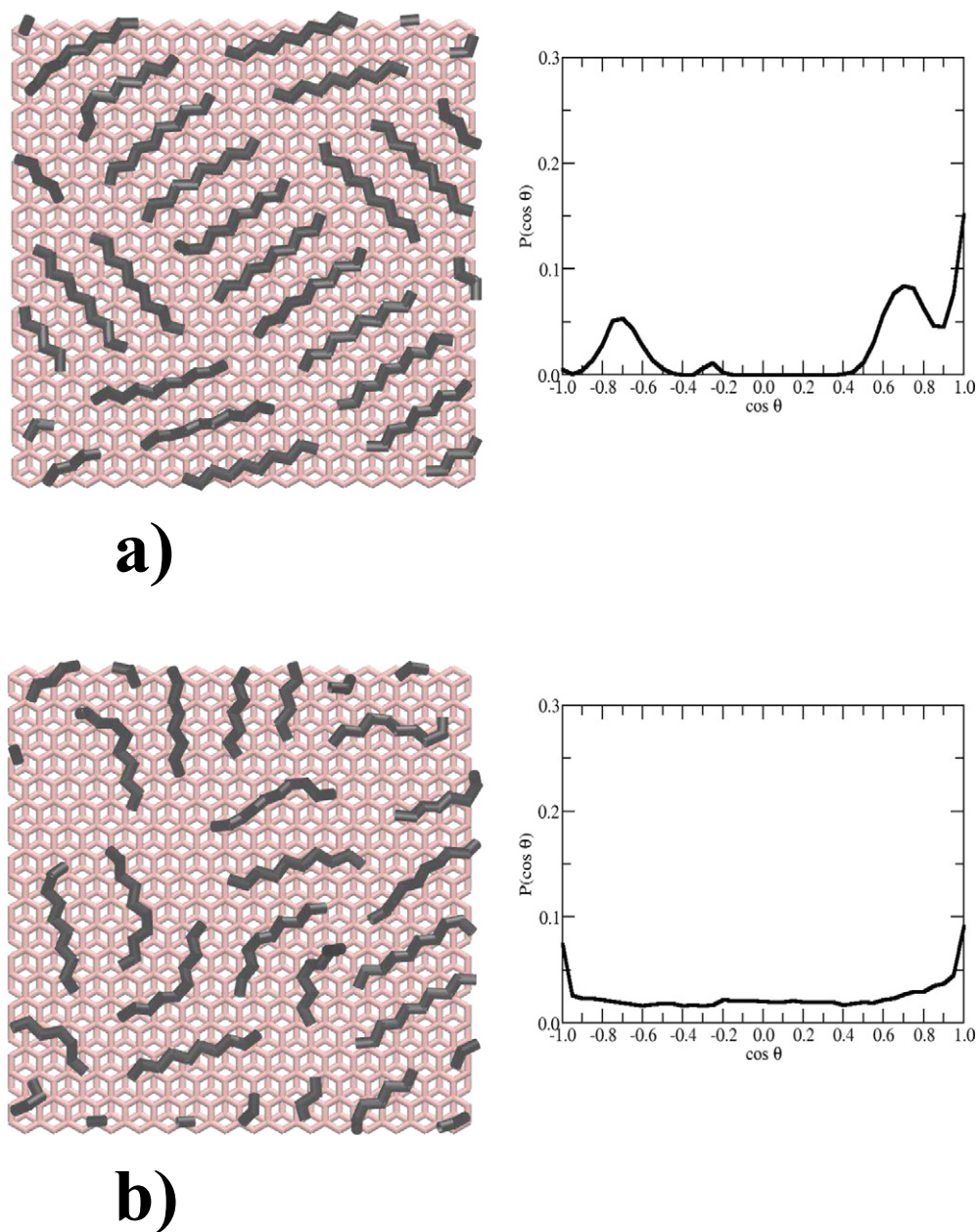


Fig. 7. Snapshots (left) and orientation probability (right) of decane molecules on the first adsorbed layer at surfactant concentration of 0.0143 for a) AOS and b) betaine. Decane molecules are given in grey and graphite substrate in pink.

reached which produced better removal of decane molecules from the solid surface.

From previous experimental works people have found that AOS and betaine surfactants exhibit good foam stability in the presence of oil while the mixture presents less stability [32,33] and that amphoteric surfactants help separation of oil-in-water emulsions [34]. Then, it seems that our systems have those contributions, on one hand the AOS helps the stability of the system and on the other hand the betaine in the mixture promotes separation of decane molecules which could explain why the mixture works better for removal of the alkane from the surface.

Finally, It is not clear if there is a unique ratio concentration in mixtures to enhance desorption from solids and more simulations will be needed to have a general conclusion (they are considered for a future work), nevertheless, we think that all of these results can give us more insights to understand much better the removal and desorption of alkane phases from solid surfaces.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.molliq.2014.11.023>.

References

- [1] M.J. Rosen, Synergism in mixtures containing zwitterionic surfactants, *Langmuir* 7 (1991) 885–888.

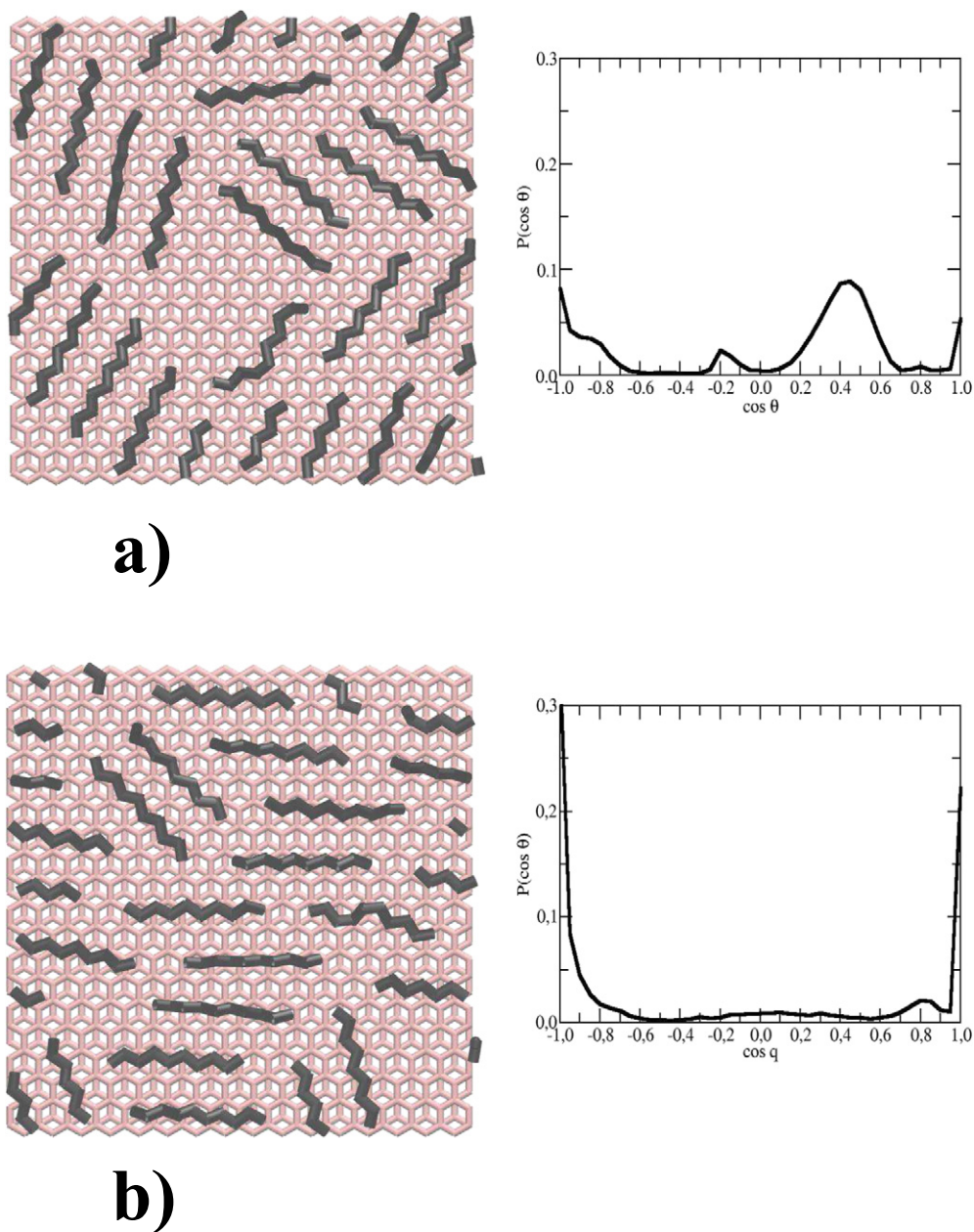


Fig. 8. Snapshots (left) and orientation probability (right) of decane molecules on the first adsorbed layer at two different betaine surfactant concentrations in the AOS/betaine mixture a) 0.0017 and d) 0.0062. Decane molecules are given in grey and graphite substrate in pink.

- [2] K. Nyuta, T. Yoshimura, K. Tsuchiya, H. Sakai, M. Abe, H. Iwase, Zwitterionic heterogemini surfactants containing ammonium and carboxylate headgroups 2: aggregation behaviour studied by SANS, DLS, and cryo-TEM, *J. Colloid Interface Sci.* 370 (2012) 80–85.
- [3] J. Saccani, S. Castano, F. Beaurain, M. Laguerre, B. Desbat, Stabilization of phospholipid multilayers at the air–water interface by compression beyond the collapse: a BAM, PM-IRRAS, and molecular dynamics study, *Langmuir* 20 (2004) 9190–9197.
- [4] Y. Tian, J. Umemura, T. Takenaka, Ultraviolet–visible absorption and resonance Raman spectra of azobenzene-containing amphiphile monolayers adsorbed at the acidic aqueous solution/carbon tetrachloride interface, *Langmuir* 4 (1998) 1064–1066.
- [5] J.C. Conboy, M.C. Messmer, G. Richmond, Effect of alkyl chain length on the conformation and order of simple ionic surfactants adsorbed at the D_2O/CCl_4 interface as studied by sum-frequency vibrational spectroscopy, *Langmuir* 14 (1998) 6722–6727.
- [6] A. Bera, S. Kissmathulla, K. Ojha, T. Kumar, A. Mandal, Mechanistic study of wettability alteration of quartz surface induced by nonionic surfactants and interaction between crude oil and quartz in the presence of sodium chloride salt, *Energy Fuels* 26 (2012) 3634–3643.
- [7] K.-D. Wantke, H. Fruhner, J. Ortegren, Surface dilatational properties of mixed sodium dodecyl sulfate/dodecanol solutions, *Colloids Surf. A Physicochem. Eng. Asp.* 221 (2003) 185–195.
- [8] P.A. Kralchevsky, K.D. Danov, V.L. Kolev, G. Broze, A. Mehreteab, Effect of nonionic admixtures on the adsorption of ionic surfactants at fluid interfaces. 1. Sodium dodecyl sulfate and dodecanol, *Langmuir* 19 (2003) 5004–5018.
- [9] C.E. McKenna, M.M. Knock, C.D. Bain, First-order phase transition in mixed monolayers of hexadecyltrimethylammonium bromide and tetradecane at the air–water interface, *Langmuir* 16 (2000) 5853–5855.
- [10] A. Bumajdad, J. Eastoe, P. Griffiths, D.C. Steytler, R.K. Heenan, J.R. Lu, P. Timmins, Interfacial compositions and phase structures in mixed surfactant microemulsions, *Langmuir* 15 (1999) 5271–5278.
- [11] J. Penfold, E.J. Staples, I. Tucker, R.K. Thomas, The structure of mixed surfactants at the airwater interface, *Colloids Surf. A: Physicochem. Eng. Asp.* 155 (1999) 11–26.
- [12] M. Jäschke, H.-J. Butt, H.E. Gaub, S. Manne, Surfactant aggregates at a metal surface, *Langmuir* 13 (1997) 1381–1384.
- [13] S. Manne, J.P. Cleveland, H.E. Gaub, G.D. Stucky, P.K. Hansma, Direct visualization of surfactant hemimicelles by force microscopy of the electrical double layer, *Langmuir* 10 (1994) 4409–4413.

- [14] D.C. McDermott, J. McCarney, R.K. Thomas, A.R. Rennie, Study of an adsorbed layer of hexadecyltrimethylammonium bromide using the technique of neutron reflection, *J. Colloid Interface Sci.* 162 (1994) 304–310.
- [15] N.C. Christov, N.D. Denkov, P.A. Kralchevsky, K.P. Ananthapadmanabhan, A. Lips, Synergistic sphere-to-rod micelle transition in mixed solutions of sodium dodecyl sulfate and cocoamidopropyl betain, *Langmuir* 20 (2004) 565–571.
- [16] K.D. Danov, S.D. Kralchevska, P.A. Kralchevsky, K.P. Ananthapadmanabhan, A. Lips, Mixed solutions of anionic and zwitterionic surfactant (betaine): surface-tension isotherms, adsorption, and relaxation kinetics, *Langmuir* 20 (2004) 5445–5453.
- [17] X. Domingo, in: E.G. Lomax (Ed.), *Amphoteric surfactants*, Surfactant Science Series, vol. 59, Marcel Dekker, New York, 1996 (Chapter 3).
- [18] K. Tsujii, *Surface Activity: Principles, Phenomena, and Applications*, Academic Press, San Diego, CA, USA, 1998.
- [19] E.S. Basheva, D. Ganchev, N.D. Denkov, K. Kasuga, N. Satoh, K. Tsujii, Role of betaine as foam booster in the presence of silicone oil drops, *Langmuir* 16 (2000) 1000–1013.
- [20] X. Hu, Y. Li, H. Sun, X. Song, Q. Li, X. Cao, Z. Li, Effect of divalent cationic ions on the adsorption behavior of zwitterionic surfactant at silica/solution interface, *J. Phys. Chem. B* 114 (2010) 8910–8916.
- [21] Q. Liu, S. Yuan, H. Yan, X. Zhao, Mechanism of oil detachment from a silica surface in aqueous surfactant solutions: molecular dynamics simulations, *J. Phys. Chem. B* 116 (2012) 2867–2875.
- [22] E. Lopez-Chavez, A. Garcia-Quiroz, R. Muñoz-Vega, J.I. Benitez-Puebla, L.S. Zamudio-Rivera, J.-M. Martinez-Magadan, E. Buenrostro-Gonzalez, R. Hernandez-Altamirano, Density functional theoretical study of the interaction of geminal zwitterionic liquids with limestone, regarding the behavior of the wettability parameter, *J. Chem. Eng. Data* 57 (2012) 3538–3542.
- [23] K.A. Rezaei, R. Denoyel, A.A. Hamouda, Wettability of calcite and mica modified by different long-chain fatty acids (C18 acids), *J. Colloid Interface Sci.* 297 (2006) 470479.
- [24] H. Dominguez, Structure of the SDS/1-dodecanol surfactant mixture on a graphite surface: a computer simulation study, *J. Colloid Interface Sci.* 345 (2010) 293–301.
- [25] H. Dominguez, Structural transition of the sodium dodecyl sulfate (SDS) surfactant induced by changes in surfactant concentrations, *J. Phys. Chem. B* 115 (2011) 12422–12428.
- [26] E. Nuñez-Rojas, H. Dominguez, Computational studies on the behaviour of sodium dodecyl sulfate (SDS) at TiO₂(rutile)/water interfaces, *J. Colloid Interface Sci.* 364 (2011) 417–427.
- [27] L. Yan, S. Zhu, X. Ji, W. Lu, Proton hopping in phosphoric acid solvated nafion membrane: a molecular simulation study, *J. Phys. Chem. B* 111 (2007) 6357–6363.
- [28] W.D. Cornell, P. Cieplak, C.I. Bayly, I.R. Gould, K.M. Merz, D.M. Ferguson, D.C. Spellmeyer, T. Fox, J.W. Caldwell, P.A. Kollman, A second generation force field for the simulation of proteins, nucleic acids, and organic molecules, *J. Am. Chem. Soc.* 117 (1995) 5179–5197.
- [29] W.L. Jorgensen, J. Tirado-Rives, The OPLS [optimized potentials for liquid simulations] potential functions for proteins, energy minimizations for crystals of cyclic peptides and crambin, *J. Am. Chem. Soc.* 110 (1998) 1657–1666.
- [30] S.K. Nath, F.A. Escobedo, J.J. de Pablo, On the simulation of vapor liquid equilibria for alkanes, *J. Chem. Phys.* 108 (1998) 9905–9911.
- [31] T.R. Forester, W. Smith, DL_POLY Package of Molecular Simulation, CCLRC, Daresbury Laboratory, Daresbury, Warrington, England, 1996.
- [32] G.J. Hirasaki, C.A. Miller, O.G. Raney, M.K. Poindexter, D.T. Nguyen, J. Hera, Separation of produced emulsions from surfactants enhanced oil recovery processes, *Energy Fuels* 25 (2011) 555–561.
- [33] M. Simjoo, T. Rezaei, A. Andrianov, P.L.J. Zitha, Foam stability in the presence of oil: effect of surfactant concentration and oil type, *Colloids Surf. A Physicochem. Eng. Asp.* 438 (2013) 148–158.
- [34] A. Andrianov, R. Farajzadeh, M. Mahmoodi, M. Talanana, P.L.J. Zitha, Immiscible foam for enhancing oil recovery: bulk and porous media experiments, *Ind. Eng. Chem. Res.* 51 (2012) 2214–2226.