Вісник Харківського національного університету, серія "Хімія", вип. 38 (61), 2022
https://doi.org/10.26565/2220-637X-2022-38-02 ISSN 2220-637X
УДК: 544.77.022.532+547.264+004.942

EXAMINATION OF MIXED SODIUM DODECYL SULFATE – 1-BUTANOL MICELLES WITH MOLECULAR DYNAMICS

I. V. Kononenko[a], **V. S. Farafonov**[b]

V. N. Karazin Kharkiv National University, 4 Svobody sq., Kharkiv, 61022, Ukraine

a) ✉ *kononenko2109@gmail.com* *https://orcid.org/0009-0009-7762-6005*
b) ✉ *farafonov@karazin.ua* *https://orcid.org/0000-0003-0785-9582*

Properties of mixed micelles composed of sodium *n*-dodecyl sulfate surfactant and 1-butanol co-surfactant were examined using molecular dynamics simulation for three experimentally observed compositions. The aggregation number varied in the range of 30 to 64, and the co-surfactant content was 75 to 32 molecules, respectively. The composition of the bulk water – 1-butanol mixture matched the experimentally studied concentrations. All-atom potential models and explicit solvent were used in order to capture the most structural details. Such characteristics as micelle size, co-surfactant location, depth of water penetration were determined. The simulated micelles were found to have compact ellipsoidal shape, except of the most co-surfactant-rich ones, which were elongated. The equilibrium composition differed little from the initial one indicating consistence of the simulations. The co-surfactant molecules were observed in different positions: either situated on the surface of surfactant aggregate or having hydrocarbon tails immersed in it. Still, the hydroxyl groups stayed on the micelle surface and preserved contact with bulk solution. Water molecules were found penetrating the mixed micelles up to 0.3 – 1.0 nm from their center. Degree of counterion binding was estimated and its dependence on micelle composition was derived. It was found to decrease with the co-surfactant content in a non-linear manner. Specifically, for co-surfactant content up to 34% the counterion binding was almost similar to that of pure sodium *n*-dodecyl sulfate micelles; the value gradually fade at higher 1-butanol content. Several positions of the boundary between bound and free counterions were considered. The approach proposed here may be employed for examination of other mixed micelles, as well.

Keywords: *radial distribution function, micelle size, hydration, degree of counterion binding.*

Introduction

At present, surfactant micellar solutions found versatile application. They serve as cleaning agents, disinfection aids, emulgators, as reaction media, and so forth. One of their valuable features is a variety of characteristics, which can be tuned to achieve desired properties: surfactant head group and hydrocarbon radical, counterion, concentration, ionic strength. Introduction of a co-surfactant provides a new degree of freedom, which extends the range of available properties of micelles and bulk solution even more.

In this paper we examine the microscopic structure and counterion binding of mixed micelles made of sodium *n*-dodecyl sulfate (SDS) surfactant and 1-butanol (BuOH) co-surfactant (Fig. 1). On one hand, this is a relevant choice because SDS is among the most widely used surfactants in technology and laboratory practice. On the other hand, extensive experimental data was collected for this system at various concentrations of the components. [1–3] It is summarized in a recent review. [4] However, intriguingly, for most cases the available data is fragmentary. Often the micelle size and composition are reported (radius, aggregation number N_{SDS} and number of co-surfactant molecules N_{BuOH}), but there is no information about degree of counterion binding. Oppositely, when counterion binding was examined, there is no data about the aggregation number and co-surfactant content. This shows that our knowledge of properties of this object is still limited.

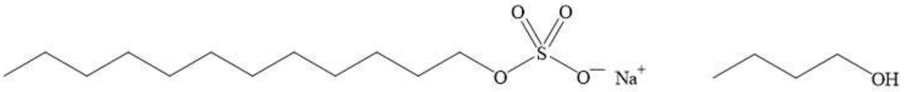


Figure 1. Structure formulas of SDS surfactant and 1-butanol co-surfactant.

Here we will use the method of molecular dynamics (MD) to get a new insight. It is a powerful instrument for identifying microscopic structure of a molecular system. When applied to micelles it can reveal water penetration into the hydrocarbon core, ordering of surfactant molecules, counterion binding, dynamics of self-assembly *etc*. At present, single-component surfactant micelles are thoroughly examined by this method. [5] Computational studies of the mixed micelles are also found in literature, although in much lesser amount. [6–8]

Notably, the chosen system has not yet been studied with MD. The closest match is the MD simulation of mixed micelles made of SDS and medium to higher alcohols (hexanol to hexadecanol) [8]. The authors were focused on structure of the micelles and its dependence on composition. Transitions between different micelle shapes were identified. Importantly, coarse-grained potential models were used there. On one hand, it allowed cover long time scale (microseconds), on the other hand, these models lack detail needed to study ion binding. The mixture of SDS and 1-butanol was investigated, as well, but in an interfacial setup only. [9] There, the effect of the co-surfactant on surface tension and density profile of the surfacial film was identified.

For the current study we chose three compositions of mixed micelles, which were experimentally observed: $N_{\mathrm{SDS}} = 30$ and $N_{\mathrm{BuOH}} = 75$ [1]; $N_{\mathrm{SDS}} = 40$ and $N_{\mathrm{BuOH}} = 40$ [1]; $N_{\mathrm{SDS}} = 64$ and $N_{\mathrm{BuOH}} = 32$ [2]. This choice covers a wide range of the co-surfactant content: from 71% to 33% by amount. For all of these systems the degree of counterion binding was not reported, and micelle radius was not reported for the last one.

Simulation methodology

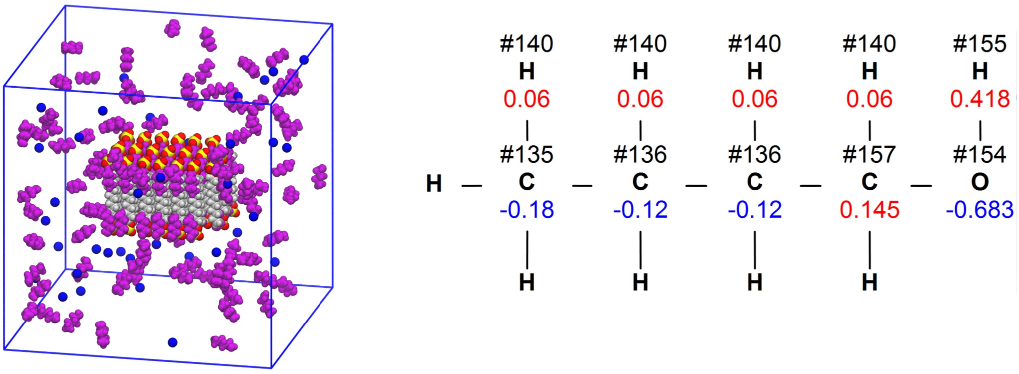
The simulation cells consisted of a preformed DS^- + BuOH aggregate placed in a water – 1-butanol mixture with distributed Na^+ counterion. The initial shape of the aggregate was a rectangular bilayer made of alternating DS^- ions and BuOH molecules. This compact shape can be easily generated and shortens the time period needed to obtain an equilibrated micelle. On one hand, close packing of hydrophobic tails resembles that in a micelle. On the other hand, the initial placement of BuOH molecules within the aggregate allows avoid waiting for their sorption from the bulk solution. The cells were cubic-shaped with edge length 8.5 nm for $N_{\mathrm{SDS}} = 64$ and 8 nm otherwise. One of simulation cells is shown in Fig. 2A. The number of 1-butanol molecules that should be placed in the bulk solution was deduced from the conditions of the experiment, where given composition of mixed micelles was observed. The calculations were done via Eq. 1 and the relevant experimental data is collected in Table 1. The principle is as follows. Let us consider 1 L of the system. Amount of BuOH in the bulk solution equals the difference between its total amount, $c_{\mathrm{BuOH}} \cdot 1$ L, and its amount in micelles. The latter equals the amount of SDS in micelles, $(c_{\mathrm{SDS}} - \mathrm{CMC}) \cdot 1$ L, multiplied by the ratio $N_{\mathrm{BuOH}} / N_{\mathrm{SDS}}$. Here CMC is critical micelle concentration of SDS; it was taken as 0.004 mol/L because in 1-butanol solutions it decreases compared with pure water [4]. Repeating the calculation for the volume of bulk solution in the MD cell V_{sol} gives the number of BuOH molecules to place in it. Because the micelle occupies a considerable fraction of the cell volume, V_{sol} should be found as the difference between volume of the whole cell V_{cell} and volume of the micelle inside V_{mic}. The latter can be approximated as the volume of a parallelepiped and measured by visual examination, *e.g.*, in VMD software. [13]

$$N_{\mathrm{BuOH}\,sol} = N_A \left(c_{\mathrm{BuOH}} - (c_{\mathrm{SDS}} - \mathrm{CMC}) \frac{N_{\mathrm{BuOH}}}{N_{\mathrm{SDS}}} \right) (V_{cell} - V_{mic}) \qquad (1)$$

where $N_{\mathrm{BUOH}\,sol}$ is number of BuOH molecules added in the bulk solution, N_A is Avogadro number.

Table 1. Compositions of the simulated cells and relevant experimental data.

system	N_{SDS}	N_{BuOH}	c_{SDS}, mol/L	c_{BuOH}, mol/L	$V_{cell} - V_{mic}$, nm^3	$N_{\mathrm{BuOH}\,sol}$	N_{water}
1 [1]	30	75	0.0316	0.764	480	201	15046
2 [1]	40	40	0.033	0.326	480	86	15683
3 [2]	64	32	0.2	0.2	570	35	18936



A **B**

Figure 2**. A:** Simulation cell for micelle with $N_{SDS} = 40$, $N_{BuOH} = 40$. Na^+ ions are colored blue, BuOH molecules are colored violet. **B:** Used OPLS-AA potential model of 1-butanol.

Atom–atom interactions in the system were described using OPLS-AA force field. The potential model for SDS was taken from literature [10]. The one for BuOH was composed using the built-in atom types and atomic point charges, which are empirical and optimized for reproducing properties of organic liquids [11]. It is depicted in Fig. 2B. Water was represented by means of the SPC model.

The simulations were carried out at standard conditions (T = 25°C, p = 1 bar), which were maintained using Berendsen thermostat and barostat. Electrostatic interactions were calculated with the PME method, while van der Waals interactions were cut at 1 nm. Three-dimensional periodic boundary conditions and bond constraints were imposed. The simulations were 50 ns long, time step equaled 2 fs. GROMACS 5.1 software was used [12].

Results and discussion

As the initial micelle shape was artificial (a bilayer), the beginning of each simulation was devoted to equilibration of the micelle. The distribution of 1-butanol between micelle and solution was equilibrated, as well. To monitor the progress we calculated number of BuOH molecules staying in contact with DS^- ions (that is located within 0.4 nm of any DS^- ion). This number shows the amount of co-surfactant in the micelle. The graphs are shown in Fig. 3.

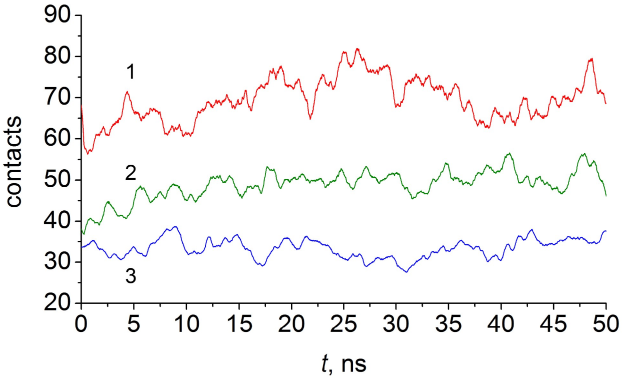


Figure 3. Evolution of number of contacts between DS^- ions and BuOH molecules for micelles of different composition. 1 — $N_{SDS} = 30$, 2 — $N_{SDS} = 40$, 3 — $N_{SDS} = 64$.

We conclude that the original composition of the micelles was mostly preserved. For systems #1, #2, and #3 the average number of BuOH molecules equals 71.4, 50.5, and 33.1, respectively, that is close to the originally placed. This additionally proves the correctness of the computational model. The graphs were also used to identify the end of equilibration phase, which was recognized at 20 ns. The quantities below were computed over the 20–50 ns interval.

The final configurations of two micelles are shown in Fig. 4. Hydroxyl groups of BuOH molecules are located among the surfactant head groups. The butyl radicals can be found either lying on the surface of the SDS aggregate or protruding inside it.

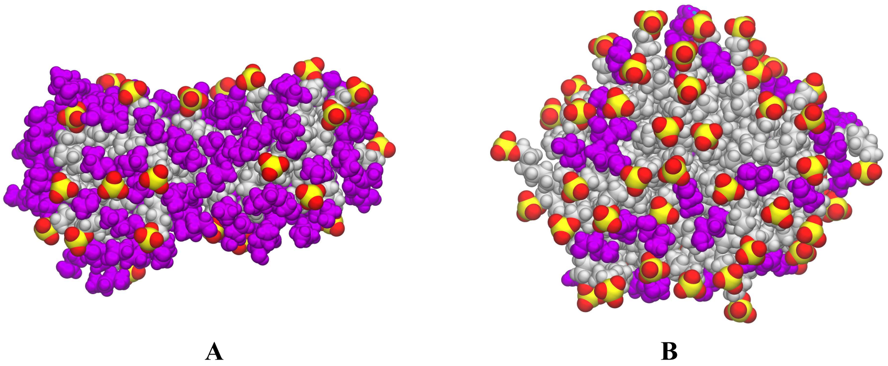


Figure 4. Final configurations for micelle with $N_{SDS} = 30$, $N_{BuOH} = 75$ (**A**) and $N_{SDS} = 64$, $N_{BuOH} = 32$ (**B**). BuOH molecules are colored violet.

To estimate size of the micelles we calculated the radial distribution function (RDF) of S atoms of DS$^-$ anions with respect to micelle center of mass, Fig. 5A. The latter was approximated by the center of mass of DS$^-$ anions, which is justified by uniform distribution of the co-surfactant across the micelle.

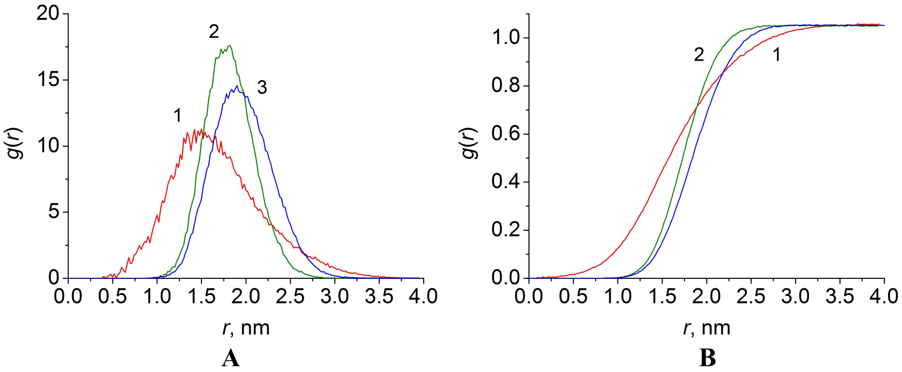
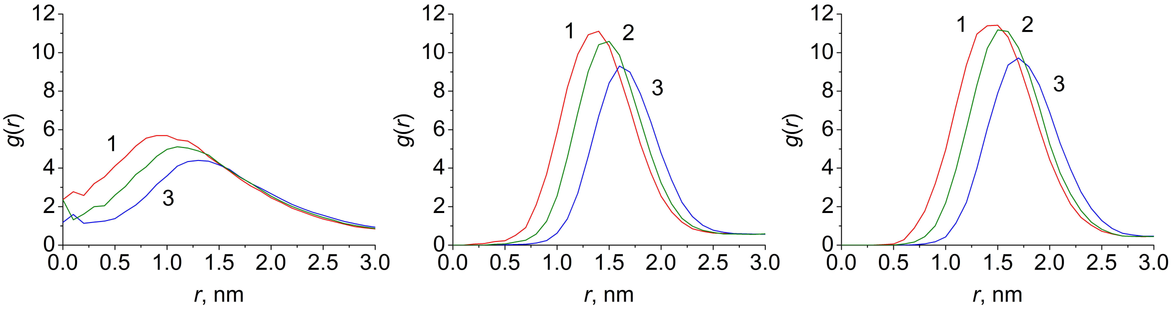


Figure 5. A: RDF of S atoms (**A**) or water molecules (**B**) with respect to micelle center of mass. 1 — $N_{SDS} = 30$, 2 — $N_{SDS} = 40$, 3 — $N_{SDS} = 64$.

Abscissa of the peak of the RDF shows the most probable position of head groups and, thus, indicates the radius of micelle. Determined in such a way it equals 1.54 nm, 1.78 nm, 1.88 nm for $N_{SDS} = 30$, 40, 64, respectively. The first two values agree quite good with the experimental numbers 1.71 nm and 1.68 nm, respectively. The last value (1.88 nm) also equals the radius of pure SDS micelles with $N_{SDS} = 60$.

The curve of micelle with $N_{SDS} = 30$ is notably wider than the other. This is because of its pronouncedly prolate shape, as is proven by visual inspection. This elongation is the probable reason why experimental radius is 0.2 nm larger than the one determined from RDF. Importantly, visual inspection also reveals that the SDS content occasionally reversibly splits into two fragments bridged by BuOH molecules for short times. Oppositely, the two other micelles are less fluid and have a more compact, although still ellipsoidal, shape.

More detailed information about co-surfactant distribution in micelles is provided by radial distribution functions of particular 1-butanol atoms with respect to micelle center of mass. The RDF's for hydroxyl O atom and C atoms in positions 2 and 4 are shown in Fig. 6. The peaks of the O atom are located ca. 0.2 nm closer to micelle center than those of S atoms of DS$^-$ anions, which corresponds to location among ester O atoms of DS$^-$. The C^2 and C^4 atoms are in average immersed deeper into micelles than hydroxyl O atoms, and this is more pronounced for $N_{SDS} = 30$: the peak of C^4 atoms is 0.35 nm ($N_{SDS} = 30$) or 0.25 nm ($N_{SDS} = 40$, 64) behind that of the O atoms. The numbers are shorter than the C^4 – O distance in a stretched BuOH molecule (0.5 nm) showing that in average the molecules are inclined or bent. Considering Fig. 4 we conclude that BuOH molecules can both lie on the surface of DS$^-$ aggregate and be immersed in it, giving average C^4 – O distance projection to micelle radius less than 0.5 nm. Still, in micelles with $N_{SDS} = 40$ and 64 the co-surfactant does not reach the micelle interior: $g(r) \approx 0$ at $r < 0.6$ nm. The micelles with $N_{SDS} = 30$ are more labile and rich with co-surfactant, so BuOH can be found in all positions there.

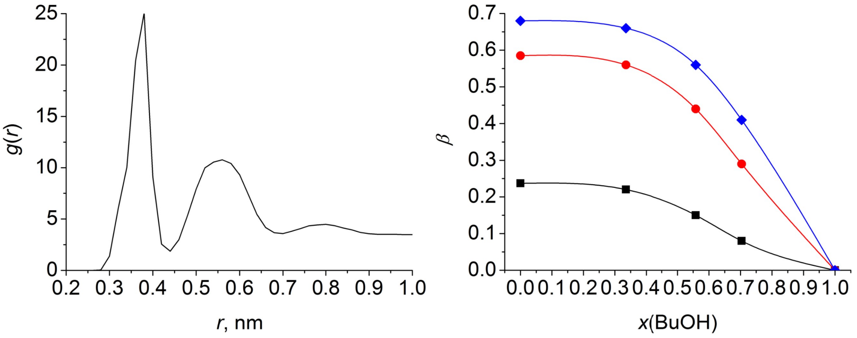


A **B** **C**

Figure 6. RDF of BuOH C^4 (1, red), C^2 (2, green), and O (3, blue) atoms with respect to the micelle center. **A:** $N_{SDS} = 30$; **B:** $N_{SDS} = 40$; **C:** $N_{SDS} = 64$.

The simulations were done with explicit water, therefore, the distribution of water in micelle can be examined. It was described using RDF of water molecules with respect to the micelle center, Fig. 5B. Compared to the bulk solution, the density of water decreases by 2 times at the distance of 1.58 – 1.84 nm from micelle center. This indicates that the head groups and adjacent methylene groups of the micelles are strongly hydrated. Except of $N_{SDS} = 30$, micelles become almost dry at 1.1 nm (RDF is <1% of the bulk value) and completely dry at 0.85 nm. The curve for micelles with $N_{SDS} = 40$ almost coincides with that of pure SDS micelles having $N_{SDS} = 60$. Therefore introduction of 1-butanol up to 50% ($N_{SDS} = N_{BuOH} = 40$) did not affect the micelle structure considerably. Contrary, low aggregation number and prolate shape of the micelle with $N_{SDS} = 30$ makes its hydrocarbon core rather thin.

The other question of interest is counterion binding by mixed micelles. To calculate the degree of counterion binding β it is necessary to place the boundary between bound and free Na^+ ions. We used the position of the first and the second minima of the RDF between Na^+ ions and DS^- S atoms as the criterion, which equal 0.44 nm and 0.7 nm, respectively. The graph for the case $N_{SDS} = 64$ is shown in Fig. 7A; in other cases RDF has similar abscissas of minima and maxima. An even longer distance of 0.9 nm was considered, as well. The ions located closer than the chosen boundary position d were considered as bound and contributed to β. The values are collected in Table 2 and depicted in Fig. 7B. For comparison the data for pure SDS micelles is shown, as well [10]. Molar fraction of BuOH was computed using equilibrium N_{BuOH} values instead of the initial ones.



A **B**

Figure 7. **A:** RDF between S atoms and Na^+ ions. **B:** Dependence of degree of counterion binding on molar fraction of 1-butanol in mixed micelle. Black squares: β(0.44 nm), red circles: β(0.7 nm), blue diamonds: β(0.9 nm). Lines are produced by spline interpolation.

Table 2. Numbers of bound Na^+ ions and corresponding degrees of counterion binding for different positions of the boundary and micelle compositions.

		$d = 0.44$ nm		$d = 0.7$ nm		$d = 0.9$ nm	
N_{SDS}	x_{BuOH}	N	β	N	β	N	β

30	0.70	2.3	0.08	8.7	0.29	12.3	0.41
40	0.56	5.8	0.15	17.5	0.44	22.4	0.56
64	0.34	14.1	0.22	35.6	0.56	42.0	0.66
60	0	14.2	0.24	35.1	0.59	40.7	0.68

A clear monotonic dependence is observed: increase of 1-butanol content lowers counterion binding. However, the effect becomes significant only when the co-surfactant content is considerable: even at $x_{\mathrm{BuOH}} = 0.34$ β remains almost equal to that of pure SDS micelles. We suggest the following explanation. The micelle with $x_{\mathrm{BuOH}} = 0.34$ contains $N_{\mathrm{SDS}} = 64$ and $N_{\mathrm{BuOH}} = 32$. Size and shape of its DS^- aggregate differ little from those of pure SDS micelle with $N_{\mathrm{SDS}} = 60$, leading to similar counterion binding. The additional 1-butanol is distributed over the surface (Fig. 4B). In two other mixed micelles the BuOH molecules incorporate into the hydrocarbon core to larger extent and pull apart the surfactant head groups. As a result, surface charge density decreases, which weakens attraction of Na^+.

For the considered compositions there was no experimental data about β to compare. However, $\beta = 0.39$ was reported for a system with $c_{\mathrm{SDS}} = 0.02$ mol/L, $c_{\mathrm{BuOH}} = 0.8$ mol/L that is quite close to system #1 (Table 1). [4] For pure micelles the value 0.71 was reported there. Both values agree with matching simulation results for boundary position at 0.9 nm.

Conclusions

Mixed micelles made of sodium *n*-dodecyl sulfate and 1-butanol at standard conditions were simulated by means of molecular dynamics. Three compositions were considered with molar fraction of the co-surfactant 33% to 71%. 1-butanol was found located both on the surface of micelles and incorporated in their hydrocarbon core. Still, its hydroxyl groups stay on the micelle surface among surfactant head groups. Degree of counterion binding was found reducing with increase of 1-butanol content. However, up to molar fraction of 33% the effect was small, and counterion binding was similar to that of the single-component micelles. The used approach may be utilizied for examination of other mixed micelles, as well.

Acknowledgements

The authors are grateful to the Ministry of Education and Science of Ukraine for the financial support of this study via grant #0120U101064, and to Dr. Dmitry Nerukh (Aston University, Birmingham, UK) for the generously provided computational resources.

References

1. Almgren, M.; Swarup, S. Size of sodium dodecyl sulfate micelles in the presence of additives i. alcohols and other polar compounds. *J. Colloid Interface Sci.* **1983**, *91*, 256–266. https://doi.org/10.1016/0021-9797(83)90330-2.
2. Caponetti, E.; Martino, D. C.; Floriano, M. A.; Triolo, R. Localization of *n*-Alcohols and Structural Effects in Aqueous Solutions of Sodium Dodecyl Sulfate. *Langmuir* **1997**, *13*, 3277–3283. https://doi.org/10.1021/la961013m.
3. Kharchenko, A. Yu. Composition of the sodium dodecylsulfate – 1-pentanol mixed micelles as determined using acid-base indicators. *Kharkov Univ. Bull., Chem. Ser.* **2016**, *27*(50), 5–15. https://doi.org/10.26565/2220-637X-2016-27-01.
4. Kharchenko, A. Yu.; Kamneva, N. N.; Mchedlov-Petrossyan, N. O. The properties and composition of the SDS – 1-butanol mixed micelles as determined via acid-base indicators. *Colloids Surf. A* **2016**, *507*, 243-254. https://doi.org/10.1016/j.colsurfa.2016.08.004.
5. Taddese, T.; Anderson, R. L.; Bray, D. J.; Warren, P. B. Recent advances in particle-based simulation of surfactants. *Curr. Opin. Colloid Interface* **2020**, *48*, 137–148. https://doi.org/10.1016/j.cocis.2020.04.001.
6. Marrink, S. J.; Mark, A. E. Molecular Dynamics Simulations of Mixed Micelles Modeling Human Bile. *Biochemistry* **2002**, *41*(17), 5375–5382. https://doi.org/10.1021/bi015613i.
7. Shang, B. Z.; Wang, Z.; Larson, R. G. Molecular Dynamics Simulation of Interactions between a Sodium Dodecyl Sulfate Micelle and a Poly(Ethylene Oxide) Polymer. *J. Phys. Chem. B* **2008**, *112*(10), 2888–2900. https://doi.org/10.1021/la00022a026.

8. Mendez-Bermudez, J. G.; Dominguez, H. Structural changes of a sodium dodecyl sulfate (SDS) micelle induced by alcohol molecules. *J. Mol. Model.* **2015**, *22*(33), 1–9. https://doi.org/10.1007/s00894-015-2904-x.
9. Parra, J. G.; Aray, Y. B.; Iza, P.; Zarate, X.; Schott, E. Behavior of the SDS/1-butanol and SDS/2-butanol mixtures at the water/*n*-octane interface through molecular dynamics simulations. *Chem. Phys.* **2019**, *523*, 138–149. https://doi.org/10.1016/j.chemphys.2019.04.021.
10. Farafonov, V. S.; Lebed, A. V. Developing and validating a set of all-atom potential models for sodium dodecyl sulfate. *J. Chem. Theory Comput.* **2017**, *13*(6), 2742−2750. https://doi.org/10.1021/acs.jctc.7b00181.
11. Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and Testing of the OLPS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *J. Am. Chem. Soc.* **1996**, *118*(15), 11225–11236. https://doi.org/10.1021/ja9621760.
12. Abraham, M. J.; Murtola, T.; Schulz, R.; Pall, S.; Smith, J. C.; Hess, B.; Lindahl E. GROMACS: High performance molecular simulations through multi-level parallelism from laptops to super-computers. *SoftwareX* **2015**, *1–2*, 19–25. https://doi.org/10.1016/j.softx.2015.06.001.
13. Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual Molecular Dynamics. *J. Mol. Graphics* **1996**, *14*, 33−38. https://doi.org/10.1016/0263-7855(96)00018-5.

Received 09.08.2022

Accepted 12.09.2022

І.В. Кононенко, В.С. Фарафонов. Дослідження змішаних міцел додецилсульфату натрію – 1-бутанолу методом молекулярної динаміки.

Харківський національний університет імені В.Н. Каразіна, хімічний факультет, майдан Свободи, 4, Харків, 61022, Україна

Властивості змішаних міцел, що складаються з поверхнево-активної речовини (ПАР) *н*-додецилсульфату натрію та ко-ПАР 1-бутанолу досліджені методом моделювання молекулярної динаміки для трьох експериментально спостережуваних складів. Число агрегації перебувало в інтервалі від 30 до 64, а вміст ко-ПАР становив від 75 до 32 молекул відповідно. Склад навколишнього розчину вода – 1-бутанол відповідав експериментально дослідженим концентраціям. Використовувалися повноатомні потенціальні моделі та явний розчинник, щоб відтворити більшість структурних деталей. Визначено такі характеристики, як розмір міцели, розташування ко-ПАР, глибина проникнення води. Змодельовані міцели мали компактну еліпсоїдальну форму, за винятком найбільш багатих на ко-ПАР, які були продовгуватими. Рівноважний склад мало відрізнявся від початкового, що вказує на узгодженість моделювання. Молекули ко-ПАР спостерігалися в різних положеннях: розташовані на поверхні агрегату ПАР або занурені в нього вуглеводневими радикалами. Проте гідроксильні групи перебували на поверхні міцели і зберігали контакт із розчином. Виявлено, що молекули води проникають у змішані міцели на відстань до 0,3 – 1,0 нм від центру. Оцінено ступінь зв'язування протиіонів та встановлено його залежність від складу міцели. Виявлено, що він нелінійно зменшується зі зростанням вмісту ко-ПАР. Зокрема, за вмісту ко-ПАР до 34% зв’язування протиіонів було майже подібним до такого в чистих міцелах *н*-додецилсульфату натрію; значення поступово зменшувалося при підвищенні вмісту 1-бутанолу. Розглянуті декілька положень границі між зв'язаними та вільними протиіонами. Запропонований підхід може бути використаний для дослідження інших змішаних міцел.

Ключові слова: *функція радіального розподілу, розмір міцели, гідратація, ступінь зв'язування протиіонів.*