Mixed Micellization and Interactional Behavior of Anionic Surfactants in Aqueous Solutions

Olena O. Streltsova, Olha V. Voliuvach*

Department of Physical and Colloidal Chemistry, Odesa I. I. Mechnikov National University, Vsevoloda Zmiienka St., 2, Odesa 65082, Ukraine

analytics_rd@onu.edu.ua

Keywords: *anionic surfactants, mixed micellization, quantitative and thermodynamic analysis.*

Mixed micellar systems have attracted considerable attention because of their unique solution properties and broad practical applications. This study investigates the micellization behavior of binary mixtures composed of two types of anionic surfactants: sodium undecylcarboxylate and sodium alkyl sulfates in aqueous media. The critical micelle concentrations of the mixed surfactant systems were determined by conductometric and tensiometric methods. The aggregation characteristics of the mixed anionic surfactant systems were calculated using Rubingh's model. To the best of our knowledge, these parameters have not previously been reported for this particular mixed micellar system. The excess free energy of micellization was evaluated and correlated with the surfactant interaction parameter in mixed micelles. The obtained results were analyzed in terms of synergistic interactions within the systems, and the influence of the chemical structure of the polar (charged) head group as well as the hydrocarbon chain length of the anionic surfactants on the self-assembly processes in mixed systems was discussed.

Introduction

Surfactants used in industrial applications are generally multicomponent systems consisting either of compounds belonging to the same homologous series or of mixtures of surfactants differing in hydrocarbon chain length, molecular structure, and, in the case of ionic surfactants, the nature of their hydrophilic head groups [1, 2]. Mixed micellar systems have attracted considerable scientific interest because of their unique physicochemical properties in solution. A detailed understanding of these systems is essential for establishing the scientific basis for the formulation of surfactant compositions intended for use as solubilizing agents, emulsifiers, gel-forming agents, and detergent formulations. Depending on the interactions between their components, surfactant mixtures may exhibit either antagonistic or synergistic behavior, resulting in colloidal and interfacial properties that differ significantly from those of the individual surfactants [3–13]. Studies of mixed surfactant systems have demonstrated their effectiveness

in controlling processes occurring in a wide variety of dispersed systems, including systems for pharmaceutical and biomedical use. Mixtures of different surfactants are capable of self-assembly and may form aggregate structures that differ substantially from those observed in single-component systems [1, 5, 14].

A survey of the recent literature indicates that both the theoretical description and the experimental characteristics of mixed micellization are unique for each binary surfactant system investigated [9–23]. Recent studies [24, 25] have emphasized the importance of simultaneously considering viscous (frictional) forces and cohesive forces associated with surface tension in liquids. These approaches provide useful tools for investigating molecular interactions in surfactant systems, nanoemulsions, and pharmaceutical formulations.

Particular attention has recently been devoted to cationic–cationic and anionic–anionic surfactant mixtures because of their potential applications in pharmaceutical dosage forms [21, 23, 26–30]. Considerable efforts have been directed toward elucidating drug-binding mechanisms to mixed micelles, which are frequently employed as biomembrane models. These studies demonstrate that electrostatic and hydrophobic interactions play a crucial role in improving drug delivery efficiency and provide valuable guidance for the rational design of mixed micellar drug-delivery systems [21, 23, 26–30]. Various theoretical approaches have been proposed for describing intermolecular interactions in mixed surfactant systems and for evaluating the influence of solution composition on the quantitative characteristics of micellization and adsorption at phase boundaries [1, 31, 32]. Among the most widely used models are Motomura's excess thermodynamic approach, Rubingh's regular solution theory, the molecular thermodynamic model proposed by Sarmoria and co-workers, and the approach developed by Puvvada et al. [31, 32]. For asymmetric mixed cationic–anionic surfactant systems, the dissociated Margules model has been shown to provide more accurate activity coefficients and improved estimates of micellar parameters than Rubingh's regular solution theory, particularly for alkyl dimethylbenzylammonium chloride–sodium dodecylbenzenesulfonate mixtures [18]. Analysis of the available literature indicates that each theoretical model possesses both advantages and limitations [1, 31, 32]. Nevertheless, the quantitative characteristics of mixed micellization obtained using the Rubingh and Motomura approaches generally agree within the limits of experimental uncertainty [31].

Previous small-angle neutron scattering studies of mixed micellar solutions containing the novel anionic surfactant sodium 5-tetradecylfuran-2-sulfonate and sodium dodecyl

sulfate (SDDS) demonstrated weak synergistic interactions accompanied by a decrease in the critical micelle concentration (CMC) and only limited incorporation of SDDS into the mixed micelles. This behavior was attributed to electrostatic repulsion between the anionic head groups [14]. In contrast, mixtures of anionic and nonionic surfactants, including sodium dodecyl sulfate with ethoxylated dodecylamine, sodium dodecylbenzenesulfonate with tristyrylphenol ethoxylate (EOT) [16], and sodium dodecylbenzenesulfonate with Tween 80 [9], exhibit considerably stronger synergistic effects during mixed micellization at appropriate component ratios [19].

The principal micellar, interfacial, and thermodynamic parameters of mixed micelles and mixed adsorption layers are commonly determined using complementary experimental techniques, including surface tensiometry, electrical conductivity measurements, and isothermal titration calorimetry (ITC) [1, 6, 7, 9, 18, 23, 30–33]. Surface tension measurements provide valuable information on the thermodynamics of micelle formation and on the influence of surfactant interactions on the surface activity of mixed systems [23]. Furthermore, changes in the standard enthalpy and entropy of mixed micellization provide evidence for the presence of different intermolecular interactions, including electrostatic, ion–dipole, hydrogen-bonding, and hydrophobic interactions between surfactant molecules [34].

These findings clearly demonstrate that investigations of mixed micellar systems are of considerable importance from both fundamental and practical perspectives. However, relatively few studies have addressed mixed micellization in aqueous solutions of anionic–anionic surfactant mixtures differing in the structure of their polar head groups [14, 23]. Moreover, the experimental behavior of each binary surfactant system remains highly system-specific. As pointed out by previous authors [16], predicting the behavior of surfactant mixtures whose individual components possess substantially different CMC values remains a particularly challenging task. To the best of our knowledge, no quantitative data have previously been reported for the intermolecular interaction parameters of sodium undecylcarboxylate (SUDC) mixed with sodium alkyl sulfates (SAS) containing R12 (sodium dodecyl sulfate, SDDS), R14 (sodium tetradecyl sulfate, STDS), and R16 (sodium hexadecyl sulfate, SHDS) hydrocarbon chains. Likewise, deviations from ideal behavior during mixed micellization and the composition of mixed micelles formed in the SUDC–SDDS, SUDC–STDS, and SUDC–SHDS systems have not been previously investigated. Consequently, the present study provides new experimental information on these mixed surfactant systems. The present work investigates the micellization behavior of binary

SUDC–SAS systems as a function of solution composition and hydrocarbon chain length of the sodium alkyl sulfates. The results are intended to provide recommendations for improving the practical application of these biodegradable and environmentally safe anionic surfactants while reducing the amount of surfactant required compared with the use of individual components.

Accordingly, the objective of this work was to perform a quantitative and thermodynamic analysis of mixed micellization in aqueous solutions containing sodium undecylcarboxylate (SUDC) and sodium alkyl sulfates (SAS), namely sodium dodecyl sulfate (SDDS), sodium tetradecyl sulfate (STDS), and sodium hexadecyl sulfate (SHDS), in order to determine the optimum component ratios that provide the most favorable conditions for the technological application of the SUDC–SDDS, SUDC–STDS, and SUDC–SHDS mixed surfactant systems.

Experimental part

Material and methods

The following anionic surfactants (SAS) were used in this study after a single recrystallization: sodium dodecyl sulfate (SDDS, $C_{12}H_{25}OSO_3Na$), sodium tetradecyl sulfate (STDS, $C_{14}H_{29}OSO_3Na$), and sodium hexadecyl sulfate (SHDS, $C_{16}H_{33}OSO_3Na$) supplied by Riika (analytical grade, purity 97%). Stock solutions of the sodium alkyl sulfates (50.0×10^{-3} mol·L^{-1}) were prepared using double-distilled water. Sodium undecylcarboxylate (SUDC, $C_{11}H_{23}COONa$) was prepared by neutralization of undecylic acid ($C_{11}H_{23}COOH$) with an aqueous sodium hydroxide solution. Prior to use, the acid (TOP, analytical grade) was recrystallized twice from ethanol. To eliminate the ageing effect characteristic of soap solutions, freshly prepared 50.0×10^{-3} mol·L^{-1} stock solutions of sodium undecylcarboxylate were used for each series of measurements. All solutions were prepared with double-distilled water in the absence of supporting electrolytes.

Working solutions of the individual surfactants and their binary mixtures ($R_{11}COONa$ – R_nOSO_3Na) in the concentration range from 5.0×10^{-2} (1.0×10^{-2}) to 1.0×10^{-6} mol·L^{-1} were prepared by dilution of the corresponding stock solutions. The mole fraction of sodium alkyl sulfate in the binary mixtures was varied between 0.2 and 0.8. To suppress hydrolysis of the carboxylate surfactant, the solution pH was maintained within the range of 9.0–9.2. The pH values were monitored using an EV-74 universal ion meter equipped with a glass electrode and adjusted by addition of 0.1–1.0 mol·L^{-1} sodium hydroxide solution.

The critical micelle concentrations of the individual surfactants and their binary mixtures were determined by conductometric [35–39] and tensiometric [40] methods. Electrical conductivity measurements were performed

using an EZODO PL-700 ALS conductivity meter. The measurement uncertainty did not exceed ±2% of the measured conductivity values.

Preliminary experiments showed that equilibrium surface tension values for aqueous SUDC–SAS binary mixtures in the concentration range (0.001–10.0) × 10^{-3} mol·L^{-1} were established after approximately three hours at 298 ± 2 K. Surface tension measurements were carried out using the Wilhelmy plate method with an accuracy of ±0.5 mJ·m^{-2}.

The critical micelle concentrations obtained by the conductometric and tensiometric methods were in excellent agreement. The CMC values were determined to be (28.40 ± 0.03) × 10^{-3} mol·L^{-1} for SUDC, (8.50 ± 0.03) × 10^{-3} mol·L^{-1} for SDDS, (2.10 ± 0.02) × 10^{-3} mol·L^{-1} for STDS, and (0.52 ± 0.003) × 10^{-3} mol·L^{-1} for SHDS. These values are in good agreement with those previously reported in the literature [1, 34, 41].

Results and discussion

Analysis of the specific conductivity isotherms obtained for the individual surfactants and their binary aqueous mixtures revealed conductivity profiles characteristic of surfactant systems undergoing micellization. In all cases, the conductivity–concentration plots (κ versus C) consist of two distinct linear regions corresponding to concentrations below and above the CMC. The breakpoint in the $\kappa = f(C)$ dependence corresponds to the CMC (**Figure 1**).

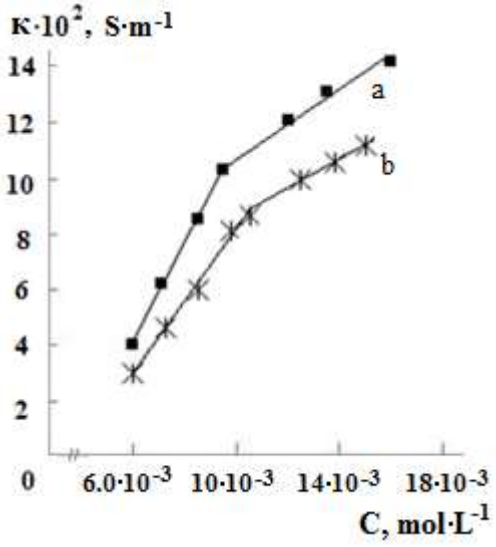

Figure 1. Conductometric isotherms of SUDC–SDDS mixtures with SDDS mole fractions (n) of 0.6 *(a)* and 0.4 *(b)*.

At surfactant concentrations below the CMC, the specific conductivity increases almost linearly with concentration, similarly to aqueous solutions of moderately strong electrolytes. Once the CMC is reached, a distinct change in slope is observed due to the formation of ionic micelles, which are predominantly spherical in shape [2]. Since ionic micelles possess considerably lower mobility than individual surfactant ions, the rate of increase in electrical conductivity decreases above the CMC.

The surface tension isotherms obtained for the individual surfactants and their binary mixtures (**Figures 2 and 3)** exhibit the characteristic behavior of micelle-forming surfactant systems. As the surfactant concentration increases, the surface tension decreases until the CMC is reached, after which it remains nearly constant or decreases only slightly because additional surfactant molecules

preferentially participate in micelle formation rather than adsorb at the air–water interface.

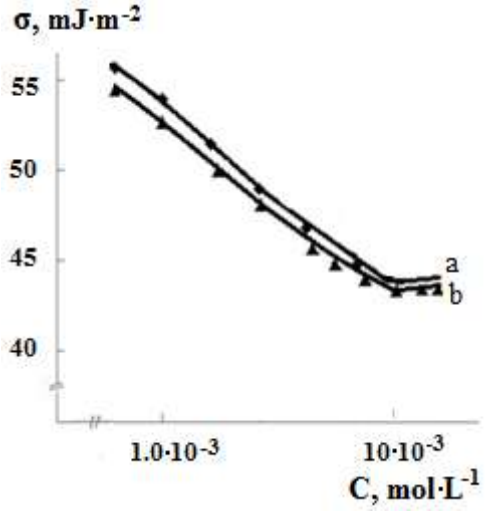

Figure 2. Surface tension isotherms of SUDC–SDDS mixtures with SDDS mole fractions (*n*) of 0.6 *(a)* and 0.4 *(b)*.

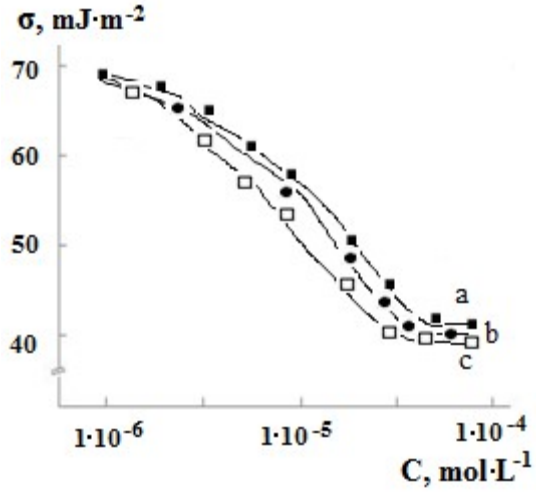

Figure 3. Surface tension isotherms of SUDC–SHDS mixtures with SHDS mole fractions (*n*) of 0.5 *(a)*, 0.6 *(b)* and 0.8 *(c)*.

The experimental results demonstrated that, over a wide range of compositions, aqueous mixtures of SUDC–STDS and SUDC–SHDS exhibit lower CMC than the corresponding individual surfactants (SUDC, STDS, and SHDS) **(Tables 1 and 2).** Furthermore, the CMC decreases with increasing hydrocarbon chain length of the sodium alkyl sulfate and with increasing mole fraction (*n*) of SAS in the binary mixture. An exception is the SUDC–SDDS binary system, composed of two anionic surfactants, one of which, SDDS, possesses only a slightly longer hydrocarbon chain than SUDC. In this case, the CMC decreases only relative to that of pure SUDC (CMC = 28.4 × 10^{-3} mol·L^{-1}) as the mole fraction (*n*) of SDDS in the mixed solution increases. According to the Davies hydrophilic–lipophilic balance (HLB) values, the sulfate head group is considerably more hydrophilic than the carboxylate head group (HLB (-SO_4Na) = 35.7; HLB (-CO_2Na) = 21.1) [1]. However, because SDDS contains only one additional methylene group (–CH_2–) compared with SUDC (R11), the enhancement of hydrophobic interactions is relatively weak, resulting in only a modest reduction of the CMC in the mixed system.

Table 1. Critical micelle concentration (CMC) values for individual anionic surfactants in aqueous solutions at 298 K

CMC×10^{-3}, mol·L^{-1}			
SUDC	SDDS	STDS	SHDS
28.40±0.4	8.50±0.3	2.10±0.03	0.52±0.02

Table 2. Critical micelle concentration (CMC) values for SUDC–SAS mixtures at different mole fractions (n) of SAS in binary aqueous solutions

n (SAS)	CMC×10^{-3}, mol·L^{-1}		
	SUDC - SDDS	SUDC - STDS	SUDC - SHDS
0.2	13.60	0.550	0.150
0.4	10.50	0.450	0.083
0.5	9.70	0.380	0.068
0.6	9.50	0.330	0.056
0.8	9.10	0.200	0.043

To evaluate the mutual influence of surfactants differing in the structure of their hydrophilic head groups, composition–property diagrams were constructed, and the properties of the investigated systems were compared with those predicted for the corresponding hypothetical ideal systems. For this purpose, the Lange equation [42] was applied:

$$\frac{1}{\mathrm{CMC}_{12}} = \frac{n}{\mathrm{CMC}_1} + \frac{(1-n)}{\mathrm{CMC}_2} \quad (1)$$

where CMC_1, CMC_2, and CMC_{12} are the critical micelle concentrations of the individual SAS, SUDC, and their binary mixtures, respectively, and n is the mole fraction of SAS in the binary aqueous solution.

A clear discrepancy was observed between the theoretical and experimental CMC values (**Figure 4**), indicating non-ideal behavior of the investigated binary surfactant systems. The degree of synergism, as reflected by the CMC values, increased with increasing hydrocarbon chain length of the sodium alkyl sulfate. The largest deviations, amounting to approximately one order of magnitude (10–15-fold), were observed for the SUDC–STDS and SUDC–SHDS systems, in which the hydrocarbon chains of the two surfactants differ substantially in length. This behavior can be attributed to enhanced hydrophobic interactions between the alkyl chains, as well as to secondary structural effects associated with changes in the packing density of SUDC and SAS molecules (ions) within curved mixed micelles.

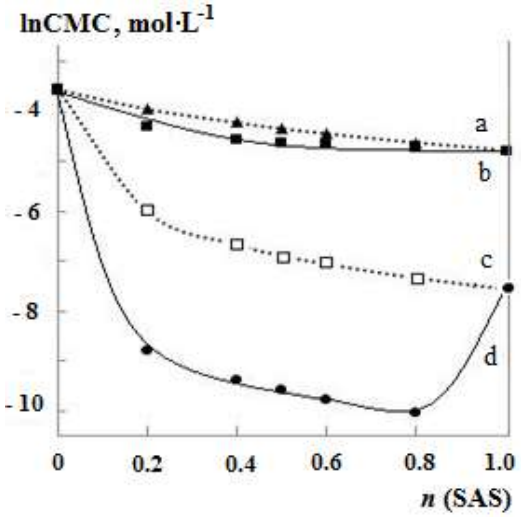

Figure 4. Dependence of the natural logarithm of the critical micelle concentration (CMC) of SUDC–SDDS (curves a, b) and SUDC–STDS (curves c, d) mixtures on the mole fraction (n) of SAS in binary aqueous solutions: a and c represent the theoretical curves calculated using the Lange equation, whereas b and d represent the experimental data.

The negative deviation of the experimental CMC values from the values predicted by the ideal mixing model indicates the formation of mixed micelles **(Figure 4)**. This conclusion is further supported by the calculated mixed micelle compositions and

intermolecular interaction parameters discussed below.

Solution of Rubingh's equation (2) [3]:

$$\frac{(x_1^m)^2 ln\,(nCMC_{12}/x_1^m CMC_1)}{(1-x_1^m)^2 ln\,[(1-n)CMC_{12}/(1-x_1^m)CMC_2]} = 1$$

where n (SAS) is the mole fraction of SAS in the binary solution containing SUDC; x_1^m is the mole fraction of SAS in the mixed micelle; and CMC_1, CMC_2, and CMC_{12} are the critical micelle concentrations of SAS, SUDC, and their binary mixtures, respectively.

The calculations demonstrated that mixed micelles are formed in the bulk aqueous phase of all the investigated binary anionic surfactant systems. The composition of these mixed micelles depends both on the mole ratio of the surfactants in solution and on the hydrocarbon chain length of the surfactant molecules (ions) **(Table 3)**. In all cases, the micellar phase is enriched with the more oleophilic surfactant component.

Over a wide range of compositions of binary anionic surfactant systems containing surfactants with different hydrophilic head groups, the composition of the mixed micelles is not constant. This behavior is attributed to the fact that the driving force for mixed micellization is the hydrophobic interaction between the surfactant molecules.

Table 3. Micellization parameters of mixed SUDC–SAS systems at different mole fractions (n) of SAS in binary aqueous solutions

n (SAS)	x_1^m	β^m	$f^m{}_1$	$f^m{}_2$	ΔG_M kJ·mol^{-1} (2)
SUDC - SDDS					
0.2	0.4720	–1.39	0.6771	0.7334	–2.57
0.4	0.6140	–1.46	0.8025	0.5769	–2.51
0.5	0.6737	–1.56	0.8437	0.4916	–2.42
0.6	0.7309	–1.19*	0.9139	0.5273	–2.03
0.8	----	----	----	----	----
SUDC - STDS					
0.2	0.5538	–11.85	0.0944	0.0265	–8.96
0.4	0.5881	–11.35	0.1451	0.0196	–8.50
0.5	0.5898	–11.14	0.1541	0.0207	–8.35
0.6	0.6065	–12.02	0.1557	0.0120	–8.77
0.8	0.6241	–14.88	0.1225	0.0030	–10.30
SUDC - SHDS					
0.2	0.5912	–13.93	0.0973	0.0077	–10.02
0.4	0.6083	–14.70	0.1044	0.0043	–10.45
0.5	0.6243	–16.04	0.1044	0.0019	–10.97
0.6	0.6245	–16.08	0.1033	0.0019	–10.98
0.8	0.6404	–17.56	0.1033	0.0007	–11.69

***** Does not satisfy the additional criterion for synergism:

$$|\ln[CMC_1\,(SDDS) / CMC_2\,(SUDC)]| < |\beta^m|$$

As the mole fraction of SAS increases in the binary SUDC–SAS solution, its mole fraction in the mixed micelles increases correspondingly. These results clearly demonstrate the dominant role of the more hydrophobic surfactant in determining the composition of the mixed micelles.

The activity coefficients of the surfactant molecules in the mixed micelles were calculated

according to the regular solution theory approximation:

$$f_1^m = exp\,[\beta^m(1-x^m)^2],$$

$$f_2^m = exp\,[\beta^m(x^m)^2]$$

The calculated activity coefficients are less than unity, indicating that the investigated binary systems exhibit significant deviations from ideal solution behavior.

The intermolecular interaction parameter (β^m), calculated using Equation (3),

$$\beta^m = \frac{ln\,(nCM_{12}/x_1^m CMC_1)}{(1-x_1^m)^2}, \quad (3)$$

provides a quantitative measure of the interactions between SUDC and sodium dodecyl sulfate, sodium tetradecyl sulfate, and sodium hexadecyl sulfate within the mixed micelles.

For all the investigated binary systems (SUDC–SDDS, SUDC–STDS, and SUDC–SHDS), the interaction parameter β^m was found to be negative **(Table 3)**, indicating attractive intermolecular interactions between SUDC and SAS in the mixed micelles. The magnitude of these interactions increases markedly with increasing hydrocarbon chain length of the sodium alkyl sulfate, with β^m changing from −1.56 for SUDC–SDDS to −14.88 for SUDC–STDS and −17.56 for SUDC–SHDS. Since the absolute value of β^m reflects the strength of the intermolecular interactions, these results demonstrate that the attractive interactions become progressively stronger as the alkyl chain length increases.

Despite the identical negative charge of their polar head groups, the long-chain surfactants STDS and SHDS exhibit strong attractive interactions with SUDC over the entire composition range investigated. These interactions arise from the combined effects of hydrophobic association and electrostatic interactions within the mixed micelles.

The synergistic behavior of the investigated mixed surfactant systems is further confirmed by the negative values of the interaction parameter β^m. The calculations showed that, for the binary SUDC–STDS and SUDC–SHDS mixtures, the following additional criteria for synergism are satisfied over the entire composition range investigated:

1. $\beta^m < 0$
2. $|\ln[CMC_1\,(SAS) / CMC_2\,(SUDC)]| < |\beta^m|$

As the proportion of the more oleophilic surfactant increases in the mixed solution, the absolute value of β^m also increases, indicating progressively stronger attractive interactions within the mixed micelles. A similar trend was reported by the authors of Ref. [23] for mixed SDDS–sodium oleate systems, where the interaction parameter increased from −9.59 to −21.28 as the mole fraction of sodium oleate increased from 0.2 to 0.8.

The excess free energy of micellization (ΔG_M) was calculated for the investigated binary surfactant systems, taking into account the

activity coefficients f^m_1 (SAS) and f^m_2 (SUDS) in the mixed micelles, according to Equation (4):

$$\Delta G_M = [x_1^m \ln x_1^m f^m_1 + x_2^m \ln x_2^m f^m_2)]RT. \quad (4)$$

From a thermodynamic standpoint, the mixed micellization of SUDC with the long-chain sodium alkyl sulfates is more favorable **(Table 3)**, particularly at a component ratio of 0.2 SUDC : 0.8 STDS and for SUDC–SHDS systems with n(SHDS) ≥ 0.5, where ΔG_M ranges from -10.97 to -11.69 kJ·mol^{-1}. The negative values of the excess free energy of micellization indicate the thermodynamic stability of the mixed micelles. The nonlinear dependence of the CMC on the composition of the mixed micelles reflects the corresponding nonlinear variation in the excess free energy of aggregation. These findings suggest that the observed synergistic effects arise predominantly from the entropic contribution associated with differences in the structures of the surfactant polar head groups.

Conclusions

In the present study, mixed micellization in aqueous solutions containing two anionic surfactants – sodium undecylcarboxylate (SUDC) and sodium alkyl sulfates (SDDS, STDS, and SHDS) – was investigated using physicochemical methods over a wide range of mixture compositions in order to elucidate the behavior of surfactant systems possessing identically charged hydrophilic head groups. The experimentally determined critical micelle concentrations were consistently lower than the corresponding theoretical values, demonstrating non-ideal interactions in the SUDC–SAS systems. The extent of this deviation depends strongly on the hydrocarbon chain length of the sodium alkyl sulfate. Pronounced synergistic effects were observed for the SUDC–STDS and SUDC–SHDS mixtures, whereas the SUDC–SDDS system exhibited predominantly antagonistic behavior during mixed micellization. This difference is attributed to the increasing contribution of hydrophobic interactions between the surfactant hydrocarbon chains. Rubingh's model was successfully applied to analyze the observed behavior. The negative values of the intermolecular interaction parameter (β^m, ranging from −1.39 to −17.56 indicate attractive interactions between SUDC and SAS in mixed micelles, which are enriched in the sodium alkyl sulfate component. Despite carrying identically charged anionic head groups, the long-chain surfactants STDS and SHDS exhibit strong attractive interactions with SUDC throughout the investigated composition range as a result of the combined effects of hydrophobic association and electrostatic interactions.

The negative excess free energy of micellization further confirms both the spontaneous nature of mixed micelle formation and the high thermodynamic stability of the mixed aggregates. Thermodynamically, the most favorable mixed micellization occurs for

systems containing 0.2 (SUDC) : 0.8 (STDS) and for SUDC–SHDS mixtures with $n \geq 0.5$, where ΔG_M ranges from –10.97 to –11.69 $kJ \cdot mol^{-1}$.

Overall, the results demonstrate that mixed micellar systems composed of anionic surfactants possessing identically charged hydrophilic head groups are of considerable scientific as well as practical interest. Such systems show promise for application as solubilizing agents, drug-delivery carriers, emulsifiers, gelling agents, and components of detergent formulations.

References

[1] Holmberg K, Jönsson B, Kronberg B, Lindman B. Surfactants and Polymers in Aqueous Solution. 2002.

[2] Mchedlov-Petrosyan NO, Lebed' AV, Lebed' VI. Kolloidnyye poverkhnestno-aktivnyye veshchestva. Uchebno-metodicheskoye posobiye. – Khar'kov : KHNU imeni Karazina, 2009;72.

[3] Rubingh D. Mixed Micelle Solutions. Solution Chemistry of Surfactants 1979:337-354.

[4] Ogino K. Solution Properties of Mixed Surfactant Systems. Journal of Japan Oil Chemists' Society 1985;34(7):568-575.

[5] Kumar Shah S, Chakraborty G, Bhattarai A, De R. Synergistic and antagonistic effects in micellization of mixed surfactants. Journal of Molecular Liquids 2022;368:120678.

[6] Rosen M, Hua X. Synergism in binary mixtures of surfactants: II. Some experimental data. Journal of the American Oil Chemists' Society 1982;59(12):582-585.

[7] Zhu B, Rosen M. Synergism in binary mixtures of surfactants. Journal of Colloid and Interface Science 1984;99(2):435-442.

[8] Szymczyk K, Jańczuk B. The Properties of a Binary Mixture of Nonionic Surfactants in Water at the Water/Air Interface. Langmuir 2007;23(9):4972-4981.

[9] AL-Saady F, H. keem s. Mixed Micelles of Binary Mixtures of Sodium Dodecylbenzene Sulfate and Tween 80 Surfactants in Aqueous Solutions. Baghdad Science Journal 2020;17(1):305-309.

[10] Russo Krauss I, Cavasso D, Ciccarelli D, Heenan R, Ortona O, D'Errico G, Paduano L. A Hofmeister series perspective on the mixed micellization of cationic and non-ionic surfactants. Journal of Molecular Liquids 2021;335:116205.

[11] Azum N, Rub M, Alotaibi M, Khan A, Asiri A. Synergistic Interaction Between Cationic Novel Gemini Surfactant and Non-ionic Conventional Surfactants in Aqueous Medium. Biointerface Research in Applied Chemistry 2021;12(6):7416-7428.

[12] Streltsova EA, Muntyan OG, Volyuvach OV. Micelle formation in aqueous solutions of surfactant binary mixtures. Ukr. Chem. J. 2002;68(3-4):91-95.

[13] Streltsova EA, Voluvach OV. Intermolecular interaction in binary mixtures of cationic and anionic surfactants. Ukr. Chem. J. 2004;70(5-6):46-50.

[14] Deeming L, Leaman N, Honecker D, Chen Y, Ma K, Edler K. Mixed micellar solutions of an oleo-furan sulfonate surfactant with anionic and non-ionic surfactants. Journal of Colloid and Interface Science 2025;699:138201.

[15] Puača G, Tepavčević V, Poša M. Interaction between Triton X100 and Brij 58 in their binary mixed micelles: Micellization in aqueous solution and aqueous solution of Poloxamer 188 at the range of temperature T = (273.15–323.15) K. The Journal of Chemical Thermodynamics 2022;173:106835.

[16] Kotsi K, Dong T, Kobayashi T, Mc Robbie I, Striolo A, Angeli P. Synergistic effects between a non-ionic and an anionic surfactant on the micellization process and the adsorption at liquid/air surfaces. Soft Matter 2024;20(3):523-534.

[17] Han W, Long W, Peng L, Zhang W, Shi B. Effect of nonionic and anionic surfactant on ecotoxicity and micellization behaviors of dodecyl trimethyl ammonium bromide (DTAB). Colloids and Surfaces A: Physicochemical and Engineering Aspects 2023;671:131588.

[18] Sood A, Sethi O, Aggarwal M. Evaluation of mixed micellar interactions of CnBCl and SDBS mixtures using dissociated Margules model and influence of different salts. Journal of Surfactants and Detergents 2022;26(1):23-32.

[19] Lang Y, Zhou J, Liang H, Sun J, Zhang K, Wang C, Liu Y, Geng T. Synergistic effects of nonionic surfactants ethoxylated alkylamines and sodium dodecyl sulfate in mixed systems. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2024;694:134192.

[20] Sarıkaya Yıldız İ, Bilgen S, Akbaş H. Micellization, aggregation, interaction, and solubilization behaviors of mixed solutions of cationic gemini and nonionic surfactants. Journal of Surfactants and Detergents 2024;27(4):547-555.

[21] Suting S, Wagay T, Charingia A, Askari H. Binary micellar schemes of cationic gemini and conventional surfactants: chain length effect. Journal of Dispersion Science and Technology 2022;44(11):2001-2012.

[22] Azum N, Rub M, Chani M, Alzahrani K, Asad M, Kamal T. Mixed Micellization and Density Functional Theory (DFT) Studies on the Molecular Interactions between Gemini and Nonionic Surfactants. Journal of Oleo Science 2025;74(1):47-59.

[23] Pathan T, Girase M, Ray D, Padsala S, Parekh P, Khimani M, Pathan S, Kuperkar K, Aswal V, Patel V. Scrutinizing micellar transitions and interfacial properties in mixed micelles comprising sodium dodecyl sulfate and sodium oleate: A tensiometric and scattering insight. Journal of Molecular Liquids 2024;397:124138.

[24] Singh M, Singh S. The Chemistry of Friccohesity for Industrial Nanoformulation. Cambridge Scholars 2023.

[25] Singh S, Agbizu Cookey G, Singh M. Friccohesity resonating energy transfer for molecular economy. Journal of Molecular Liquids 2025;427:127176.

[26] Rafaet Hossain M, Abdul Rub M, Mahbub S, Rana S, Asiri A, Anamul Hoque M, Kabir M. Assembly nature and physicochemical variables of a mixture of cetyltrimethylammonium bromide + tetradecyltrimethylammonium bromide in aq. levofloxacin hemihydrate drug medium: A conductivity and theoretical approach. Journal of Molecular Liquids 2022;367:120372.

[27] Sohal P, Kaur R, Singh M, Banipal T, Banipal P, Kang T. Binding studies of dopamine HCl drug with the mixed {sodium bis(2-ethylhexyl) sulfosuccinate + sodium dodecylsulfate} micelles: Physicochemical, spectroscopic, calorimetric and computational approach. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2022;640:128386.

[28] Kumar M, Khushi K, Singh S, Deb D, Khan J, Ahmad A, Singh O, Singh N, Srivastava A. Binding and occupancy properties of gabapentin in mixed surfactant systems. Journal of Surfactants and Detergents 2023;27(3):433-444.

[29] Srivastava A, Tiwari S, Khan J, Deb D, Ullah M. Investigating the binding interactions of cetirizine and diphenhydramine in SDS-SDBS mixed micelles. Colloid and Polymer Science 2025;303(6):985-1001.

[30] Sharma J, Banipal T, Banipal P. Mixed micellization and interactional behavior of anionic surfactants in aqueous betaine hydrochloride drug solutions. Journal of Dispersion Science and Technology 2025:1-16.

[31] Streltsova OO, Voliuvach OV. Pro mitseloutvorennya i adsorbtsiyu poverkhnevo-aktyvnykh rechovyn na mezhi podilu faz binarnyy rozchyn poverkhnevo-aktyvnykh rechovyn – povitrya. Visnyk

Odes′koho natsional′noho universytetu. Khimiya 2003;8(4):163-175.

[32] Haque M, Das A, Rakshit A, Moulik S. Properties of Mixed Micelles of Binary Surfactant Combinations. Langmuir 1996;12(17):4084-4089.

[33] Zheng P, Cai D, Zhao J, Shen W. Thermodynamic properties of mixed surfactants of dodecyltrimethylammonium bromide and 1-dodecyl-3-methylimidazolium bromide. The Journal of Chemical Thermodynamics 2017;113:394-398.

[34] Alam M, Mahbub S, Alfakeer M, Hoque M, Mustafa S, Ahmad M, Kabir S. The Assembly of the Mixture of Two Ionic Surfactants in Polyols Media at Variable Temperatures: Combined Conductivity and Theoretical Investigations. Journal of Surfactants and Detergents 2021;25(1):37-52.

[35] Garcia-Mateos I, Mercedes Velazquez M, Rodriguez L. Critical micelle concentration determination in binary mixtures of ionic surfactants by deconvolution of conductivity/concentration curves. Langmuir 1990;6(6):1078-1083.

[36] Scholz N, Behnke T, Resch-Genger U. Determination of the Critical Micelle Concentration of Neutral and Ionic Surfactants with Fluorometry, Conductometry, and Surface Tension—A Method Comparison. Journal of Fluorescence 2018;28(1):465-476.

[37] Perger T, Bešter-Rogač M. Thermodynamics of micelle formation of alkyltrimethylammonium chlorides from high performance electric conductivity measurements. Journal of Colloid and Interface Science 2007;313(1):288-295.

[38] Pérez-Rodríguez M, Prieto G, Rega C, Varela L, Sarmiento F, Mosquera V. A Comparative Study of the Determination of the Critical Micelle Concentration by Conductivity and Dielectric Constant Measurements. Langmuir 1998;14(16):4422-4426.

[39] Carey E, Patil S, Stubenrauch C. Conductivity Measurements as a Method for Studying Ionic Technical Grade Surfactants. Tenside Surfactants Detergents 2008;45(3):120-125.

[40] Adamson AW, Gast AP. Physical Chemistry of Surfaces. John Willey Sonc. Inc. New York, 1997.

[41] Kochkodan O, Slobodianiuk N, Kovshun L, Khyzhan O. Molecular Interactions in Binary Surfactant Solutions: Effect of Ionic Counterpart. Journal of the Mexican Chemical Society 2020;64(3).

[42] Lange H, Beck K. Zur Mizellbildung in Mischlösungen homologer und nichthomologer Tenside. Kolloid-Zeitschrift und Zeitschrift für Polymere 1973;251(6):424-431.