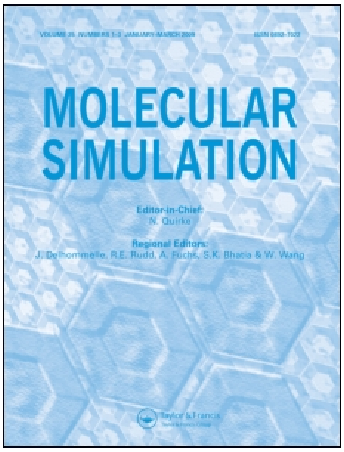

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

A molecular dynamics study of Na-dodecylsulfate/water liquid crystalline phase

A. H. Poghosyan[a]; G. A. Yeghiazaryan[a]; H. H. Gharabekyan[a]; J. Koetz[b]; A. A. Shahinyan[c]
[a] International Scientific-Educational Centre of National Academy of Sciences of Armenia, Yerevan, Republic of Armenia [b] Universität Potsdam, Institut für Chemie, Potsdam (Golm), Germany [c] The Institute of Applied Problems of Physics of the National Academy of Sciences of Armenia, Yerevan, Republic of Armenia

To cite this Article Poghosyan, A. H. , Yeghiazaryan, G. A. , Gharabekyan, H. H. , Koetz, J. and Shahinyan, A. A.(2007) 'A molecular dynamics study of Na-dodecylsulfate/water liquid crystalline phase', Molecular Simulation, 33: 14, 1155 — 1163

To link to this Article: DOI: 10.1080/08927020701613631

URL: http://dx.doi.org/10.1080/08927020701613631

Molecular Simulation, Vol. 33, No. 14, December 2007, 1155–1163

A molecular dynamics study of Na–dodecylsulfate/water liquid crystalline phase

A. H. POGHOSYAN†*, G. A. YEGHIAZARYAN†, H. H. GHARABEKYAN†, J. KOETZ‡ and A. A. SHAHINYAN¶

†International Scientific-Educational Centre of National Academy of Sciences of Armenia, 0019 Yerevan, Republic of Armenia
‡Universität Potsdam, Institut für Chemie, Karl-Liebknecht-Straße 24-25, Haus 25, 14476 Potsdam (Golm), Germany
¶The Institute of Applied Problems of Physics of the National Academy of Sciences of Armenia, 0014 Yerevan, Republic of Armenia

(Received June 2007; in final form August 2007)

We have performed a Series of long (about 130 ns) molecular dynamics simulations of a sodium dodecylsulfate/water liquid crystalline (LC) phase, consisting of 512 sodium dodecylsulfate and 15,000 water molecules, where the initial starting configuration is varied. In addition, the all atom and the united atom model were compared using NAMD and GROMACS codes with CHARMM27 and modified GROMOS87 force fields, respectively. Characteristic parameters, such as area per molecule, bilayer thickness, roughening, and orientation of the hydrocarbon chains in the hydrophobic core of the bilayer have been calculated. In general, the data obtained by means of molecular dynamics simulation are in agreement with the experimental X-ray diffraction data. However, only for the all-atom model, we found an excellent agreement with the experimental values of area per molecule and hydrocarbon chain packing parameters. Therefore, one can conclude that the use of a CHARMM27 all-atom force field, implemented in NAMD code, is the best approach for simulations of a SDS LC-phase.

Keywords: Lyotropic liquid crystals; Molecular dynamics; SDS bilayers

1. Introduction

It is already well established that surfactants, i.e. molecules consisting of a polar head and a long alkyl tail, can generate quite different self-assembled structures, e.g. lyotropic liquid crystalline ones, composed of individual lamellae of fluid amphiphilic molecules separated by a solvent. Surfactant bilayers have been intensively studied for many years, and can be considered as a simple model for biological membranes [1–3]. It has to be mentioned here that surfactants have been found already a wide range of applications in everyday life as well as in industrial processes. For instance they are present in detergents, cosmetics, pharmaceuticals, food processing, agrochemicals, paints, paper coatings, etc. [4,6,7]. In addition, they play a vital role in the oil industry, e.g. in enhanced oil recovery [5]. In many applications the solubilization of hydrophobic probes in surfactant based self-assembled systems, e.g. microemulsions or lamellar liquid crystalline structures, is of high importance [8].

For a more detailed characterization of the surfactant bilayer different methods can be used, such as small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS; [1,9,10]). For example, the compressibility modulus of lamellar liquid crystalline systems can be measured directly using a surface force apparatus [11], and the elasticity of the bilayer (expressed in terms of the bending elasticity constant) can be obtained by neutron spin echo experiments.

By using the well-known ionic surfactant molecule SDS, i.e. sodium dodecylsulphate, a simple model of micelles was discussed by Woods and coworkers [13]. Anianson and Wall developed a model to describe the dynamics of micellization by a fast and slow relaxation process. Therefore, the fast relaxation (in the s range) is related to the kinetic constants $k-$ and $k+$ for a monomer exchange from the micelle [21]. Watanabe and Klein investigated the structural and dynamical aspects of the two-dimensional hexagonal mesophase of sodium octanoate and water, discussing the amphiphilic aggregated micelles [14]. During the last decade, with the

---

*Corresponding author. Email: sicnas@sci.am

ISSN 0892-7022 print/ISSN 1029-0435 online
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020701613631

increase of computational power, the atomic-level computer simulations have been used as an additional method to study such self-assembled systems in more detail [12]. Recently computer simulations of thin SDS-films, i.e. the so called "Newton black films", coated on water [18–20] were performed. Furthermore, interesting features of water and SDS molecules have been investigated by Faraudo *et al.* [19,20].

A 5 ns atomic scale MD simulation of a 60 SDS/7579 water micellar system has been published by Bruce and coworkers [12,15] where the behavior of water in different electrostatic environments was examined, as well as some structural properties of micelles. Shelley and coauthors performed an 182 ps MD simulation of 42 SDS micelles in water [16] and MacKerell reported about a 120 ps simulation of 60 SDS micelles [17]. That means MD simulations of SDS-based systems were focused predominantly on micellar structures [12–17]. In the present study, we perform the molecular dynamics (MD) simulation of the Na–dodecylsulfate/water system in order to improve our knowledge of the dynamical and structural properties of the SDS-based LC-phase. Overall, our MD simulations last about 130 ns with 512 SDS/15,000 water molecules, accordingly reaching up to ~55,000 atoms for Series A and B (united atom), and about 67,000 atoms for Series C (all atom). The main structural parameters, such as area per molecule, bilayer thickness, surface roughening parameter, diffusion coefficients, and hydrocarbon chain orientation have been calculated and compared with X-ray experimental data in order to verify the accuracy of MD simulations. Three series of MD experiments (Series A, B, and C) were realized.

2. Construction and simulation details

Construction of Series A

The SDS molecule was built using Hyperchem (Hypercube Inc.) software and was replicated to create a bilayer consisting of 64 SDS plus 64 counterions using MDesigner [22] software. After adding 15,000 water molecules to 512 SDS molecules, that means about 29 water molecules per SDS molecule, the final system was created by replication of the initial system (by placing 4 × 64 patches), and subjected to an energy minimization and 50 ns MD simulation (in the *NPT* ensemble).

Construction of Series B

The starting configuration of Series A was subjected to the ~20 ns MD simulation taking into account the surface tension ($NP_N\gamma T$ ensemble), by varying the value of surface tension between 50 to 200 dyn/cm. This procedure was applied in order to increase the area per molecule, and to decrease the bilayer thickness, respectively. Finally, we received a bilayer thickness of about 8 nm starting with an initial projected area per molecule of about 0.31 nm^2. After a short 200 ps MD simulation with constant volume, the additional 50 ns of MD simulation in the isothermal-isobaric *NPT* ensemble was performed. It has to be mentioned here, that it is better to start with a canonical *NVT* ensemble, before proceeding to another ensemble.

Simulation details (Series A and B)

By using the SPC [23] water model, the partial charges and force field parameters of SDS molecule were generated using the Dundee PRODRG server [24] with some modification from GROMOS87 united atom force field [25].

Due to the united atom model implemented in the force field, each SDS molecule contains 17 atoms, and on the whole the system contains about 55,000 atoms. The simulations were performed using the GROMACS software [26] with a 3 fs time step. Three-dimensional periodic boundary conditions were used. For both simulations (Series A and B) the temperature was fixed at $T = 298$ K and the pressure at 1 atm. The temperature was controlled on the one hand by means of the Berendsen coupling method [27] using separate thermostats for the SDS surfactants and water molecules, and on the other hand the pressure was maintained using the Parrinello-Rahman method [28] scaling all directions isotropic to 1 atm with the time constant of 1.0 ps. The *semi*-explicit SHAKE algorithm [29] for constraining lengths of the bonds was used with a tolerance of 10^{-5}. The list of non-bonded pairs was updates every 20 fs. The non-bonded van der Waals interaction was truncated to 2 nm and for long-range Coulomb interactions the PME [30] was used with the tolerance of 10^{-6}. During the simulation the coordinates of atoms were saved every 30 ps.

The simulation was performed on Linux cluster (ARMCLUSTER) using 50 processors and the total CPU time was estimated about 50,000 CPU/h.

Construction of Series C

The SDS molecule was constructed using the Hyperchem (Hypercube Inc.) software. The SDS molecule was inserted into the bulk water and simulated for 200 ps to minimize the energy. After the minimizing it was randomly rotated and replicated to create a bilayer with 512 SDS plus 512 counterions using VMD package [31]. Adding about 15,000 water molecules (29 water molecule per SDS), the system was equilibrated by minimizing the potential energy for 2.000 steps. After realizing the simulation in *NPT* ensemble about 500 ps with constraining atom's movement in *z* direction, till the time when the value of area per SDS comes close to the experimental value. Totally, the 10 ns of MD simulation was carried out in *NPT* ensemble.

Simulation details (Series C)

Basing on the TIP3P [32] model simulations were done using NAMD code with CHARMM27 all-atom force field [33]. The reference temperature was set to 298 K and to normal pressure (1 atm) using Langevin dynamics [34] with damping (or coupling) coefficient of 1 ps^{-1} and the modified Langevin piston [35] method, respectively. The PME [30] with the precision of 10^{-6}, was used for the long-range electrostatic interactions, and the van der Waals interactions were truncated at 12 Å with smoothly switching at 10 Å. The bonds were constrained using SHAKE [29] algorithm involving the hydrogen atoms. A 1 fs time step was used during the run. The list of non-bonded pairs was updates every 2 fs and the coordinates of atoms were saved every 25 ps.

The simulation were performed on ARMCLUSTER using 30 processors and the total CPU time was about 11,000 CPU/h.

3. Results and discussion

Structural parameters

One of the most important characteristics of the bilayer, which can be compared with the experimental data, is the area per molecule and the thickness of the bilayer. The average area per molecule for Series A was determined as to be seen in figure 1a. This parameter was calculated multiplying the *x* and *y* values of size of system divided by the number of molecules in a layer/256. At the end of simulation, between 40 and 50 ns, an average value of $\sim 0.2175\ \mathrm{nm}^2$ can be obtained, which is not in agreement with the experimental one. Note that our earlier experimental data on X-ray diffraction shows that the area per molecule of liquid crystalline SDS/water system (about 20–23 wt% of SDS) corresponds to $0.406\ \mathrm{nm}^2$ [1]. The area per surfactant molecule can be calculated experimentally from the slope of the surface tension vs. log[*c*] just before the cmc is reached. For ionic surfactant molecules, such as SDS, the experimentally given value is in the order of $0.40\ \mathrm{nm}^2$, as a result of the lateral repulsion between the head groups. By adding electrolytes, the lateral repulsion is reduced, and the area/surfactant ion for vertical orientation will decrease up to $0.2\ \mathrm{nm}^2$ [39]. The second parameter is the system thickness, i.e. the interlayer spacing, which is shown in figure 1b (for Series A).

The thickness was calculated from the bilayer normal *z* value obtained during the simulation time. With the 29 water/per SDS molecule hydration the estimated thickness fluctuates in the range between 11 and 11.44 nm. However, the experimental finding by means of SAXS measurements, performed by Koetz *et al.* [9], yield to an interlayer spacing of 8 nm at a water/SDS-decanol ratio of 2:1. Nevertheless, the interlayer spacing strongly depends on the weight ratio of water/amphiphile due to the swelling of the bilayer, as well as on the cosurfactant incorporated into the bilayer. The experimental result of pure SDS/water systems performed by us [1,40] shows $d = 5.9$ nm at 20–23 wt% of SDS.

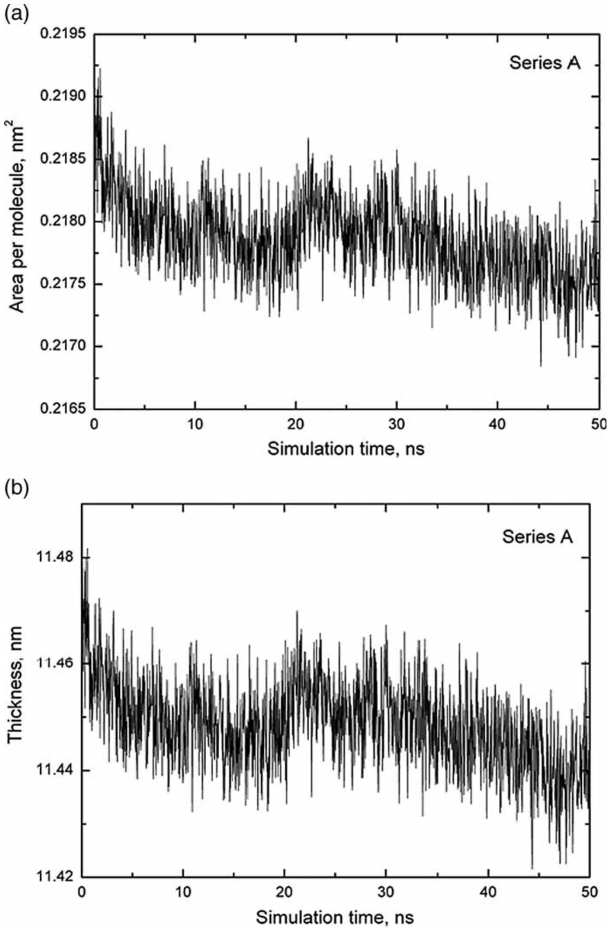

Figure 1a,b. Area per molecule and system thickness plotted against the time for Series A.

Therefore, we have performed additional 50 ns MD simulation changing the initial configuration (Series B). As the starting configuration for Series B, we decrease the interlayer spacing, and therefore the area per molecule increases to $0.31–0.32\ \mathrm{nm}^2$, which is in much better agreement with the experimental data. The time evaluation of area per molecule and bilayer thickness is shown in figure 2a,b. During the 50 ns long simulation the system thickness value is fluctuated in the range of 8 nm and the value of area per molecule is about $0.31\ \mathrm{nm}^2$. However, the value of area per molecule is still far from the experimental value. One can assume that the underestimated value of the area per molecule can be related to the united atom character of the system. That means, the increase of the van der Waals radius of the C—H pairs may lead to the increase of area per molecule and therefore, to a decrease of the interlayer spacing. However, it seems to be much better to testify the system in presence of all H-atoms, the so called “all-atom” character. In order to check this assumption an additional 10 ns of MD simulation (Series C) was performed. The corresponding curves of area per molecule and bilayer thickness are presented in figure 3a,b. After a couple of ns,

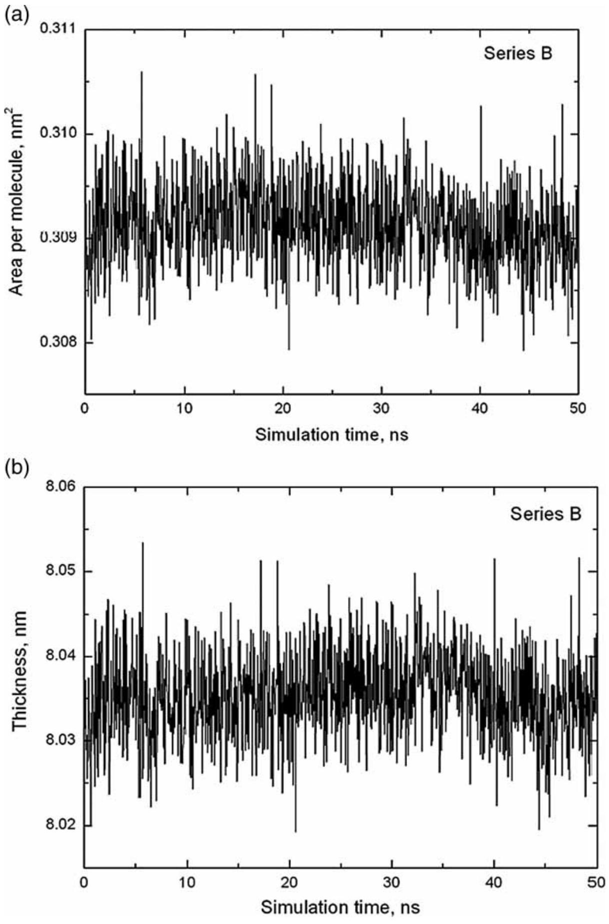

Figure 2a,b. Area per molecule and system thickness plotted against the time for Series B.

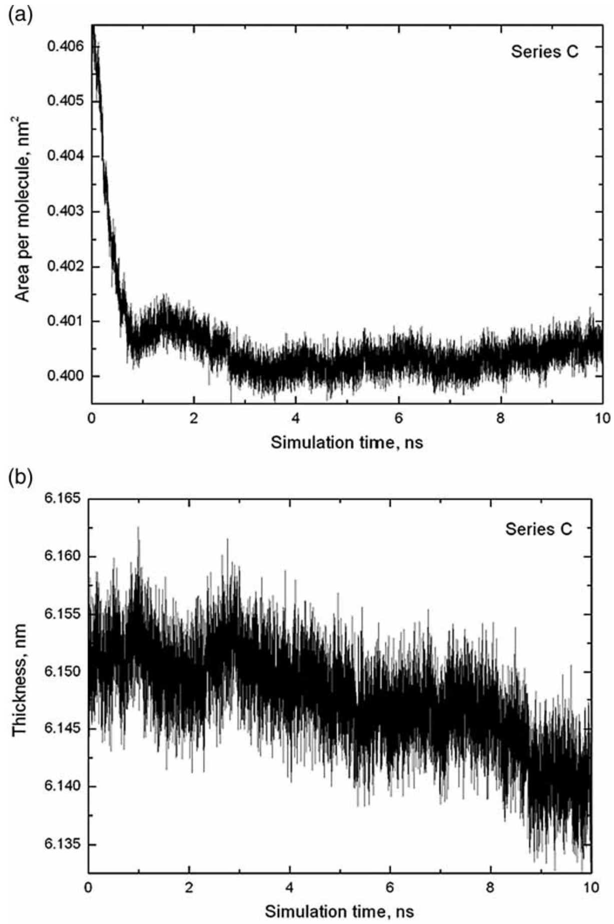

Figure 3a,b. System thickness and area per molecule plotted against the time for Series C.

the value was fluctuated in the range of 0.40 nm^2 and remains almost the same at the whole period of simulation, which is in excellent agreement with the experimental data. The corresponding bilayer thickness with an average value of 6.14 nm, is also in good agreement with experimental data [40]. Keep in mind, that the SAXS measurements in Ref. [9], indicating an interlayer spacing of 8 nm, were done in a cosurfactantbased system containing decanol as a cosurfactant. Therefore, the calculated pure SDS/water bilayer of about 6 nm is in good agreement.

Generally, it has to be mentioned here that the interlayer spacing, observed from SAXS measurements, is the layer repeat unit, i.e. the water layer with headgroup of amphiphiles and the hydrophobic core including the hydrocarbon chains of amphiphilic molecules. Respectively, the MD simulation thickness means the bilayer thickness plus water layers from each leaflet.

In fact, for both cases (united and all-atom characters), we receive a lamellar phase during a long time MD and the main structural parameters are in agreement with X-ray diffraction data [1], however, according to the phase diagram performed by Kekicheff and coworkers [41] the transition temperature related to lamellar L_α phase is detected above than room temperature (about 49.8°C) and at low water content. Hence, instead of bilayer structure the micellar structure might be observed and the question of how long we should simulate the surfactants to reach the micellar phase is still unclear. We suppose that in fact such metastable phase exists and further calculation of parameters will give us answer on this question.

In order to visualize the structure in more detail, we provide snapshots of the SDS/water at the end of simulation for Series A, B and C, which is a cross-section view perpendicular to the bilayer plane. In Series A, after the long time simulation, undulations occur due to the z-axis normal motions of amphiphilic molecules, while in Series B and Series C one can see a roughening of the surface with vertical displacement of SDS molecules. Therefore we estimated the roughness function, which is computed as:

$$\xi(\vec{R}) = \sqrt{< (z(\vec{r}) - z(\vec{r} + \vec{R}))^2 >} \qquad (1)$$

where the $z(\vec{r})$ and $z(\vec{r} + \vec{R})$ are the z-axis coordinates of two sulfur atoms in the same leaflet. The curves calculated from Series B and C is presented in figure 5. Note that the theoretical calculations claim a value of ~2.4 Å [37], assuming that the surface tension of corresponding monolayer is ~38 mN/m, and the experiment reveal a

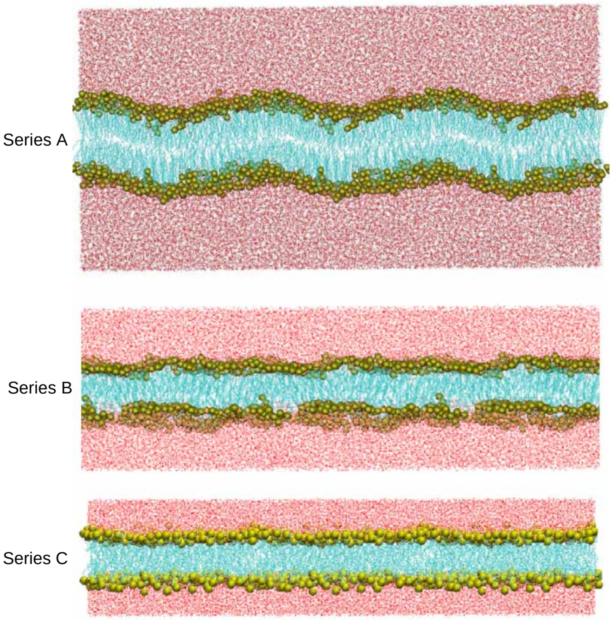

Figure 4a,b and c. The cross-sectional snapshot view of SDS/water bilayer at the end of simulation (Series A, B and C). The S is drawn as a sphere, while the chains and water molecules are given as sticks. The colouring scheme C is cyan, O is red, H–silver. The system is replicated in *y*-direction (colour in online version).

value of 2.7 Å [38]. Our calculations show that the roughness function receives a value of $\xi(R \rightarrow \infty) \sim 2.6$ Å for Series B and ~ 2.5 Å for Series C, which is a bit lower than the experimental data. One can see well melted and disordered distributions of hydrocarbon chains for both simulations.

In addition the radial distribution functions (RDF) from sulphur to sodium and from sulphur to water oxygen were calculated for both series. However, there are no significant differences in both cases, instead of a more sharp peak in case of Series B. From RDF curves, given in figure 6a (S—Na) and 6b (S—O_w), one can detect peaks for S to water oxygen at 0.386 nm, which is in agreement with MD data in [14]. From RDF curve one can differ between three water regions, that means a first shell at 0.386 nm, a second shell at 0.667 nm and bulk water. Figure 6b shows the distribution of sodium counterions indicating an ordering of counterions. There are two peaks, one sharp in the region of 0.3–0.33 nm and another one at the distance of 0.62 nm. It must be noted that about 70–80% of sodium counterions are in the first shell covered at about 0.4–0.45 nm from sulphur atoms, which is a hint for the counterion condensation.

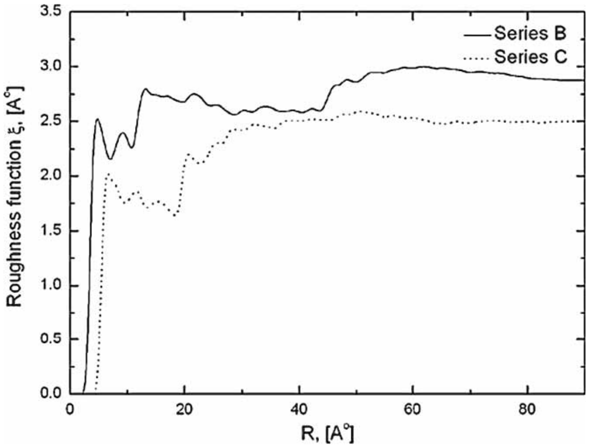

Figure 5. The monolayer roughness function calculated for Series B and C.

Chain orientation

It's also important to examine the orientation of hydrocarbon chain molecules. Therefore, the average hydrocarbon chain and the orientation order parameter, later formulated as:

$$S_{zz}^{\mathrm{mol}} = \frac{3}{2} < \cos^2 \alpha_i > -\frac{1}{2} \tag{1}$$

have to be considered.α_i- is the angle between the z -axis of the simulation box and the molecular axis, defined as a vector from C_{i-1} to C_{i+1} C carbon atom and the brackets

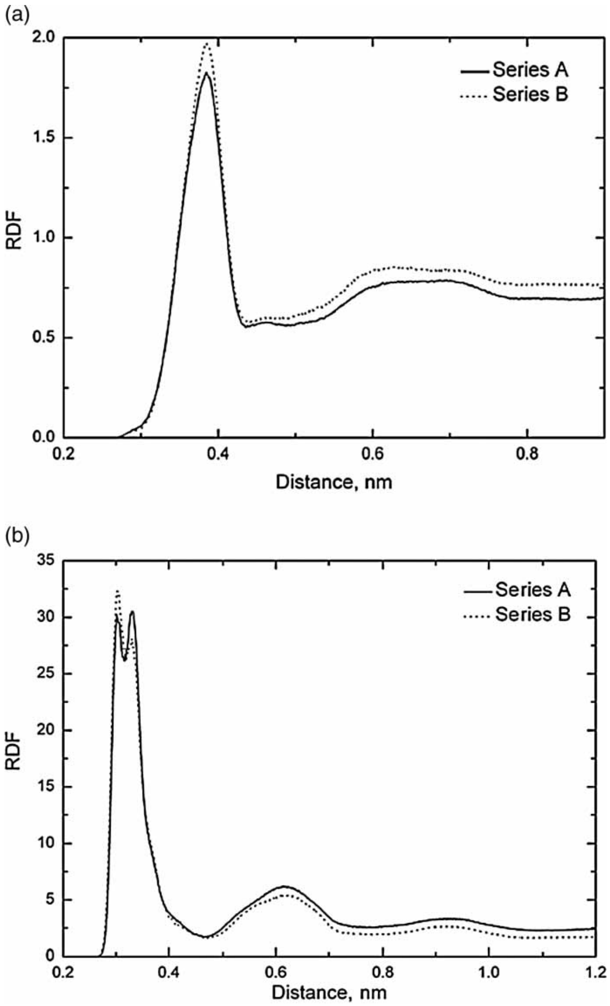

Figure 6. (a) The radial distribution functions from sulphur to water oxygen for Series A and B. (b) The radial distribution function from sulphur to sodium counterions for Series A and B.

denote the ensemble and time average. By means of deuterium magnetic resonance spectroscopy the S_{CD} can be obtained experimentally, which is related to the orientation parameter $-2S_{\mathrm{CD}} = S_{zz}^{\mathrm{mol}}$ assuming axial symmetry in the segment motion. We have estimated the S_{CD} from MD simulation data and plotted in figure 7, together with an another MD simulation data of hydrocarbon chain orientation order parameters of the pure L_{α} phase of SDS given by Bandyopadhyay *et al.* [36]. Our simulation data from Series A and B are not in agreement with data provided in [36], however, the calculated data from Series C are in excellent agreement with the data in Ref. [36]. We obtained almost the same value in the middle of hydrocarbon tail (C_2—C_6) and a little shift from the experimental data at the end of the hydrocarbon chain.

In order to better understand the conformation of SDS hydrocarbon chains in case B, we have calculated the distribution of dihedral angles and the corresponding curves are demonstrated in figure 8. The symmetry of the plots shows the equilibrium state of the system and the typical behavior expected for hydrocarbon chains in the SDS bilayer. One can see the maximums at *gauche* $^{\pm}$ ($\pm 60°$) conformations and at 180° for the *trans* conformation, although the presence of some *gauche* defects (*gauche* maxima is shifted from $\sim 65°$), which is due to the disordered arrangement of hydrocarbon chains of SDS molecules.

The mean hydrocarbon chain length is also calculated and the average value of ~ 1.28 nm is received for Series B and ~ 1.12 nm for Series C. The distance is computed from the mean (time averaged) distance between the terminal CH_3 group and ester oxygen bonded CH_2 group. The mean hydrocarbon chain length also can be estimated from the electron density peak-to peak distance. The obtained lengths was compared with the data (11.68 ± 0.64 Å for the pure lamellar phase of the surfactant in Ref. 36) and it is obvious that the values calculated from Series C are in good agreement with provided data ($l \approx 11.6$ Å).

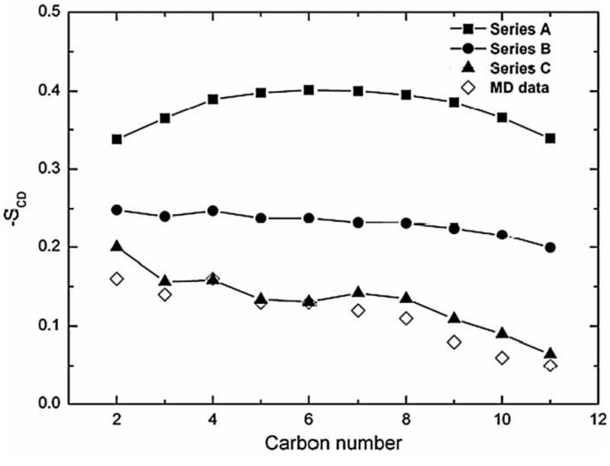

Figure 7. The orientation order parameters for Series A, B and C in comparison to another simulation data from Ref. [36].

Comparing the chain orientation parameters, one can conclude that the allatom character is in much better agreement with the experimental data.

Electron density

We have determined also the electron densities of different components of the amphiphilic molecule and water, including whole SDS, Na, water and the SO_4 headgroup.

In figure 9a–c, the electron density curves are plotted obtained from MD simulation trajectories by averaging all the conformations. It is obvious, that there is asymmetry, although some slightly differences at the hydrocarbon volume between two layers from Series A and B are

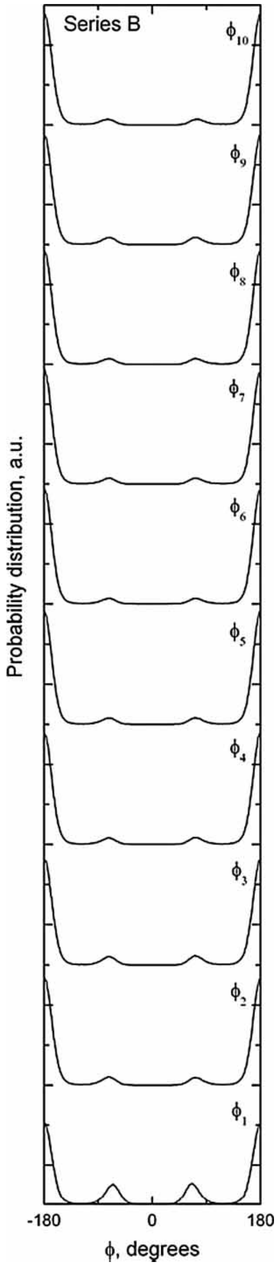

Figure 8. The probability distribution of dihedral angles of the SDS chain. Numeration of angles start from O. e.g. $\phi_1 = O - C1 - C2 - C3$.

available. From EDP one can estimate an average distance between the head group maxima on both leaflets of bilayer, which can be related to *ca.* 3 nm for case A, *ca.* 2.25 nm for Series B, and about 2 nm for Series C. If we take into account that the length of one SDS molecule in all-trans conformation, consisting of n hydrocarbon atoms can be defined by the following formula:

$$l \doteqdot (1.265n + 3A^{\circ}) \qquad (2)$$

where 3 Å is the length of the headgroup of the surfactant molecule and n is the number of carbon atoms $n = 12$, the length of the SDS molecule can be calculated to $l \doteqdot 1,9$ nm. Considering that the value of head group maxima for both cases corresponds to both tilting and penetration of hydrocarbon chains, it can be also calculated from MD simulation trajectories and snapshots from figure 4a–c.

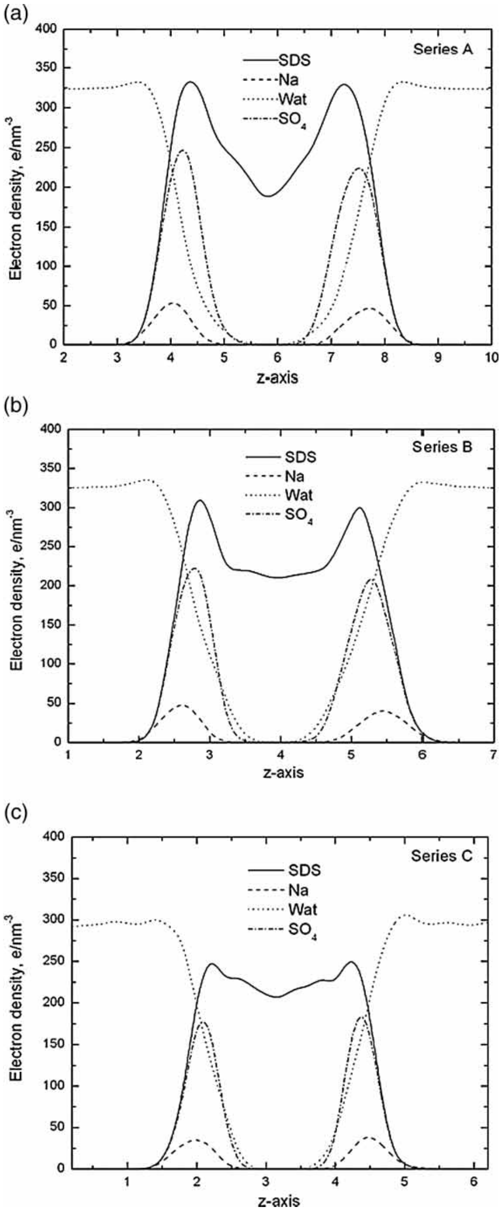

Figure 9a,b and c. The electron density profiles for SDS, sodium, water and headgroup. The center of bilayer is in ~5.7 nm for Series A, ~4 nm for Series B and ~3.2 nm for Series C.

The experimentally given electron density diagrams, demonstrated by us in Ref. [39], show peak pairs that distances indicate the interlayer spacing at a certain water concentration in the range between 2.8 and 10 nm. However, the interlayer spacing of 2.8 nm is related to the extrapolated value at zero water concentration. The sodium counterions are situated near the headgroup as to be seen in the profile.

Water properties

We also examine the movements of amphiphilic molecules and calculate the lateral diffusions and the corresponding coefficients for SDS and water molecules. To understand the lateral motions, we calculate the average mean displacement (MSD), defined as follows:

$$\mathrm{MSD} = \sum_{i}^{\mathrm{all}} < |\vec{r}_i(t) - \vec{r}_i(0)|^2 > \qquad (3)$$

where, the r_i (t) is the center of mass (COM) position of particle i at time t. Therefore, the lateral diffusion coefficient can be determined from the slope of MSD at long period. The diffusion coefficient for SDS $D_{\mathrm{SDS}}^{\mathrm{Series\,A}} = 4 \times 10^{-7}\,\mathrm{cm}^2/\mathrm{s}$, $D_{\mathrm{SDS}}^{\mathrm{Series\,B}} = 2.6 \times 10^{-7}\,\mathrm{cm}^2/\mathrm{s}$ and for water molecules the coefficient is $D_{\mathrm{wat}}^{\mathrm{Series\,A}} = 2.5 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{s}$, $D_{\mathrm{wat}}^{\mathrm{Series\,B}} = 2.33 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{s}$. These calculated values are in good agreement with experimental data, which claims that the diffusion coefficient of water is $\sim 5 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{s}$. In order to qualify the movements of sodium counterions, we have also calculated the sodium diffusion coefficient: $D_{\mathrm{wat}}^{\mathrm{Series\,A}} = 5 \times 10^{-7}\,\mathrm{cm}^2/\mathrm{s}$. In order to determine the orientation of water molecules, the average cosine of the angle between the dipole moment of water molecules and bilayer normal was calculated, as to be seen in figure 10. In profile near the headgroup, the dominant angle is $\sim 30 - 50°$. In addition we have calculated the charge density of SDS and sodium, and also the electric potential (data not shown).

4. Conclusions

Performing a Series of long MD simulations of SDS/water liquid crystalline system, we have analyzed the structural and dynamical parameters of the system and compared with available experimental findings. To check the united-atom model, we started two Series of long MD simulations with various initial startup configurations and received a disagreement of area per molecule and bilayer thickness with experimental data. In addition, we checked other parameters, in particular diffusion coefficients, radial distribution functions, orientational order parameters of hydrocarbon chains, surface roughness and electron densities. Our results for radial distribution function for

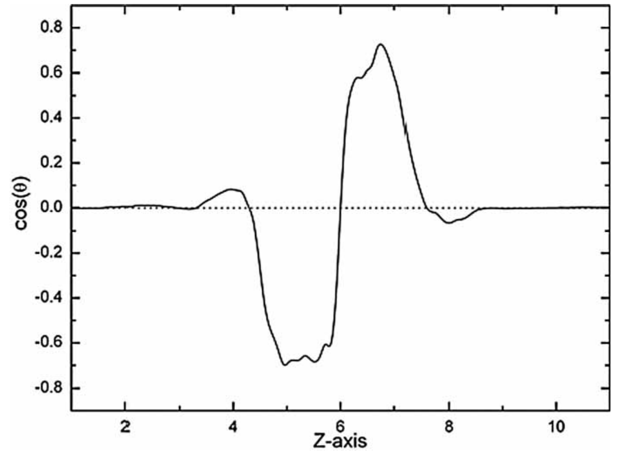

Figure 10. The mean cosine of the angle between the water dipole and the bilayer normal (*z*): Series A.

S—Ow and S—Na + display similar results as reported in previous simulations and show the ordered distribution of counterions, and give a hint for counterion condensation. The electron density profiles depending on the initial starting configuration are calculated and compared with experimental data. Differences occur only in the middle of the bilayer, i.e. the hydrocarbon core of bilayer. In case of Series B we have obtained a smeared part of profile in the middle of bilayer. Depending on initial starting configuration, we have calculated the orientation of hydrocarbon chains of SDS molecules. It is obvious that our simulation results are not in agreement with MD data. Although, the calculation of the probability distribution for rotation about the dihedrals of the chains of SDS molecules, shows the typical behavior expected for hydrocarbon chains in SDS bilayer. The later calculation was done for Series B.

To compare the models, we have also investigated the CHARMM27 force field with all-atom model, implemented in NAMD package. The all-atom model gave the best results in comparison to the experimental data. We have obtained $0.40\,\mathrm{nm}^2$ for area per molecule, which is in excellent agreement with the experiment [1]. Investigating the roughness function, we received the value of ~ 2.5 Å, being in the range of theory and experiment. Calculating the orientational order of hydrocarbon chains, we found a strong agreement with MD data [36] that means the all-atom model accurate reproduces the experiment. However, even the MD results are somewhat in agreement with experimental findings, it is obvious that the force field is still need to be improved in order to better reproduce experimental results. Anyway, we recommend the use of all-atom models for surfactant simulations.

It is also important to note that with a given concentration and temperature we receive a lamellar L_α phase with the accordance of our X-ray experimental data [1,40], however, on the other hand according to Kekicheff's calorimetric study [41], the transition temperature of L_α phase is 49.8°C and the concentration range is from 66.5 to ~87.3% SDS, i.e. lamella exists at SDS-rich content and high temperatures. As discussed previously, our simulations, which were done at ~20 wt% SDS (there is no data on 20 wt% SDS in phase diagram [41]) and at room temperature, were compared with small and wide angle X-ray diffraction data and the main parameters are in good agreement with data.

Unfortunately, we have no explanation of this disagreement, although it may be supposed that about 100 ns simulation time is not enough to reach equilibrium or such intermediate intervals really contain a number of metastable phases/mesophases with narrow range of compositions and in order to fill this gap it's better either to continue the simulation with same physical conditions to see further changes or do a new simulation at high temperature and SDS-rich content. On the other hand, we should take into account the initial configuration, and additional MD simulations are therefore essential by changing the startup configuration from bilayer to micellar with same properties. Anyway, these obtained effects should be subjected to the experimental re-checking.

The next step is to perform all-atom MD simulations to reveal the influence of polyelectrolytes on the structure of these liquid crystalline SDS/water bilayers.

Acknowledgements

The authors would like to express gratitude to Dr Vladimir Sahakyan and Dr Mikayel Gyurjian for great assistance and providing us with the access to the cluster (ARMCLUSTER).

References

[1] M.K. Minasyanc, V.A. Zakaryan, A.A. Shahinyan, I.G. Chistyakov. X-ray analysis of Na-dodecylsulfate–water system. *Kristallografiya (in Russian)*, **24**, 319 (1979).
[2] C. Tanford. *Hydrophobic Effect*, 2nd ed., Wiley, New York (1980).
[3] R.G. Larson. *The Structure and Rheology of Complex Fluids*, Oxford University Press, Oxford, New York (1999).
[4] L.L. Schramm, E.N. Stasiuk, D.G. Marangoni. Surfactants and their applications. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.*, **99**, 3 (2003).
[5] C.A. Miller, S. Qutubuddin. Enhanced oil recovery with microemulsions. In *Apolar Media*, H.F. Eicke, G.D. Parfitt (Eds.), p. 117, Marcel Dekker, New York (1987).
[6] S.A. Lacks, S.S. Springhorn, A.L. Rosenthal. Effect of the composition of sodium dodecyl sulfate preparations on the renaturation of enzymes after polyacrylamide gel electrophoresiset. *Anal. Biochem.*, **100**, 357 (1979).
[7] D. Attwood, A.T. Florence. *Surfactant Systems*, Chapman and Hall, London (1983).
[8] C. Tanford, J.A. Reynolds. Characterization of membrane proteins in detergent solutions. *Biochim. Biophys. Acta*, **457**, 133 (1976).
[9] J. Koetz, S. Kosmella. Polymers in lyotropic liquid crystalline systems. *Colloids Surf. A*, **123**, 265 (1997).
[10] S.E. Friberg, T. Moaddel, K.R. Morris, R. Abramowich, K.L. Arnsberry. A lamellar liquid crystal with fosinopril sodium. *J. Pharm. Sci.*, **83**, 677 (1994).
[11] E. Freyssingeas, E. Atelmi, D. Kekicheff, P. Richetti, A.M. Belloqc. Softening of the interactions between surfactant bilayers in a lamellar phase due to the presence of a polymer. *Eur. Phys. J. B*, **9**, 123 (1999).

[12] C.D. Bruce, S. Senapati, M.L. Berkowitz, L. Perera, M.D.E. Forbes. Molecular dynamics simulation of sodium dodecyl sulfate micelle in water: The behavior of water. *J. Phys. Chem. B*, **106**, 10902 (2002).

[13] M.C. Woods, J.M. Haile, J.P. O'Conell. Internal structure of a model micelle via computer simulation. 2. Spherically confined aggregates with mobile head. *J. Phys. Chem.*, **90**, 1875 (1986).

[14] K. Watanabe, M.L. Klein. Molecular dynamics studies of sodium octanoate and water: The liquid–crystal mesophase with two-dimensional hexagonal symmetry. *J. Phys. Chem.*, **95**, 4158 (1991).

[15] C.D. Bruce, M.L. Berkowitz, L. Perera, M.D.E. Forbes. Molecular dynamics simulation of sodium dodecyl sulfate micelle in water: Micellar structural characteristics and counterion distribution. *J. Phys. Chem. B*, **206**, 3788 (2002).

[16] J. Shelley, K. Watanabe, M.L. Klein. Simulation of a sodium dodecylsulphate micelle in aqueous solution. *Int. J. Quantum Chem.*, **17**, 103 (1990).

[17] A.D. MacKerell. Molecular dynamics simulation analysis of a sodium dodecylsulfate micelle in aqueous solution. Decreased fluidity of the micelle hydrocarbon interior. *J. Phys. Chem.*, **99**, 1846 (1995).

[18] F. Bresme, J. Faraudo. Computer simulation studies of Newton black films. *Langmuir*, **20**, 5127 (2004).

[19] J. Faraudo, F. Bresme. Anomalous dielectric behavior of water in ionic Newton black films. *Phys. Rev. Lett.*, **92**, 236102 (2004).

[20] J. Faraudo, F. Bresme. Origin of the short-range, strong repulsive force between ionic surfactant layers. *Phys. Rev. Lett.*, **94**, 077802 (2005).

[21] E.A.G. Aniansson, S.N. Wall. Kinetics of step-wise micelle association. *J. Phys. Chem.*, **78**, 1024 (1974).

[22] A.A. Shahinyan, A.H. Poghosyan, G.A. Yeghiazaryan, H.H. Gharabekyan. A software tool for construction of biomembranes. *Electronic J. Nat. Sci.*, **1**, 56 (2004).

[23] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, J. Hermans. *Intermolecular Forces*, pp. 331–342, Reidel, Dordrecht (1981).

[24] A.W. Schuettelkopf, D.M.F. van Aalten. PRODRG – a tool for high-throughput crystallography of protein-ligand complexes. *Acta Crystallogr. D*, **60**, 1355 (2004).

[25] W. van Gusteren, H.J.C. Berendsen. *GROMOS96 Manual*, Groningen, The Netherlands (1996).

[26] H.J.C. Berendsen, D. van der Spoel, R. van Drunen. GROMACS: A message-passing parallel molecular dynamics implementation. *Comp. Phys. Commun.*, **91**, 43 (1995).

[27] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. DiNola, J.R.J. Haak. Molecular dynamics with coupling to an external bath. *Chem. Phys.*, **81**, 3684 (1984).

[28] M. Parrinello, A. Rahman. Crystal structure and pair potentials: A molecular dynamics study. *Phys. Rev. Lett.*, **45**, 1196 (1980).

[29] J.P. Ryckaert, G. Ciccotti, H.J.C. Berendsen. Numerical integration of Cartesian equations of motion of a system with constraints: Molecular dynamics of n-alkanes. *J. Comp. Phys.*, **23**, 327 (1977).

[30] T. Darden, D. York, L. Pedersen. Particle mesh Ewald: An N log (N) method for Ewald sums in large systems. *J. Chem. Phys.*, **98**, 10089 (1993).

[31] W.F. Humphrey, A. Dalke, K. Schulten. VMD – Visual molecular dynamics. *J. Mol. Graphics.*, **14**, 33 (1996).

[32] W.L. Jorgensen, J. Chandrasekhar, J.D. Medura, R.W. Impey, M.L. Klein. Comparison of simple potential function for simulating liquid water. *J. Chem. Phys.*, **79**, 926 (1983).

[33] L. Kale, R. Skeel, M. Bhandarkar, R. Brunner, A. Gursoy, N. Krawetz, J. Phillips, A Shinozaki, K. Varadarajan, K. Schulten. NAMD2: greater scalability for parallel molecular dynamics. *J. Comput. Phys.*, **151**, 283 (1999).

[34] R.M. Levy, J.A. McCammon, M. Karplus. Diffusive Langevin dynamics of model alkanes. *Chem. Phys. Lett.*, **64**, 4 (1979).

[35] S.E. Feller, Y.H. Zheng, R.W. Pastor, B.R. Brooks. Constant pressure molecular dynamics simulation – the Langevin piston method. *J. Comp. Phys.*, **103**, 4613 (1995).

[36] S. Bandyopadhyay, J.C. Shelley, M.L. Klein. Molecular dynamics study of the effect of surfactant on a biomembrane. *J. Phys. Chem. B*, **105**, 5979 (2001).

[37] J. Daillant, L. Bosio, J.J. Benattar. Capillary waves and bending elasticity of monolayers on water studied by X-ray reflectivity as a function of surface pressure. *J. Meunier. Europhys. Lett.*, **8**, 453 (1989).

[38] O. Belorgey, J.J. Benattar. Structural properties of soap black films investigated by X-ray reflectivity. *Phys. Rev. Lett.*, **66**, 313 (1991).

[39] S. Kosmella, J. Koetz, S. Friberg, R.E. Mackay. Interactions of polyelectrolytes with the Lyotropic liquid crystalline system Na-dodecylsulfate/decanol/water. Ber. Bunsenges. *Phys. Chem.*, **100**, 1059 (1996).

[40] A.A. Shahinyan. The role of structural organization of ionic micelles at the mechanism of forming macromolecules in emulsions. *NAS RA*, pp. 181 Yerevan (1985).

[41] P. Kekicheff, C. Grabielle-Madelmont, M. Ollivon. Phase diagram of sodium dodecyl sulfate–water system: 1. A calorimetric study. *J. Colloid Interface Sci.*, **131**, 112 (1989).