Can sodium 1-alkylsulfonates participate in the sodium dodecyl sulfate micelle formation?

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Abstract

The aggregation behavior of sodium dodecyl sulfate (SDS) was studied in an aqueous solution in the presence of increasing concentrations of selected sodium 1-alkylsulfonates, namely sodium 1-octanesulfonate, sodium 1-decanesulfonate, and sodium 1-dodecanesufonate. The critical micelle concentration (CMC) of SDS was determined by conductivity and fluorescence intensity measurements. The steady-state fluorescence quenching experiments with pyrene as a fluorescent probe were performed to obtain micellar aggregation numbers (N_{agg}) of the surfactant. The thermodynamic parameters of micellization ($\Delta G^0_{\mathrm{mic}}$ for all studied systems; $\Delta H^0_{\mathrm{mic}}$ and $\Delta S^0_{\mathrm{mic}}$ for sodium 1-dodecanesufonate) have been determined and compared. The influence of alkyl chain length and concentration of the selected sodium 1-alkylsulfonates on the values of CMC, N_{agg}, $\Delta G^0_{\mathrm{mic}}$, $\Delta H^0_{\mathrm{mic}}$, and $\Delta S^0_{\mathrm{mic}}$ of SDS has been discussed. As it was found, all selected for the experiments electrolytes decrease significantly the CMC of the surfactant, while an opposite effect is observed for N_{agg} values. The obtained experimental results have been supported by theoretical calculations. Interestingly, it has been proven that solely the molecules of sodium 1-dodecanesufonate (of the same carbon chain length) may act as the SDS mimetics – they are not recognized by SDS as the ones with a different structure and consequently are allowed to participate in the formation of the surfactant's micelles.

Keywords: sodium dodecyl sulfate; sodium 1-alkylsulfonates; critical micelle concentration; micellar aggregation number; thermodynamic parameters; fluorescence spectroscopy; conductivity; molecular dynamics.

1. Introduction

Surfactants, considering their structure and charge of the hydrophilic parts of the molecule, can be divided into cationic, anionic, amphoteric and nonionic ones [1]. The surface properties of these amphiphilic molecules, such as lipophilicity, viscosity, solubilization capacity, adsorption at the interface, self−assembly or micelle formation [2], are induced by the hydrophobic interaction between hydrocarbon parts of the surfactant molecules balanced by their hydration and electrostatic repulsive effects [3] and play an important role in many natural and industrial applications, *i.e.* detergent and pharmaceutical industries, food technology, and petroleum recovery processes [4]. The tendency of surfactants to self-aggregate is with no doubt one of the most fascinating aspects of these particles, while micelles remain one of the central topics of study within surface and colloid chemistry [5]. Important experimental characteristics describing micelles are the critical micelle concentration (CMC; the concentration where they are formed) [6], kinetic features (such as the micellar lifetime and reaction rates) [7], their size, shape, dispersity in a solution [8], aggregation numbers (N_{agg}; the amount of surfactant molecules making up a micelle) [9] as well as the thermodynamics [10] of the micellization process (entropy is believed to be the major driving force for micellization in aqueous solutions). All these parameters are sensitive to numerous internal (*e.g.*, hydrophobic structure and head group type [11]) and external (surfactant concentration [12], pressure [13], pH [14], temperature [15], ionic strength [16], solvent properties [17], presence of electrolyte [18] and non-electrolyte [19] additives, applied technique [20], *etc.*) factors and impact even on biological properties (it has been proven for example that the highest antimicrobial properties are observed at concentrations below CMC [21]). Therefore, it is of great importance from the practical point of view – particularly when the real systems are investigated – to consider the influence of additives and other factors on the features of surfactants [22].

Generally, added electrolytes are known to affect the aggregation behavior of the ionic surfactants, which is attributed entirely to the counter-ion effect [23]. However, there are reports indicating that a co-ion, depending upon its and surfactant's structures, can also affect the micellization phenomenon [24]. In this paper, we report the aggregation behavior of sodium dodecyl sulfate (SDS) in the presence of selected sodium 1-alkylsulfonates of different chain lengths, namely sodium 1-octanesulfonate (K8S), sodium 1-decanesulfonate (K10S), and sodium 1-dodecanesufonate (K12S) studied by steady-state fluorescence spectroscopy and conductivity measurements and supported by molecular dynamics simulations. All chosen sodium 1-alkylsulfonates are structurally very similar to the SDS surfactant (**Figure 1**). In sodium dodecyl sulfate the sulfur of a headgroup is linked to the carbon atom via an oxygen atom, while in sulfonates it is linked directly to a carbon chain of an appropriate length (8, 10, and 12 carbon atoms in the case of K8S, K10S, and K12S, respectively). According to our knowledge, the determination of critical micelle concentrations (CMC), micellar aggregation numbers (N_{agg}) and thermodynamic parameters of micellization of SDS in the presence of the chosen sulfonates has been never performed, although such a need has been signalized previously [25]. Can molecules with a structure similar to SDS act as the surfactant's mimetics and be incorporated into its micelles? Or maybe SDS molecules recognize that other molecules have a slightly different structure and consequently do not allow them to participate in the formation of the surfactant's micelles? The search for the answers to questions raised has prompted us to embark on these studies.

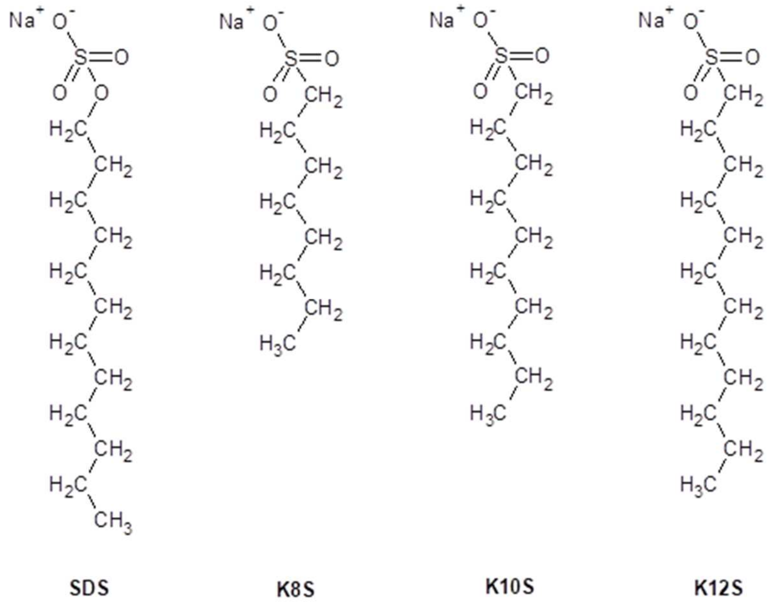


Figure 1. Chemical structures of SDS, K8S, K10S, and K12S.

2. Experimental

2.1. Materials

Sodium dodecyl sulfate (SDS, ≥99.0%), sodium 1-octanesulfonate (K8S, ≥99%), sodium 1-decanesulfonate (K10S, ≥99%), sodium 1-dodecanesulfonate (K12S, ≥99%), pyrene (≥97%), cetylpyridinium chloride (CPC, ≥98%), and sodium chloride (≥99%) were acquired from Merck (Poland) and used without additional purification as received. For all solutions preparation, double-distilled water with a conductivity of less than 0.18 μS cm^{-1} was employed. The studies of the aggregation behavior of SDS were performed in aqueous solutions of K8S, K10S, K12S, and NaCl used at low concentrations (1-8 mM), because it is difficult to get reliable conductivity results in the high ionic strength [25,26]. Due to the limited solubility of K12S in water its highest concentration was set at 4 mM.

2.2. Methods

2.2.1. Steady-state fluorescence spectroscopy

The Cary Eclipse Varian (Agilent, Santa Clara, CA, USA) spectrofluorometer, equipped with a temperature controller and a 1.0 cm multicell holder, was used to measure the fluorescence intensities. All experiments were conducted at 298.15 K.

The fluorescence emission spectra of pyrene (c = 2 μM; V = 2 mL; λ_{ex} = 340 nm; the excitation and emission slit widths set at 5 nm) dissolved in: (i) 1, 2, 4, and 8 mM K8S; (ii) 1, 2, 4, and 8 mM K10S; (iii) 1, 2, and 4 mM K12S; (iv) water, 1, 2, 4, and 8 mM NaCl were recorded from 360 to 500 nm in both the absence and presence of increasing amounts of SDS in order to determine the CMC values (up to 11 mM). The values obtained are the means of two separate experiments. All spectra were recorded in triplicate for each experiment.

In order to determine the N_{agg} values the fluorescence intensity of pyrene (c = 2 μM; V = 2 mL; λ_{ex} = 340 nm; λ_{em} = 375 nm; the excitation and emission slit widths set at 5 nm) dissolved in a mixture of 10 mM SDS and: (i) 1, 2, 4, and 8 mM K8S; (ii) 1, 2, 4, and 8 mM K10S; (iii) 1, 2, and 4 mM K12S; (iv) water, 1, 2, 4, and 8 mM NaCl was measured in the absence and presence of increasing concentrations of the quencher, cetylpyridinium chloride, CPC (up to 19.5 μM). The same titration was performed four times, thus all obtained values are means from four separate experiments.

2.2.2. Conductivity measurements

Conductometric measurements for all studied systems were performed at 298.15 K using a microtitration unit (Cerko Lab System, Poland) fitted with a 5 mL syringe (Hamilton, Poland) and a CD-201 conductometric cell (Hydromet, Poland). The details of the measuring devices and experimental setup have been described previously [27]. The experiment consisted of injecting 0.01 mL of the titrant solution comprising SDS (c = 60 mM) and the appropriate ligand of different concentrations (1, 2, 4, and 8 mM K8S; 1, 2, 4, and 8 mM K10S; 1, 2, and 4 mM K12S; water, 1, 2, 4, and 8 mM NaCl), into the reaction cell containing the ligand solution only. In the case of 1, 2, and 4 mM K12S the conductometric titrations were additionally performed at 308.15 K and 318.15 K.

2.2.3. Molecular Dynamics (MD) simulation protocol

All simulated systems were built using CHARMM-GUI server [28] and were performed using Gromacs 2020 [29] with Plumed 2.6 plugin [30] and applying CHARMM36m force field [31]. TIP3P model was used for water molecules. The simulations were carried out in the isothermal-isobaric (NPT) ensemble using periodic boundary conditions. Nose-Hoover algorithm [32] with a coupling constant of 1 ps was used to keep the temperature at 300.15 K, while the Parrinello-Rahman algorithm [33] with a coupling time of 5 ps was used to maintain the pressure of 1 bar. Electrostatic interactions were calculated with the Particle Mesh Ewald method [34] using a cut-off radius equal to 1.2 nm (with the switching function applied from the distance of 1 nm) and the Fourier grid spacing of 0.12 nm. Van der Waals interactions were calculated with Lennard-Jones potential with a cut-off radius of 1 nm. The Hydrogen Mass Repartitioning approach [35] was used, which enabled us to use the 4 fs time step of integration of the equations of motion. Minimization and equilibration of the systems were performed following the default CHARMM-GUI Membrane Builder protocol [36].

The initial micelle system was composed of 70 dodecyl sulfate anions placed in an 8.1x8.1x8.1 nm rectangular box filled with 16998 water molecules and 116 Na^+ and 46

Cl^- ions to provide 0.15 M ionic strength. Systems with mixed micelle compositions were prepared by exchanging the proper amount of dodecyl sulfate anions (7, 21 or 35) to 1-alkylsulfonate anions; for each system, 2.5 μs-long trajectories were obtained.

2.2.4. Free energy calculations

The free energy profiles for the sulfonates association to SDS micelle were determined with replica-exchange umbrella sampling method [37], using center-of-mass distance between SDS micelle and sodium sulfonate as the reaction coordinate. The initial configurations for US simulations were obtained with 100 ns-long steered-MD simulations, in which one SDS molecule was replaced by sodium sulfonate molecule and was pulled away from the SDS micelle with the harmonic constant of 500 kJ mol^{-1} nm^{-2}.

9 equally spaced US windows were used, spanning a 1-5.0 nm range of the reaction coordinate. The spring constant of the harmonic biasing potential was set to 75 kJ mol^{-1} nm^{-2} in each US window. Each of the US windows were simulated for 1.5 μs and free energy profiles were determined using the weighted histogram analysis method [38]. The same procedure was used to calculate the referential free energy profile for SDS association to the micelle. Uncertainties were estimated using bootstrap error analysis taking into account the correlation in the analyzed time series.

3. Results and discussion

3.1. Critical micelle concentration

The CMC values of SDS in the presence of various concentrations of K8S, K10S, and K12S (and NaCl as a reference) were obtained – among others – from steady-state fluorescence spectroscopy measurements using pyrene, a well-known fluorescent probe utilized for the micropolarity studies of its solubilization site in the micellar interior [39]. When pyrene is excited at approximately 335-340 nm, its fluorescence emission spectrum exhibits five typical vibronic peaks. The intensity ratio $\frac{F_{373}}{F_{384}}$ of the first (solvent-sensitive band at 373 nm) and the third (solvent-insensitive band at 384 nm) vibronic peaks [40] is very sensitive to solvent polarity and therefore has been widely used to measure the polarity of the microenvironment of the polycyclic aromatic hydrocarbon (high values indicate polar environment) and CMC of surfactants [41]. Thus, the ratio $\frac{F_{373}}{F_{384}}$ for pyrene was determined in the absence and presence of increasing amounts of SDS (at various concentrations of K8S, K10S, K12S, and NaCl). For all studied systems it decreased significantly with the increase of SDS concentration (**Figure 2**). The inflection points of these curves indicate the CMC values of the micellization of SDS, which are presented in **Table 1**.

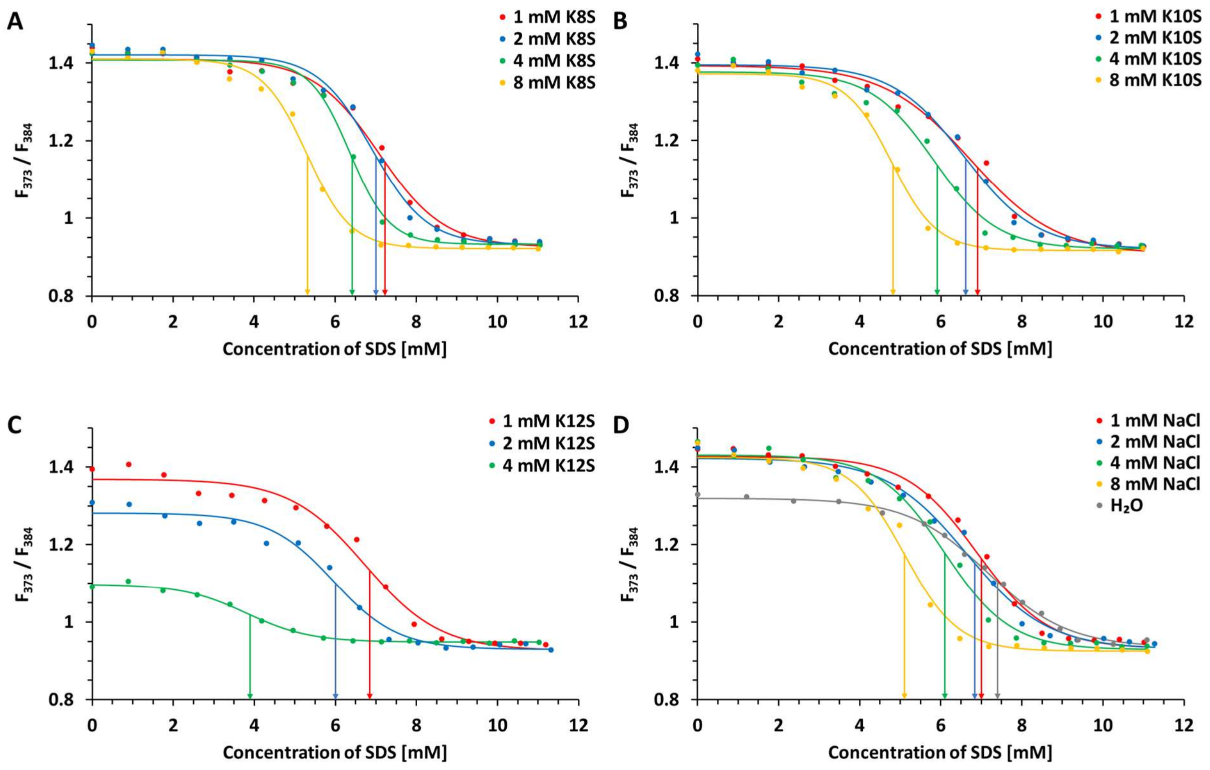
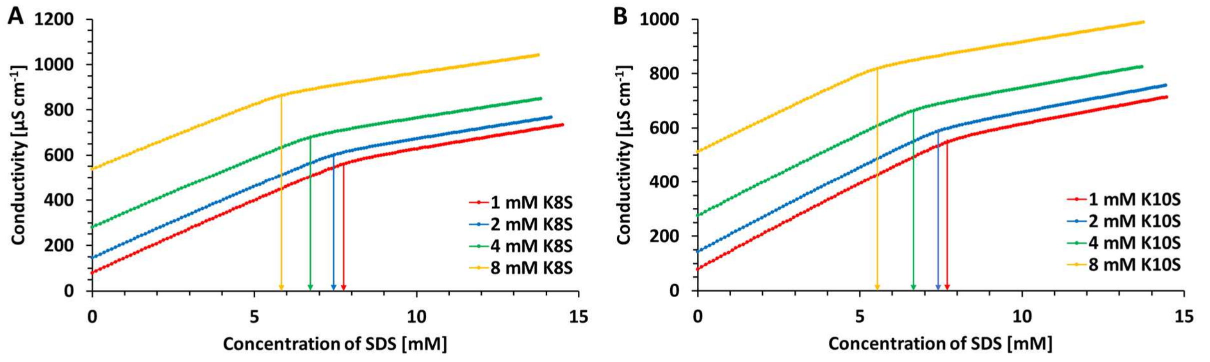


Figure 2. Plots of fluorescence intensity ratio $\frac{F_{373}}{F_{384}}$ for pyrene as a function of SDS concentration in the presence of various concentrations of K8S (A), K10S (B), K12S (C), and NaCl (D); λ_{ex} = 340 nm; c_{pyrene} = 2 μM; 298.15 K.

Furthermore, the CMC values of SDS were obtained for all studied systems from conductivity measurements. The plots of conductivity (κ) *vs* the concentration of SDS determined in the presence of different concentrations of K8S, K10S, K12S, and NaCl are shown in **Figure 3**. It is known that the specific conductivity is linearly correlated to the surfactant concentration in both the premicellar and postmicellar regions, with the slope in the premicellar region greater than that in the postmicellar region [3], which is due to lower mobility of micelles when compared to monomers [26]. Indeed, the plots exhibit two straight lines (both increasing with the increase of the concentration of SDS in the solution) intersecting at the point indicating the formation of the micelle. The CMC values are gathered in **Table 1**.



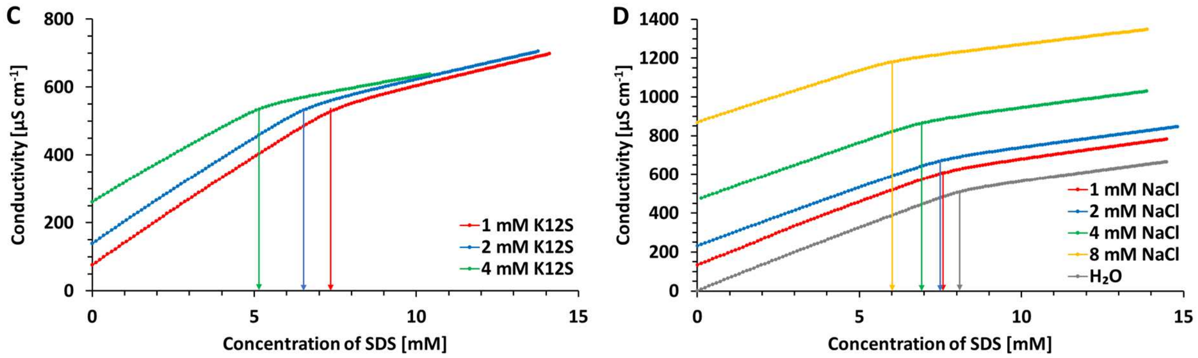


Figure 3. Plots of conductivity (κ) as a function of SDS concentration in the presence of various amounts of K8S (A), K10S (B), K12S (C), and NaCl (D); 298.15 K.

The value of CMC of SDS in water (in the absence of any added electrolyte) is in a great agreement with the previous reports [25,42]. From the inspection of **Figure 2**, **Figure 3**, and **Table 1** it can be clearly noticed that the CMC of SDS decreases very significantly with the increase of the concentration of the studied sodium 1-alkylsulfonates and sodium chloride. The lower values of CMC of SDS in the presence of K8S, K10S, K12S, and NaCl suggest its stronger tendency to self-assemble (SDS solutions containing sulfonates are more associated [43]) and form micelles under these conditions (micellization is favored in the occurrence of all studied salts in comparison to pure surfactant) [26,44]. In the case of sodium chloride the significant reduction of CMC values is related to the presence of additional ions from salt dissociation and their interactions with the SDS hydrophilic parts, monomers which are in the equilibrium with micelles or interactions with water molecules from the aqueous pseudophase [22,45]. The interactions of sodium cations with the negatively charged head of SDS micelles result in the reduction of electrostatic repulsions thereby increasing micelle stability and consequently, lowering the critical micelle concentration [22]. Such a trend has been observed previously for SDS/NaCl and SDS/KCl systems [22,25,46,47]. Furthermore, a comparison of CMC values of SDS determined in the presence of homologous series of the studied sodium sulfonates demonstrates that increasing the length of their hydrocarbon chain has the tendency of lowering the concentration of surfactant at which aggregation is initiated. However, NaCl exhibits very similar to K8S and K10S effect on the lowering the CMC of SDS – the values of critical micelle concentration in these two sulfonates are comparable and the co-ions seem not to have any other effect on the CMC of SDS than chloride ion. It means that the organic anions of K8S and K10S do not participate in the stabilization of micelles. It is in great accordance with previous reports concluding that there is indeed no co-ion effect on the micellization parameters of anionic surfactants by acetate, propionate and butyrate ions [25,48]. Interestingly, this is not the case for K12S – all studied solutions of that sodium 1-alkylsulfonate reduce CMC much stronger than K8S, K10S, and NaCl at the same concentrations. Specifically, 2 mM K12S decreases the CMC similarly to K8S, K10S, and NaCl, but at concentrations twice higher, while 4 mM K12S exhibits significantly greater impact when compared to 8 mM K8S, 8 mM K10S, and 8 mM NaCl. Hence, it can be supposed that K12S participates in the formation of the SDS micelles on account of identical to SDS hydrophobic chain length.

Table 1. Critical micelle concentration (CMC) obtained by both, conductometric titration (^{C}) and steady-state fluorescence spectroscopy (^{F}), degree of counter-ion binding (β), standard Gibb's free energy change (ΔG^0_{mic}) and aggregation number (N$_{agg}$) values of the micellization of SDS in the presence of various concentrations of K8S, K10S, K12S, and NaCl.

System	CMC [mM]	β	$\Delta G^0_{\mathrm{mic}}$ [kJ mol^{-1}]	N$_{agg}$	System	CMC [mM]	β	$\Delta G^0_{\mathrm{mic}}$ [kJ mol^{-1}]	N$_{agg}$
1 mM K8S	7.8 ^{C} 7.2 ^{F}	0.622	− 35.65	59	**1 mM K12S**	7.3 ^{C} 6.8 ^{F}	0.631	− 36.12	66
2 mM K8S	7.4 ^{C} 7.0 ^{F}	0.626	− 35.95	62	**2 mM K12S**	6.5 ^{C} 6.0 ^{F}	0.642	− 36.83	68
4 mM K8S	6.7 ^{C} 6.4 ^{F}	0.626	− 36.35	67	**4 mM K12S**	5.1 ^{C} 3.9 ^{F}	0.674	− 38.55	76
8 mM K8S	5.8 ^{C} 5.3 ^{F}	0.628	− 36.98	69	**Water**	8.1 ^{C} 7.4 ^{F}	0.643	− 35.96	58
1 mM K10S	7.7 ^{C} 6.9 ^{F}	0.630	− 35.88	64	**1 mM NaCl**	7.6 ^{C} 7.0 ^{F}	0.630	− 35.93	60
2 mM K10S	7.3 ^{C} 6.6 ^{F}	0.631	− 36.12	67	**2 mM NaCl**	7.5 ^{C} 6.8 ^{F}	0.622	− 35.81	65
4 mM K10S	6.6 ^{C} 5.9 ^{F}	0.640	− 36.72	68	**4 mM NaCl**	6.9 ^{C} 6.1 ^{F}	0.621	− 36.12	68
8 mM K10S	5.5 ^{C} 4.8 ^{F}	0.657	− 37.85	72	**8 mM NaCl**	6.0 ^{C} 5.1 ^{F}	0.622	− 36.70	70

3.2. Thermodynamics of micelle formation

The micellization behavior of surfactants can be influenced by structural/environmental modification which can be assessed by evaluating numerous thermodynamic parameters [26]. The standard Gibb's free energy change of micellization ($\Delta G^0_{\mathrm{mic}}$) per mole of monomer of SDS was calculated for all the studied systems from conductivity measurements using the following equation: $\Delta G^0_{\mathrm{mic}} = (1+\beta)RT\ln X_{\mathrm{CMC}}$, where X_{CMC} denotes CMC in mole fraction unit, R is the gas constant, T is the absolute temperature, and β (= 1 − α) is a degree of counter-ion binding (the values of the micelle ionization degree α were calculated as the ratio of the slopes of the two linear fragments of conductivity-concentration plot above and below CMC) [49]. The appropriate values of $\Delta G^0_{\mathrm{mic}}$ are listed in **Table 1**. It can be clearly observed that with increasing the alkyl chain length and concentration of the added sodium 1-alkylsulfonate the micellization process becomes more favorable ($\Delta G^0_{\mathrm{mic}}$ decreases). An opposite effect is observed for β – its values increase very slightly (the electrolyte anions are known to cause a much smaller change in the values of β for SDS than the cations [50]) with increasing the concentration and length of the sulfonates, which means that the binding of the counter-ions to the micelles increases [25]. The additional studies conducted at various temperatures for 1, 2, and 4 mM K12S (**Figure S1** in Electronic Supplementary Information) enabled determination of the values of the standard enthalpy ($\Delta H^{0}_{\mathrm{mic}}$) and then the standard entropy ($\Delta S^{0}_{\mathrm{mic}}$) changes of micellization per mole of surfactant according to the following equations: $\Delta H^{0}_{\mathrm{mic}} = -(1+\beta)RT^{2}\frac{\mathrm{dln}X_{\mathrm{CMC}}}{\mathrm{d}T}$ (where $\frac{\mathrm{dln}X_{\mathrm{CMC}}}{\mathrm{d}T}$ corresponds to the slopes of the plots in Figure S1) and $\Delta S^{0}_{\mathrm{mic}} = \frac{\Delta H^{0}_{\mathrm{mic}} - \Delta G^{0}_{\mathrm{mic}}}{T}$ [49]. The standard enthalpy changes of micellization of SDS in 1, 2, and 4 mM K12S are – 6.74, – 6.24, and – 4.68 kJ mol^{-1}, respectively. $\Delta H^{0}_{\mathrm{mic}}$ are rather small and negative indicating that micellization process is exothermic. The standard entropy changes of micellization of SDS are 99, 103, and 114 J mol^{-1} K^{-1} in 1, 2, and 4 mM K12S, respectively. $\Delta S^{0}_{\mathrm{mic}}$ is positive and increases with the increase of K12S concentration. The large entropy change values support the spontaneous micellization and hint that process is driven by an increase in entropy [42].

3.3. Aggregation number of SDS micelles

The mean aggregation numbers of SDS micelles were determined by fluorescence quenching method using pyrene as fluorescent probe and cetylpyridinium chloride as quencher molecule. The most important advantage of this method is that the aggregation number can be determined also when the micelles interact in solution [51]. $\mathrm{N_{agg}}$ values of SDS in the presence of various concentrations of K8S, K10S, K12S, and NaCl were calculated from the slopes of the plots of $\ln\left(\frac{\mathrm{F_0}}{\mathrm{F}}\right)$ versus [Q] according to the equation: $\ln\left(\frac{\mathrm{F_0}}{\mathrm{F}}\right) = \frac{\mathrm{N_{agg}[Q]}}{\mathrm{c-CMC}}$, where $\mathrm{F_0}$ and F are the fluorescence intensities in the absence and presence of quencher, respectively, c is the total surfactant concentration (higher than CMC; here 10 mM), and [Q] is quencher (CPC) concentration [52]. The highest CPC concentration (~20 μM) was much below its CMC (~100 μM), while the concentration of pyrene (2 μM) was much lower than the micelle concentration, what ensures quenching of the fluorescence of pyrene molecules that are solubilized in the micelles. This is indicated by the high values of the Stern–Volmer constants (K_{SV} from 11860 M^{-1} to 41300 M^{-1}) obtained from the strictly linear (R^2 from 0.988 to 0.997) plots of Stern–Volmer equation, $\frac{\mathrm{F_0}}{\mathrm{F}} = 1 + K_{\mathrm{SV}}[\mathrm{Q}]$ (**Figure 4**). The plots of $\ln\left(\frac{\mathrm{F_0}}{\mathrm{F}}\right)$ vs the concentration of CPC for 10 mM SDS are shown in **Figure 5**. The $\mathrm{N_{agg}}$ values as obtained from the slopes of the straight lines are listed in **Table 1**. It can be observed that aggregation number of SDS increases in the presence of studied sodium 1-alkylsulfonates and sodium chloride, as is always observed for ionic surfactants [41]. Furthermore, the higher the length of the hydrocarbon chain of the present in the system sulfonates salts, the higher the average micellar aggregation number. This is an expected behavior because, in general, the value of the micelle aggregation number increases as the CMC value decreases [41,42].

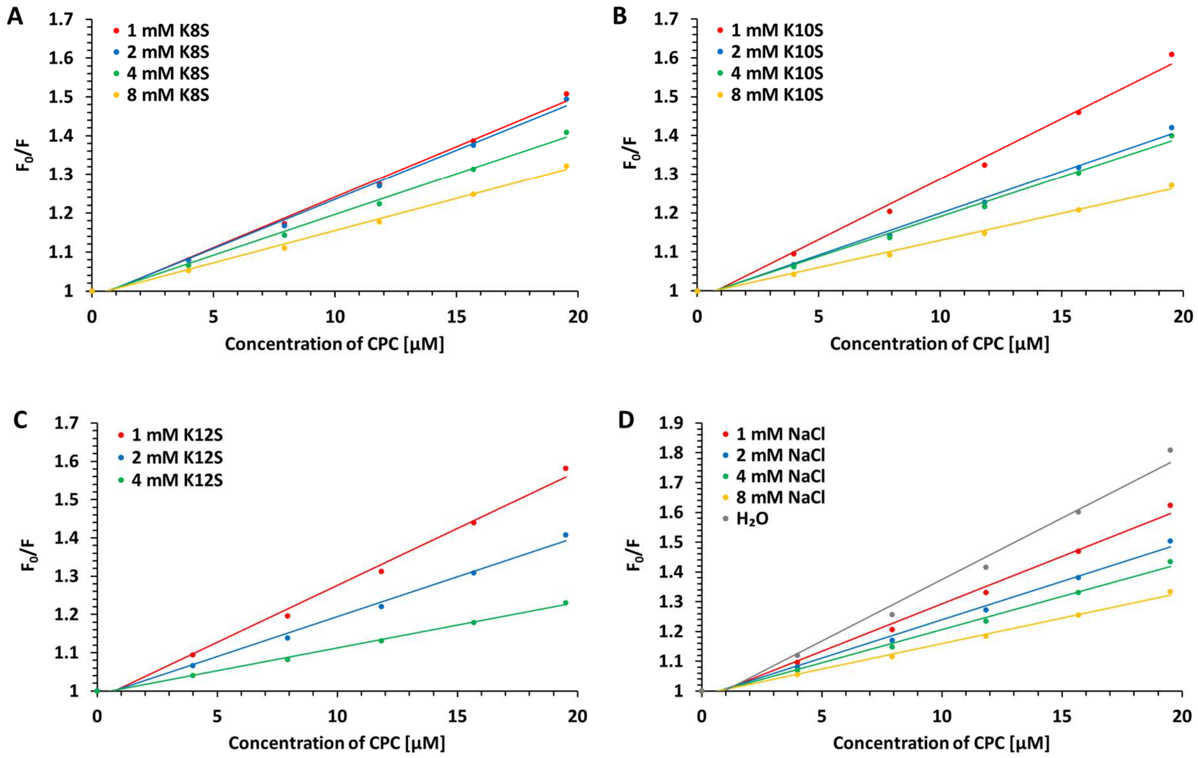


Figure 4. Stern-Volmer plots for the quenching of pyrene as a function of CPC concentration (for 10 mM SDS; in the presence of various concentrations of K8S, K10S, K12S, and NaCl); λ_{ex} = 340 nm; λ_{em} = 375 nm; c $_{pyrene}$ = 2 µM; 298.15 K.

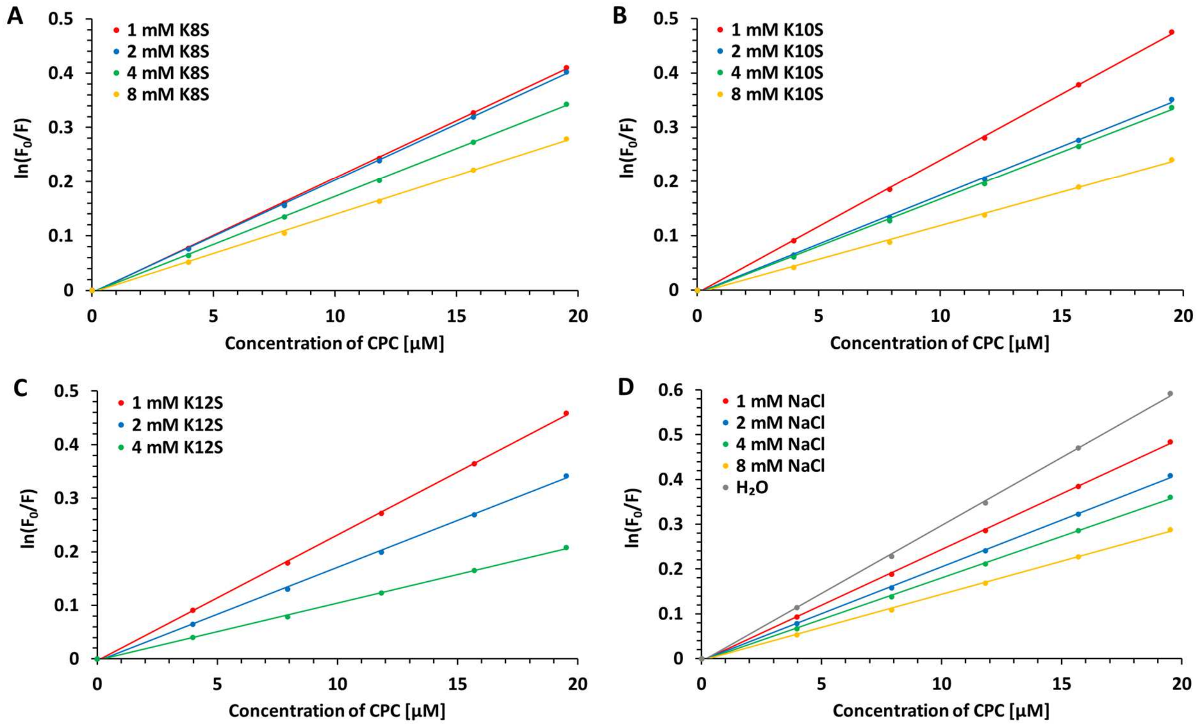


Figure 5. Plots of $\ln\frac{F_0}{F}$ of pyrene as a function of CPC concentration (for 10 mM SDS; in the presence of various concentrations of K8S, K10S, K12S, and NaCl); λ_{ex} = 340 nm; λ_{em} = 375 nm; c $_{pyrene}$ = 2 µM; 298.15 K.

3.4. Free energy of sulfonates association to SDS micelles

To investigate the possibility of sodium 1-alkylsulfonates participation in the SDS micelle formation, we firstly used umbrella sampling method to calculate the free energy profiles for sulfonates association to the SDS micelle. As can be seen on **Figure 6**, our results clearly illustrate that elongating of the alkyl chain results in growing affinity of the sulfonate to the SDS micelle. Furthermore, the free energy profile for K12S matches exactly the referential profile for the SDS association to the micelle. As affinities to the micelle for K8S and K10S are lower than affinity for SDS self-association to the micelle, one can expect that in the presence of either K8S or K10S and SDS in solution, formed micelle will be composed of only SDS molecules. In the case of K12S however, the resemblance of the affinities for K12S to the micelle and SDS self-association hints that K12S molecules can form micelles along with the SDS molecules, which may explain the significant reduction of CMC observed in the experiments.

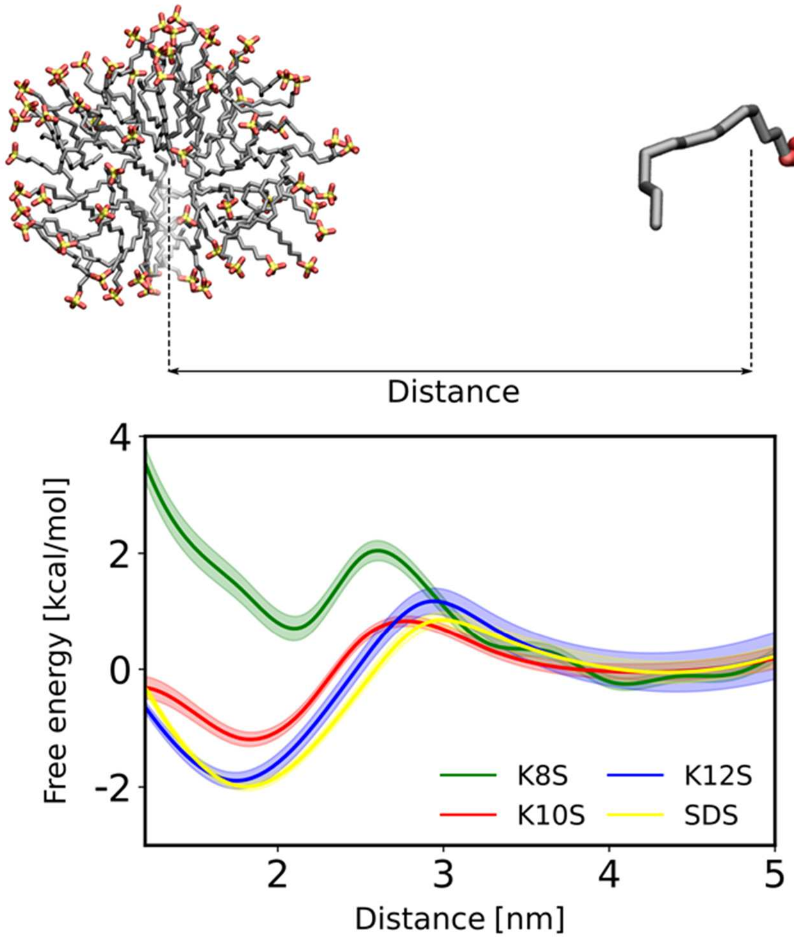


Figure 6. (Top) Structural representation of the reaction coordinate used in the study. The image was created using VMD [53]. (Bottom) Free energy profiles for the sulfonates association to the SDS micelle.

3.5. Stability of the mixed-composition micelles

In order to explore the stability of the mixed-composition micelles, we prepared systems with 10, 30 or 50% of dodecyl sulfate anions replaced by 1-alkylsulfonate anions, which were then simulated for 2.5 μs. During the simulations, the SDS core of the micelles remained intact, however, we observed events of sulfonates dissociation from the micelle to the solvent. To compare this effect between simulated systems, we calculated the actual composition of micelles from the last microsecond of simulation (**Table 2**). The sulfonate molecules were treated as the part of micelle when their distance to the centre-of-mass of SDS molecules were smaller than 2.7 nm.

Table 2. Average composition of the micelles during the last 1 μs of simulations.

Initial composition of micelle (fraction of sulfonates [%])	**Average fraction of sulfonates in the micelles [%]**		
	K8S	**K10S**	**K12S**
10	8,1 (±2,4)	3,7 (±2,8)	8,7 (±1,7)
30	17,3 (±6,1)	19,4 (±4,5)	21,0 (±3,6)
50	28,1 (±10,2)	22,7 (±12,1)	34,4 (±8,1)

As, according to the calculated free energy profiles, K8S and K10S molecules are less preferred to participate in the micelle formation than SDS, the K8S/SDS and K10S/SDS micelles can be treated as the referential states, stabilized mostly by the fact that the resultant number of SDS molecules in the systems is below their aggregation number. Although highly dynamic nature of the sulfonates exchange between the solvent and micelle, on average more K12S molecules participate in the micelle formation, in contrast to shorter sulfonates, what is particularly visible in the initial 50:50 investigated systems.

4. Conclusions

The aggregation behavior of sodium dodecyl sulfate (SDS) surfactant was studied in aqueous solutions of selected 1-alkyl sulfonates, namely sodium 1-octanesulfonate (K8S), sodium 1-decanesulfonate (K10S), and sodium 1-dodecanesufonate (K12S). The present work establishes that co-ions like octanate and decanate (similarly to shorter acetate, propionate, and butyrate [25,48]) do not have any significant effect on the CMC and N_{agg} of SDS. In contrary, dodecanate ions show an influence on the micellization behavior of the surfactant. It seems that K12S molecules (of the same carbon chain length as SDS) may act as the surfactant's mimetics and be incorporated into its micelles. In other words, SDS does not recognize K12S molecules as the ones with a different structure and consequently allows them to participate in the formation of the surfactant's micelles. The presented results may have important implications to understand the nature of the interactions between surfactants and various electrolytes.

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