Conductometric study of sodium dodecyl sulfate–nonionic surfactant (Triton X-100, Tween 20, Tween 60, Tween 80 or Tween 85) mixed micelles in aqueous solution

Dejan M. Ćirin, Mihalj M. Poša, Veljko S. Krstonošić, Maja Lj. Milanović

University of Novi Sad, Faculty of Medicine, Department of Pharmacy, Novi Sad, Serbia

Abstract

The present study is concerned with the determination of the critical micelle concentration (*cmc*) of mixed micelles of sodium dodecyl sulfate with one of five nonionic surfactants (Triton X-100, Tween 20, Tween 60, Tween 80 or Tween 85) from conductance measurements. Based on the calculated values of the β parameter we have noticed that SDS–nonionic surfactants mostly showed strong synergistic effects. It was found that nonionic surfactants with mainly longer and more hydrophobic tails show stronger interactions with hydrophobic parts of SDS, thus expressing stronger synergism. The strongest synergistic effect was noticed in an SDS–Tween 80 binary system. The SDS–Tween 85 micellar system showed antagonistic effect, most probably because the presence of the double bond in its three hydrophobic tails (three C18 tails) makes it sterically rigid.

Keywords: Conductometric study; mixed micelles; *cmc*; anionic surfactant; SDS; nonionic surfactants; Triton X-100; Tween.

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Mixtures of different surfactants have many Industrial applications because they show better characterristics than their building units [1–4]. These features can be explained by synergistic interactions between building units in mixed micelles [1–4].

Similar to individual molecules, the mixed surfactant systems form micelles at a concentration called critical micelle concentration (*cmc*). The *cmc* is the solution concentration at which the quantity of micelles is large enough to produce measurable changes in physico-chemical characteristics of a system.

Recently, determination of the *cmc* of SDS–nonionic systems by means of conductometry has been reported in several studies [5–7].

In this study, conductometric analysis of binary mixtures of sodium dodecyl sulfate (SDS) and one of five different nonionic surfactants (Triton X-100, Tween 20, Tween 60, Tween 80 or Tween 85) is presented.

SDS has significant application as very effective surfactant in a number of industrial products and in recent studies it is considered as a novel microbicide against different viruses [8,9]. Triton X-100 is important nonionic surfactant in biochemical and chemical processes and in various industrial applications [10,11]. The polysorbates used in this study (Tween 20, Tween 60, Tween 80 and Tween 85) are stable and relatively nontoxic amphihiles [12]. This makes them very useful surfactants and emulsifiers in many nutritional, domestic, scientific, and pharmaceutical products [10,12].

Knowledge of physico–chemical parameters of mixed micelles – experimental *cmc* values of individual surfactants, the *cmc* of mixed micelles, and the mole fractions of the surfactants in binary systems – are necessary to calculate the β interaction parameter [13–17]. The β interaction parameter is important in quantifying synergistic interactions in binary mixtures. A less negative value of a β interaction parameter means a weaker synergistic interaction between components. In general, a synergistic effect is expected in anionic-nonionic surfactant mixtures [1–3,5–7,18–23]. The interaction parameter can be calculated using Clint [13] and Rubingh [14] theories.

There have been many recent studies on the mixed surfactant systems comprising SDS and nonionic surfactants in anionic–nonionic binary mixtures [5–7,18–23]. Certain authors, Xui *et al*. [20] and Patel *et al*. [22], studied the micellization properties of SDS–nonionic surfactant mixed micelles. Xui *et al*. investigated mechanism of SDS–Triton X-100 mixed micelles formation by ^{1}H-NMR spectroscopy [20]. However, these studies have not determined neither quantified interactions in the mixed micelles.

In separate studies of SDS–Triton X-100 [24–26] and SDS–Tween 20 binary systems [27], the interaction parameter (β) has been calculated. However, these reports do not provide enough information on how various structures of hydrophobic tails of the nonionic co-

Correspondence: I.D. Ćirin, Department of Pharmacy, Faculty of Medicine, University of Novi Sad, Hajduk Veljkova 3, 21000 Novi Sad, Serbia.

E-mail: dejan.cirin@gmail.com

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-surfactant affect the synergism in the SDS–nonionic mixed micelles.

Therefore, the aim of our study was to investigate and compare the influence of varying structures of the hydrophobic regions of selected nonionic co-surfactants on the physico–chemical properties and the synergism in the SDS–nonionic binary systems.

Investigated polysorbates have the same polar head with variations in hydrophobic tails. Tween 20 and Tween 60 were studied to find the effect of a hydrophobic tail length on the synergism. Tween 80 and Tween 85 were selected to better understand the influence of a double bond in a hydrophobic tail on the physico–chemical parameters of the mixed micelles.

Triton X-100 was investigated as an extensively used nonionic surfactant as well as polysorbates. This surfactant has different polar head and hydrophobic region than polysorbates. Therefore the additional goal was to investigate the effect of these structural differences on interaction with SDS.

MATERIALS AND METHOD

Materials

Sodium dodecyl sulfate was purchased from Sigma-Aldrich (Germany). The degree of purity is >99 %.

Nonionic surfactants: polyoxyethylene octylphenyl ether (Triton X-100), polyoxyethylene (20) sorbitan monolaurate (Tween 20), polyoxyethylene (20) sorbitan monostearate (Tween 60), polyoxyethylene (20) sorbitan monooleate (Tween 80) and polyoxyethylene (20) sorbitan trioleate (Tween 85) were obtained from J.T. Baker (Holland). The degree of purity is >99%.

Deionised water (conductivity < 1 µS cm^{-1}, at 25 °C) was used for all purposes.

Critical micelle concentration determination

The critical micelle concentrations of the SDS–nonionic binary mixtures were determined using conductivity measurements. The *cmc* of the nonionic surfactants were obtained through surface tension measurements, since these amphiphiles do not have influence on electric conductance. The *cmc* of pure SDS was acquired by means of conductometry and tensiometry.

Conductivity measurements

Conductivity measurements were carried out on aqueous solutions of mixtures of SDS and five different nonionic surfactants (Triton X-100, Tween 20, Tween 60, Tween 80 and Tween 85).

Surfactant solutions were prepared by dissolving the relevant surfactants in deionised water at concentrations above the theoretical *cmc* values of binary mixtures, calculated according to Clint's theory. The *cmc* of binary mixtures was obtained for the different molar ratios of SDS and the nonionic surfactants.

Conductivities were measured by gradual dilution of surfactant solutions with the deionised water. The data were acquired using Consort C 860 conductometer. The cell containing solutions was immersed in a water bath, controlling the temperature variation at ±0.1 °C. The temperature was kept constant at 25 °C. The break in conductivity (specific conductivity, κ) *versus* concentration curve indicated the onset of the micellization process. Trials were repeated (n = 3) for reproducibility. The *cmc* determination error did not exceed 3%.

Surface tension measurements

Surface tension measurements were carried out on aqueous solutions of five different nonionic surfactants (Triton X-100, Tween 20, Tween 60, Tween 80 and Tween 85) in order to determine their individual *cmc*.

Surface tension measurements were carried out on a Sigma 703D tensiometer (Finland) using a du Nouy ring method. All measurements were repeated three times. In all measurements temperature was kept constant at 25 ± 0.1 °C. The *cmc* determination error did not exceed 3%.

RESULTS AND DISCUSSION

The critical micelle concentrations of the binary surfactant solutions were studied through conductivity measurements at different mole fractions of the nonionic surfactants (α). Prepared mixtures consisted of 0.1, 0.2, 0.3, 0.4 or 0.5 mole fractions of nonionic surfactant (α), as seen in Tables 1 and 2. A break in the conductivity against concentration plots, characteristic of micelle formation, was observed (Figures 1 and 2).

For SDS–polysorbate mixtures (SDS-Tween 20, SDS–Tween 60, SDS–Tween 80 and SDS–Tween 85) two breaks in conductivity against surfactant concentration were noticed, for all investigated mole fractions of nonionic surfactant (α). The presence of these two breaks suggests the existence of two types of mixed micelles, where each break corresponds to one *cmc*. Existence of two break points in SDS-Tween 20 mixtures was also found by Munoz *et al*. [28]. For mixed SDS–Triton X-100 binary system, only one *cmc* (one break) was noticed, for all molar ratios. The presence of a single *cmc* for SDS–Triton X-100 mixtures is confirmed in literature, as well [24–26]. Figures 1 and 2 depict only one break point in order to show the first and the second critical micelle concentration more noticeable.

Table 1 summarizes the *cmc* values experimentally obtained through conductivity measurements (cmc^{ex}).

The first *cmc* for mixtures of SDS–Tween 85 (α = 0.4 or 0.5) could not be studied since conductivities corresponding to these dilute solutions are too low.

Table 1. Experimentally obtained critical micelle concentrations (mM)of the mixed micelles of SDS and nonionic surfactants (Triton X-100, Tween 20, Tween 60, Tween 80 or Tween 85), at diferrent mole fractions of nonionic surfactant in solution (α)

α	Triton X-100		Tween 20		Tween 60		Tween 80		Tween 85	
	cmc^{ex} I	cmc^{ex} II	cmc^{ex} I	cmc^{ex} II	cmc^{ex} I	cmc^{ex} II	cmc^{ex} I	cmc^{ex} II	cmc^{ex} I	cmc^{ex} II
0	8.2	–	8.2	–	8.2	–	8.2	–	8.2	–
0.1	1.7	–	0.33	2.21	0.146	1.0	0.064	2.2	0.07	0.9
0.2	0.808	–	0.195	1.72	0.075	0.85	0.053	1.19	0.0375	0.43
0.3	0.593	–	0.14	1.1	0.0524	0.61	0.020	0.91	0.0259	0.2
0.4	0.48	–	0.106	0.84	0.046	0.37	0.019	0.73	–	0.11
0.5	0.398	–	0.0897	0.61	0.037	0.24	0.015	0.39	–	0.059

Table 2. Critical micelle concentrations of the ideal mixed micelles, experimentally obtained critical micelle concentrations of the mixed micelles, mole fractions of more hydrophobic surfactant in the ideal and real mixed micelles and the β interaction parameter of the mixed micelles of SDS and nonionic surfactants (Triton X-100, Tween 20, Tween 60, Tween 80 or Tween 85), at diferrent mole fractions of nonionic surfactant in solution (α)

α	cmc^{id} / mM	cmc^{ex} / mM	x^{id}	x_1	β
		Triton X-100			
0	–	8.2	–	–	–
0.1	1.9	1.7	0.791	0.739	–0.62
0.2	1.074	0.808	0.895	0.757	–1.98
0.3	0.749	0.593	0.936	0.804	–2.11
0.4	0.575	0.48	0.958	0.843	–2.12
0.5	0.466	0.398	0.972	0.865	–2.32
		Tween 20			
0	–	8.2	–	–	–
0.1	0.474	0.33	0.948	0.773	–3.07
0.2	0.244	0.195	0.976	0.841	–2.98
0.3	0.164	0.14	0.986	0.878	–2.97
0.4	0.12	0.106	0.991	0.886	–3.37
0.5	0.1	0.0897	0.994	0.917	–3.2
		Tween 60			
0	–	8.2	–	–	–
0.1	0.22	0.146	0.976	0.792	–4.09
0.2	0.109	0.075	0.989	0.812	–4.94
0.3	0.073	0.0524	0.994	0.831	–5.29
0.4	0.055	0.046	0.996	0.886	–4.44
0.5	0.044	0.037	0.997	0.891	–4.87
		Tween 80			
0	–				
0.1	0.118	0.064	0.987	0.76	–6.15
0.2	0.060	0.053	0.994	0.911	–3.89
0.3	0.040	0.020	0.996	0.771	–8.26
0.4	0.03	0.019	0.997	0.815	–7.37
0.5	0.024	0.015	0.998	0.817	–7.99
		Tween 85			
0	–	8.2	–	–	–
0.1	0.0695	0.07	0.992	0.734	6.55
0.2	0.0349	0.0375	0.997	0.74	7.75
0.3	0.0233	0.0259	0.999	0.746	8.55
0.4	0.0175	–	–	–	–
0.5	0.014	–	–	–	–

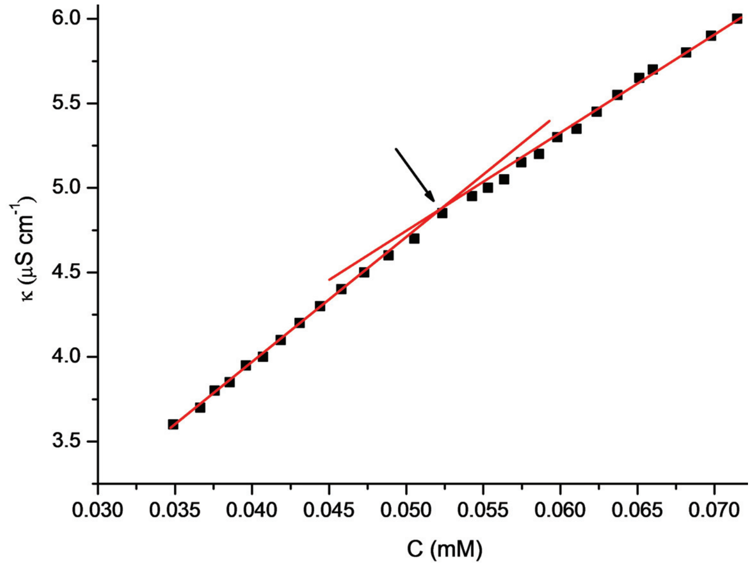

Figure 1. Dependence of the specific conductivity, κ; on concentration of mixed SDS–Tween 60 (α = 0.3) micellar solution, at 25 °C. The arrow denotes the first cmc.

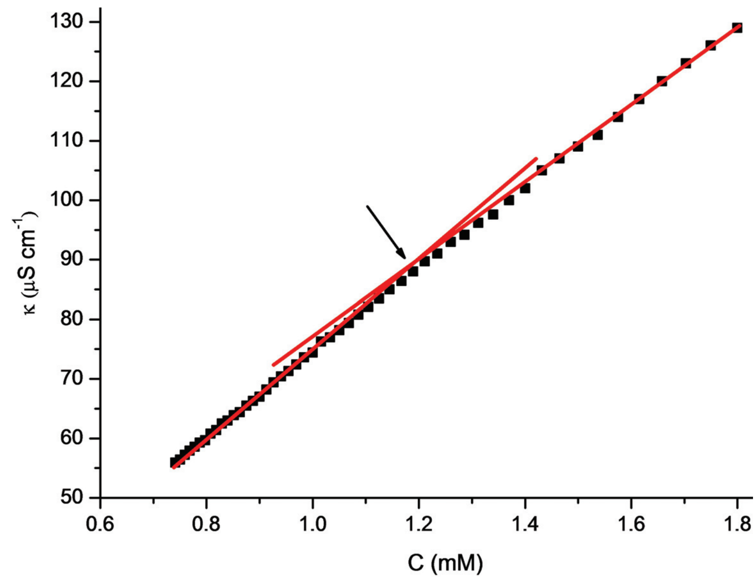

Figure 2. Dependence of the specific conductivity, κ; on surfactant concentration of mixed SDS–Tween 80 (α = 0.2) micellar solution, at 25 °C. The arrow denotes the second cmc.

The first break at low surfactant concentration corresponds to mixed micelles richer in nonionic surfactant, as found by Munoz *et al*. [28]. The second break, at higher surfactant concentrations represents another type of mixed micelles with unknown mole fractions of the surfactants because pure or mixed micelles are formed previously [28].

The *cmc* values for individual nonionic surfactants were obtained through surface tension measurements (Table 3). The *cmc* of SDS was determined by conductometric and surface tension measurements and both values were identical.

Table 3. Experimetnally obtained critical micelle concentrations of the individual surfactants

Surfactant	Triton X-100	Tween 20	Tween 60	Tween 80	Tween 85	SDS
cmc^{ex} / mM	0.24	0.05	0.022	0.012	0.06	8.2

In order to study the influence of the structure of the nonionic co-surfactants on formation of mixed micelles with SDS, physico-chemical parameters of the micellar systems were calculated and presented in Table 2. The physico–chemical parameters of the mixed micelles for the first *cmc* were calculated using experimentally obtained *cmc* values presented in Tables 1 and 2. The calculated parameters are: critical micelle concentration of ideal mixtures (cmc^{id}), the mole fraction of the more hydrophobic surfactant in the ideal mixed micelle (x^{id}), the mole fraction of the more hydrophobic surfactant in the real mixed micelle (x_1) and the β parameter. The cmc^{id} parameter indicates nonideal behaviour if it differs from experimentaly obtained critical micelle concentration, cmc^{ex}. The x^{id} and the x_1 are required to calculate the β parameter.

Critical micelle concentrations according to Clint's theory of ideal mixtures (cmc^{id}) were calculated using following equation [13]:

$$\frac{1}{cmc^{id}} = \sum_i \frac{\alpha_i}{cmc_i} \tag{1}$$

where α_i is the mole fraction in the solution of component *i*, cmc_i is experimentally obtained *cmc* of component *i*.

The cmc^{id} values are presented and compared to the experimental *cmc* (cmc^{ex}) in Table 2. Deviation of the experimentaly obtained *cmc* values from those calculated according to Clint's theory indicates nonideal behaviour of examined surfactant mixtures and mutual interactions of the surfactants in the micelles.

The mole fraction of the more hydrophobic surfactant in the ideal mixed micelle (x^{id}), according to Motomura [15], was calculated using the relationship:

$$x^{id} = \frac{cmc_2\alpha}{cmc_2\alpha + cmc_1(1-\alpha)} \tag{2}$$

where cmc_1 is experimentally obtained *cmc* of the more hydrophobic (nonionic) surfactant, cmc_2 is *cmc* of SDS and α is the mole fraction of the more hydrophobic surfactant in the solution.

The x^{id} value was used to calculate the mole fraction of the more hydrophobic surfactant in the real mixed micelle (x_1), according to Rubingh [14]. The x_1 value was obtained using following relation:

$$\frac{x_1^2 \ln(cmc^{ex}\alpha / cmc_1 x_1)}{(1-x_1)^2 \ln(cmc^{ex}(1-\alpha) / cmc_2(1-x_1))} = 1 \tag{3}$$

Eq. (3) was solved iteratively to obtain value of x_1.

The x^{id} and the x_1 values for the mixed micelles are presented in Table 2. The x_1 value was used to calculate the β interaction parameter, according to Rubingh [14], through the equation:

$$\beta = \frac{\ln(cmc^{ex}\alpha / cmc_1 x_1)}{(1-x_1)^2} \tag{4}$$

The negative values of a β indicate attractive interactions (synergism) between components of mixed micelles while positive values mean antagonistic interactions between surfactants in a mixture. This parameter quantifies the synergism or antagonism between two surfactants in mixed micelles. The less negative value of a β interaction parameter means the weaker synergistic interaction between components.

The value of the β interaction parameter coincides with the deviation between experimentaly obtained (cmc^{ex}) and calculated (cmc^{id}) *cmc* values.

The values of the β interaction parameter for the investigated binary mixtures of SDS–Triton X-100, SDS–Tween 20, SDS–Tween 60, SDS–Tween 80 and SDS–Tween 85 are presented in Table 2.

For the SDS–Triton X-100, SDS–Tween 20, SDS–Tween 60 and SDS–Tween 80 binary systems interaction parameters have negative values indicating synergism in the micellar systems.

SDS–Triton X-100 mixed micelles clearly showed the weakest synergistic effect. Phenoxy part of Triton X-100 is shorter and less hydrophobic than hydrocarbon tails of examined Tween surfactants, creating the weakest synergistic effect.

Furthermore, it is possible that the repulsive forces between the anionic heads of SDS are weaker at the surface of SDS–Tween mixed micelles than at the surface of SDS–Triton X-100 mixed micelles. The polar heads of Tween molecules are larger than the polar head of Triton X-100 and captivate larger surface area of the mixed micelles. Larger polar groups of Tween molecules create greater distance between anionic heads of SDS, thus reducing repulsive forces, increasing synergistic effect and favoring mixed micelle formation.

In SDS–Tween binary systems, SDS–Tween 80 showed the strongest synergistic effect while SDS–Tween 20 expressed the weakest synergistic effect.

The possible explanation for these results is that longer and more hydrophobic tails of nonionic surfactants show stronger interactions with hydrophobic part of SDS, thus expressing stronger synergism in the mixed micelles. Stronger synergistic effect was found in SDS–Tween 60 than in SDS–Tween 20 mixed micelles because of the longer hydrophobic tail in Tween 60 (C18) than in Tween 20 (C12).

SDS–Tween 80 showed stronger synergistic effect than SDS–Tween 60 although hydrocarbon tails are of the same length (C18). Our assumption is that this behavior is a consequence of the presence of two sp^2 hybridized C-atoms in Tween 80 hydrophobic tail, which behave as a weak dipole. This weak dipole can polarize hydrocarbon chains of SDS, creating weak induced dipoles. We suppose that this electrostatic attractive interaction between dipole and induced dipole contribute to enchased synergistic effect in SDS–Tween 80, compared to SDS–Tween 60 mixed micelles. Contrary to previous results, in SDS–Tween 85 micellar systems interaction parameters have positive values showing antagonistic effect between surfactants in the mixed micelles. This could be because the presence of the double bond in its three hydrophobic tails (three C18 tails) makes it sterically rigid, decreasing hydrophobic interactions. Rigid conformation of the hydrophobic tails disrupts steric packaging of the micellar core and leads to partial hydration of the hydrophobic core of SDS-Tween 85 mixed micelles. This partial hydration of the hydrophobic tails in the micellar core decreases the hydrophobic interactions between the hydrophobic regions of co-surfactants in the mixed micelles. This effect is described by Tanford [29], and it raises system entropy making it more unstable therefore raising *cmc* of SDS-Tween 85 binary system above cmc^{id}, as seen in Table 2.

Reported values in previous studies for critical micelle concentrations of mixed micelles and average β parameter of SDS–Triton X-100 [26] and SDS–Tween 20 [28] micellar systems are in good correlation with the values for β obtained in our study. Critical micelle concentrations and β parameters for SDS–Tween 60, SDS–Tween 80 and SDS–Tween 85 micellar systems have not been previously studied and no data were found in literature concerning *cmc* and β values of these binary systems.

CONCLUSIONS

In this study, conductometric analysis of binary mixtures of SDS and five different nonionic surfactants (Triton X-100, Tween 20, Tween 60, Tween 80 and Tween 85) was presented.

Micellization behavior of the binary surfactant solutions was studied by conductivity measurements at different molar ratios of surfactants. For mixed SDS–Tween 20, SDS–Tween 60, SDS–Tween 80 and SDS–Tween 85 binary solutions two different *cmc* values were noticed. In SDS–Triton X-100 binary system only one *cmc* was found.

The critical micelle concentration of the ideal mixed micelle, the mole fraction of the more hydrophobic surfactant in the ideal mixed micelle, the mole fraction of the more hydrophobic surfactant in the real mixed micelle, and the β interaction parameter of the mixed micelles for the first *cmc* were calculated using experimental data.

Based on the established values of the β parameters we concluded that SDS–nonionic surfactants mainly showed strong synergistic effect. It is evident that nonionic surfactants with longer and more hydrophobic tail show stronger interactions with hydrophobic region of SDS, thus expressing stronger synergism in mixed micelles. SDS–Tween 80 micellar system showed the strongest synergistic effect. Our assumption is that electrostatic attractive interactions between dipole and induced dipole contribute to enchased synergistic effect in SDS–Tween 80 mixed micelles.

SDS–Tween 85 micellar system showed antagonistic effect, most probably because the presence of the double bond in its three hydrophobic tails (three C18 tails) makes it sterically rigid.

We can conclude that for SDS-Triton X-100, SDS–Tween 20, SDS–Tween 60 and SDS–Tween 80 mixed micelles, hydrophobicity of the micellar core is increased while repulsive forces between anionic heads of SDS decreased. These effects make micellar systems more stable. Consequently the *cmc* values of SDS–Triton X-100, SDS–Tween 20, SDS–Tween 60 and SDS–Tween 80 mixed micelles are lower than those predicted by Clint's theory of ideal mixtures.

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IZVOD

KONDUKTOMETRIJSKO ISPITIVANJE MEŠOVITIH MICELA NA-DODECILSULFATA I NEJONSKOG SURFAKTANTA (TRITON X-100, TWEEN 20, TWEEN 60, TWEEN 80 ILI TWEEN 85) U VODENIM RASTVORIMA

Dejan M. Ćirin, Mihalj M. Poša, Veljko S. Krstonošić, Maja Lj. Milanović

Univerzitet u Novom Sadu, Medicinski fakultet, Katedra za farmaciju, Novi Sad, Srbija

(Naučni rad)

Poznavanje kritične micelarne koncentracije (*kmk*) mešanih micela je neophodno kako bi se dobile željene osobine micelarnih sistema koji imaju veliku industrijsku primenu. U skladu sa tim, u ovom radu su konduktometrijski određene *kmk* mešanih micela Na-laurilsulfata (SDS) sa pet nejonskih surfaktanata (Triton X-100, Tween 20, Tween 60, Tween 80 ili Tween 85). Cilj našeg rada je bio ispitivanje i komparacija uticaja različitih struktura hidrofobnih regija izabranih nejonskih ko-surfaktanata na fizičko–hemijske karakteristike i sinergističke interakcije SDS–nejonskih binarnih smeša. Ispitivani polisorbati imaju identičnu polarnu glavu, ali različitu strukturu hidrofobnog repa. Triton X-100 je ispitivan jer je to često korišćen nejonski surfaktant kao i polisorbati. Ovaj surfaktant ima drugačiju polarnu glavu i hidrofobni region od polisorbata, tako da je dodatni cilj bio da se ustanovi kako ove strukturne razlike utiču na interakciju sa SDS-om. Na osnovu izračunatih β parametara može se zaključiti da se između SDS-a i ispitivanih nejonskih surfaktanata uglavnom javlja izražen sinergistički efekat. Sinergistički efekat je izraženiji kod nejonskih surfaktanata sa dužim hidrofobnim nizom. Najslabiji sinergistički efekat je zapažen u binarnom sistemu SDS–Triton X-100. Ovakav rezultat je, najverovatnije, posledica kraćeg i hidrofilnijeg ugljovodoničnog lanca Triton-a X-100 u odnosu na hidrofobne nizove kod Tween-ova. Moguće je i da kod SDS–Tween mešovitih micela postoje slabije repulzivne interakcije između anjonskih, hidrofilnih glava SDS-a. Polarne glave Tween-ova su veće od hidrofilne glave Triton-a X-100 i zauzimaju veći prostor na površini mešovitih micela. Veće polarne grupe Tween-ova više udaljavaju anjonske, hidrofilne grupe SDS-a, čime se smanjuju repulzivne interakcije koje destabilišu micele. U SDS–Tween 80 binarnom sistemu primećen je najizraženiji sinergistički efekat između surfaktanata. Pretpostavljamo da se ovaj efekat javlja zbog prisustva sp^2 hibridizovanih ugljenikovih atoma u hidrofobnom repu Tween-a 80 koji stvaraju slab dipol, koji potom indukuju slab dipol u hidrofobnim lancima SDS-a unutar jezgra mešane micele. Smatramo da ove elektrostatičke interakcije između slabog dipola i indukovanog dipola najverovatnije doprinose sinergističkom efektu. SDS–Tween 85 micelarni sistem pokazuje antagonistički efekat, najverovatnije zbog prisustva dvostruke veze u sva tri hidrofobna niza (tri C18 niza), koje čine ovaj molekul sterno krutim i smanjuju hidrofobne interakcije. Može se zaključiti da je kod SDS–Triton X-100, SDS–Tween 20, SDS–Tween 60 i SDS–Tween 80 sistema povećana hidrofobnost micelarnog jezgra, uz smanjene repulzivnih interakcija anjonskih glava SDS-a. Ove pojave povećavaju stabilnost mešovitih micela, te su *kmk* ovih sistema niže od onih koje su predviđene Klintovom teorijom idealnih smeša.

Ključne reči: Konduktometrijsko ispitivanje • Mešovite micele • *kmk* • Anjonski surfaktant • SDS • Nejonski surfaktanti • Triton X-100 • Tween