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A conductometric investigation of hydroxypropylmethyl cellulose/sodium dodecyl sulfate/nonionic surfactant systems

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Abstract: Surfactant mixtures are very often used in various cosmetic and pharmaceutical products because they commonly act in synergism and provide more favorable properties than a single surfactant. Simultaneously, the presence of polymers in mixtures of surfactants may lead to molecular interactions and thereby affecting product stability and activity. For these reasons, it is very important to determine the influence of surfactant interactions on micellization and mixed micellization, as well as polymer–surfactant mixed micelles interactions. In this study, the self-aggregation of nonionic surfactants, polysorbate 20 (Tween 20), polyoxyethylene octylphenyl ether (Triton X100) and polyoxyethylene–polyoxypropylene block copolymer (Pluronic F68), with an ionic surfactant, sodium dodecyl sulfate, was examined in aqueous solution at 40 °C using a conductometric titration method. It was found that the concentration region for mixed micelle formation depends on the characteristics of the nonionic surfactant and its concentration. The formation of mixed micelles of surfactants in the presence of a nonionic polymer, hydroxypropylmethyl cellulose, and their binding to the hydrophobic sites of the polymer were also investigated. An analysis of obtained results indicated to different kinds of interactions in the investigated systems, which are crucial for their application.

Keywords: nonionic surfactants; sodium dodecyl sulfate; mixed micelles; surfactant/polymer interactions.

INTRODUCTION

Surfactant mixtures are commonly used in surfactant-based formulations because they often behave in synergism and provide more favorable properties than single-surfactant systems. A significant amount of work has been devoted to the investigation of the physicochemical properties of mixed micelles containing two or more surfactants of variable structures in solutions. Their extensive use

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has currently been promoted by their much more favorable practical applications than single compound system.[1–3] In this respect, industrial, pharmaceutical, chemical, and biochemical fields are of great importance. Thus, in pharmaceutical products, mixed micelles were found to enhance the absorption of various drugs in the human body.[4–6] Due to their synergistic behavior at the critical micellar concentration (*CMC*), cosmetic industries employ mixed micelles in low concentrations in order to avoid potential skin irritation.[7,8] According to the great application potentials and economical consideration of mixed micelles, it is necessary to search for the most suitable surfactant combinations with desired properties, such as surface activity and solubility.

From a theoretical point of view, mixed surfactant systems have been the subject of a great number of investigations and have attracted much interest in recent years. In an aqueous medium, pure and mixed surfactants can form micelles after reaching the *CMC*, which can be assessed by various methods to understand the self-organizing behavior of surfactants. Similar to the behavior of the individual surfactants on self-aggregation, mixed system undergo significant changes in their physicochemical properties that can be monitored using suitable experimental methods, such as conductometry, tensiometry, calorimetry, fluorometry, NMR spectroscopy,[9–15] *etc*.

In mixed micellar systems of ionic, nonionic, and zwitterionic surfactants, three types of interactions may occur: favorable (ionic–nonionic, ionic–zwitterionic and cationic–anionic), unfavorable and ideal mixing (nonionic mixtures). Ionic–nonionic surfactant mixtures exhibit highly non-ideal behavior on mixing and can change the interfacial and colloidal properties of the system. A mixture of two different surfactants can be characterized by the presence of two kinds of micelles, each essentially containing a pure surfactant, or mixed micelles formed by both surfactants. Compared to pure surfactant micelles, the formation of mixed micelles is accompanied by a series of more complex thermodynamic and structural changes.[9–12]

Polymers and surfactants are very commonly included in many industrial products, and their mixtures can exhibit molecular interactions affecting the properties of the product. In this respect, the mechanism of interaction between a water-soluble polymer, hydroxypropylmethyl cellulose (HPMC), and an anionic surfactant, sodium dodecyl sulfate (SDS), was investigated in detail.[16–18] The presence of a nonionic surfactant in an aqueous HPMC/SDS solution makes the system more complex, considering that various interactions between three different species could occur.

In the present study, conductometric measurements were performed on mixed anionic–nonionic micellar solutions. The anionic surfactant was sodium dodecyl sulfate, SDS, and the nonionic surfactants were Tween 20, Triton X100 and Pluronic F68 (polysorbate 20, polyoxyethylene octylphenyl ether and poly-

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oxyethylene–polyoxypropylene block copolymer, respectively). The micellization behavior of Tween 20/SDS mixtures was previously studied by Gosh and Moulic[12] at 20 °C and by Munoz *et al*. at 25 °C.[14] With regard to the Triton X100/SDS and Pluronic F68/SDS binary mixtures, to the best of our knowledge, no previous information has been provided in the literature concerning these binary systems. It is also interesting to note that no studies have been reported regarding the interaction and micellization behavior of nonionic surfactant/SDS systems in the presence of a nonionic polymer, HPMC.

EXPERIMENTAL

Chemicals

SDS, purity >99 %, was obtained from Merck, Germany. Tween 20 (M = 1200 g mol^{-1}), Triton X100 (M = 625 g mol^{-1}) and Pluronic F68, [$EO_{75}PO_{30}EO_{75}$] (M = 8400 g mol^{-1}), were obtained from Sigma, USA. The *CMC* values of Tween 20, Triton X100 and Pluronic F68, determined at 40 °C by tensiometry, were 0.0915, 0.786 and 0.202 mmol dm^{-3}, respectively.

Pharmaceutical grade HPMC, trade name Methocel K100M, was obtained as a gift from Colorcon Ltd., UK. The viscosity average molecular mass, $\bar{M}_v$, measured at 20 °C was 155.000 g mol^{-1}.[20] and the critical overlap concentration, c*, determined at 40 °C was 6.25 10^{-3} mmol dm^{-3}.

All samples were used without any further purification.

Preparations of the binary mixtures

Stock solutions of surfactants: 0.277 mmol dm^{-3} SDS, 1.67 mmol dm^{-3} Tween 20, 6.4 mmol dm^{-3} Triton X100 and 2.38 mmol dm^{-3} Pluronic F68 were prepared by dissolving in water with gentle stirring. Stock solution of 0.13 mmol dm^{-3} HPMC was prepared by dispersing the required mass in water at 80 °C under gentle stirring.[17] All solutions were prepared in double distilled water having a specific conductance 2–4 μS cm^{-1} at 40 °C.

Binary mixtures of nonionic surfactants and SDS were prepared by mixing the required volumes of stock solutions. Before further use, the mixtures were left for 24 h at room temperature.

Binary mixtures of HPMC, below (3.22 10^{-3} mmol dm^{-3}) and above (19.35 10^{-3} mmol dm^{-3}) critical overlap concentration, c*, and the nonionic surfactants were prepared by mixing the required masses of HPMC stock solution with suitably diluted stock solutions of surfactants. Before further use, the mixtures were left for 24 h at room temperature.

Conductometry

Conductivity measurements were realized at 40 °C, in a jacked beaker, by adding 0.2 cm^3 portions of titrant to 50 cm^3 of analyte. After the addition of each portion, the solution was stirred until a steady conductance value was achieved. Specific conductance was measured using conductivity meter INOLAB Level 1, WTW, Germany and conductivity cell with the cell constant of 1.00 cm^{-1}.

The temperature was maintained using a Phoenix II C25P thermostat, Thermo HAAKE, Germany.

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RESULTS AND DISCUSSION

Nonionic surfactant/SDS interaction

Conductometric titration is one of the most often used techniques to determine the critical micelle concentration (*CMC*) of ionic surfactants, as well as to examine their interaction with nonionic surfactants and the formation of mixed micelles in dilute solutions.[9–12] The results of the determination of the critical micelle concentration of SDS and an investigation of the nonionic surfactant/SDS interactions are presented in Fig. 1.

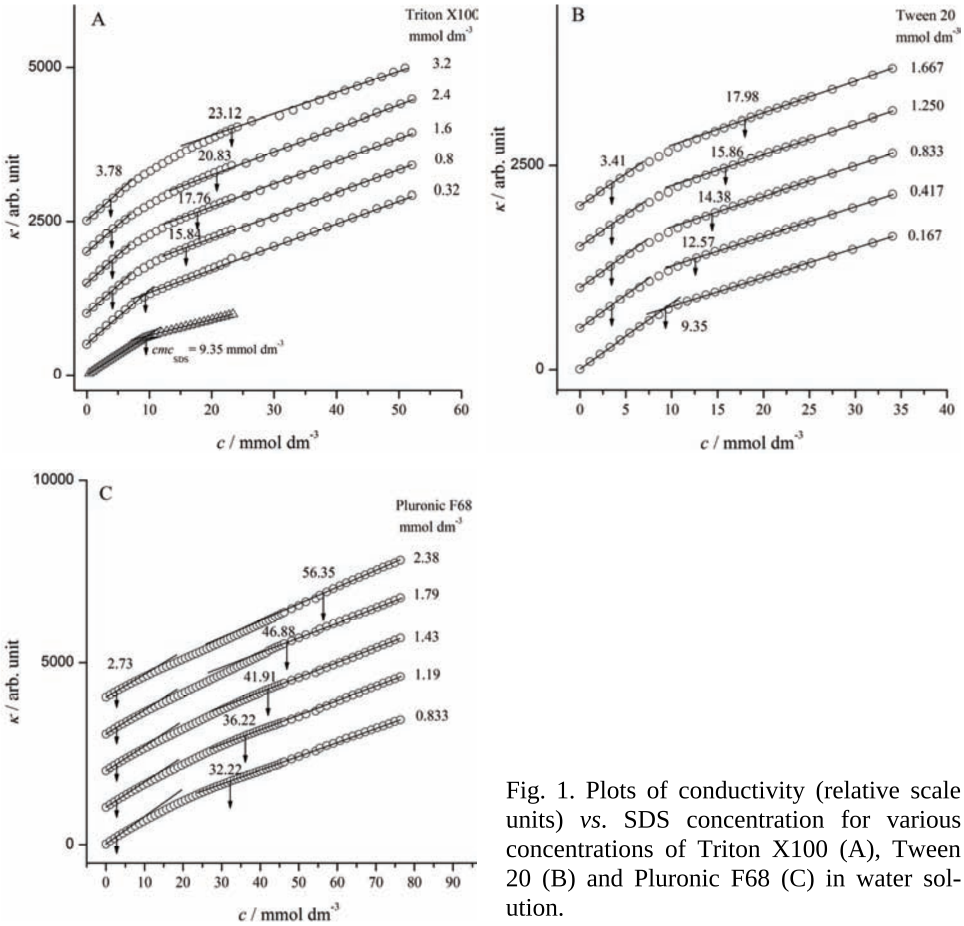

Fig. 1. Plots of conductivity (relative scale units) *vs*. SDS concentration for various concentrations of Triton X100 (A), Tween 20 (B) and Pluronic F68 (C) in water solution.

The addition of SDS to the water caused a linear increase in the specific conductance up to the surfactant concentration at which micelle formation began, *i.e.*, up to the *CMC*. After the *CMC* was attained, the conductance further increased linearly, but with a lower slope than before the *CMC* and the break in the conductance–concentration titration curve gives the *CMC* of the surfactant. For

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SDS, the *CMC* determined by conductometric titration at 40 °C was 9.35 mmol dm^{-3} (Fig. 1A). In the presence of the nonionic surfactant, the relationship between the conductance and the SDS concentration (Fig. 1), as with most ionic/ /nonionic surfactant mixtures, showed two break points. The first was when the formation of mixed associates, *i.e.*, micelles, began and the second was when the formation of mixed micelles ended. Between these break points, there was a region of nonlinearity indicating the incorporation of SDS molecules into the mixed micelles and their structural changes with increasing SDS concentration, *i.e.*, mixed micellization. For solutions of Triton X100 and Tween 20, at concentrations of 0.32 and 0.167 mmol dm^{-3}, respectively, the conductometric curves had only one break point that corresponded to the *CMC* of SDS. This indicated that at concentration of the nonionic surfactants close to their *CMC* value, due to the weak interaction with the SDS molecules, there was no mixed micelle formation.

At concentrations of nonionic surfactants well above the *CMC*, the formation of the mixed micelles started at SDS concentration lower than the *CMC* (9.35 mmol dm^{-3}) and it depended on the characteristics of the nonionic surfactant (Fig. 1A–C). Simultaneously, the end of process depended not only on surfactant type, but on its concentration as well. After reaching the second break point, the mixed micellization was finished, the conductivity increased linearly again, but with a higher slope than for SDS without nonionic surfactant after reaching the *CMC*. Namely, further addition of SDS caused only the formation of free SDS micelles that, together with the charged mixed micelles, contributed to the specific conductance.[19]

The amount of SDS molecules that were incorporated in the mixed associates at the end of micellization is presented in Fig. 2.

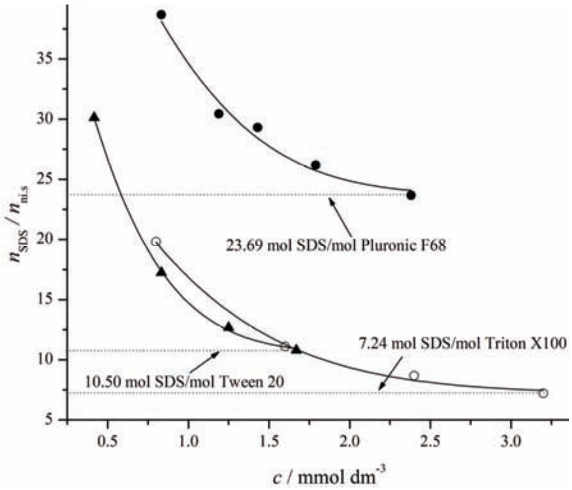

Fig. 2. Dependence of the SDS/ /nonionic surfactant mole ratios (n_{SDS}/$n_{ni.s}$) at the end of mixed micellization on the nonionic surfactant concentration.

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As can be seen, the mixed micelles of Pluronic F68 contained the highest mole partition of SDS molecules, 23.6 mol mol^{-1}, and the mixed micelles of Triton X100 the lowest one, 7.24 mol mol^{-1}. These findings could be attributed to the differences in the structures of the nonionic surfactants that affected the packing of SDS molecules into mixed micelles.[20] As reported before,[21,22] a strong attractive interaction of SDS with the ethylene oxide–propylene oxide–ethylene oxide triblock copolymer exists in the micelles and therefore the highest molar ratio of SDS could be expected. With regards to Triton X100, the presence of a phenolic group in the hydrophobic chain of the molecule causes steric hindrance that leads to poor packing of the SDS molecules in the mixed micelles.[13] The concentration of nonionic surfactant, as mentioned before, affects the structure of the mixed micelles; thus, an increase in the concentration causes a decrease in mole share of SDS molecules present in the mixed micelles, *i.e.*, the structure of the micelles.

Interactions of HPMC/nonionic surfactant mixtures with SDS

In our previous work, interactions between HPMC and SDS in aqueous solution, at 30 °C, had been investigated in detail using various experimental techniques.[16,17] Characteristic points, *i.e.*, SDS concentration at which interaction begins, the critical aggregation concentration, *CAC*, and ends, the polymer saturation point, *PSP*, were determined and it appeared that the *CAC* did not depend on the HPMC concentration, whereas the *PSP* was linearly dependent on the HPMC concentration. In order to define the region of interaction between HPMC and SDS at 40 °C, conductometric titrations of HPMC solutions at concentrations below (3.22×10^{-3} mmol dm^{-3}) and above (19.35×10^{-3} mmol dm^{-3}) the critical overlap concentration, c^*, were performed. The obtained results presented in Fig. 3 are in good agreement with those of a previous studies.[16,17]

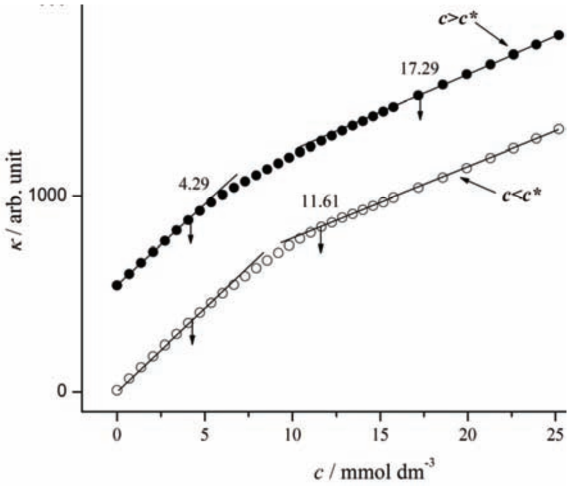

Fig. 3. Dependence of specific conductance (relative scale units) on the SDS concentration for HPMC solutions of concentrations less than 3.22×10^{-3} mmol dm^{-3} and higher than 19.35×10^{-3} mmol dm^{-3}; the critical overlap concentration was 6.25×10^{-3} mmol dm^{-3}.

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Namely, the interaction region, observed as a nonlinear conductance–concentration dependence, was much wider for HPMC concentrations higher than c^*. Under such conditions, the hydrophobic substituents of the HPMC molecules are close and interaction with SDS is intermolecular in nature. With increasing SDS concentration, micellar structures are formed around each individual substituent until saturation of all available sites on the polymer molecules.

Considering that HPMC/SDS interactions in solution are influenced by various factors (temperature, the molecular characteristics and concentration of HPMC, ionic strength,[23] *etc.*) and that they could induce changes in the properties of mixed systems, it was interesting to examine the interactions of these two species in the presence of a nonionic surfactant. For these reasons, conductometric titrations of binary mixtures of HPMC and nonionic surfactants with SDS were performed. The concentrations of HPMC in the mixtures were below 3.22×10^{-3} mmol dm^{-3} and above 19.35×10^{-3} mmol dm^{-3}, the critical overlap concentration. Concentrations of Triton X100, Tween 20 and Pluronic F68 in the binary mixtures were 1.6, 8.33 and 1.19 mmol dm^{-3}, respectively. The results of these investigations are presented in Fig. 4.

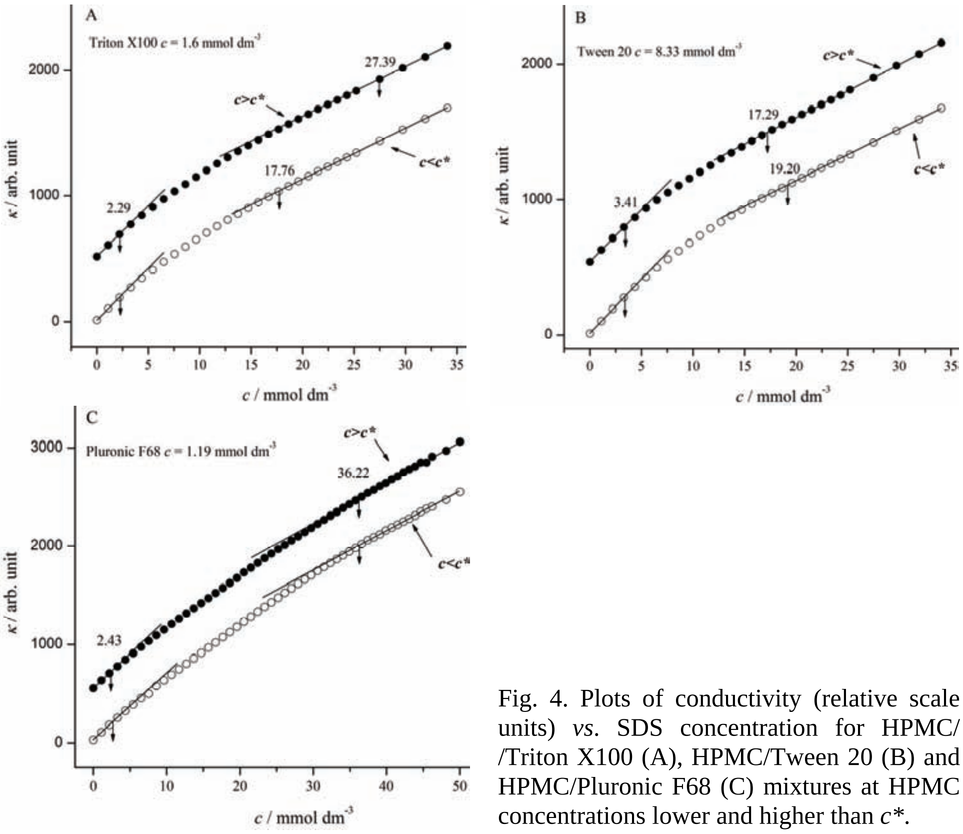

Fig. 4. Plots of conductivity (relative scale units) *vs*. SDS concentration for HPMC/ /Triton X100 (A), HPMC/Tween 20 (B) and HPMC/Pluronic F68 (C) mixtures at HPMC concentrations lower and higher than c^*.

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The addition of SDS to the mixture of HPMC and Triton X100 below *c** of HPMC (Fig. 4A) caused changes in the slope of the conductance–concentration curve at characteristic SDS concentrations (2.29 and 17.76 mmol dm^{-3}), which are the same as for the Triton X100/SDS system presented in Fig. 1A. This means that in such a system mixed micellization was a more favorable process than HPMC/SDS interaction. After mixed micellization was finished, the conductometric curve became linear again, indicating that only free micelles of SDS molecules were being formed, *i.e.*, there was no interaction with HPMC. When the HPMC concentration in a binary mixture is above *c**, the second break point is much higher (27.39 mmol dm^{-3}) meaning that after the formation of mixed micelles, the SDS molecules started to form micellar aggregates around the hydrophobic substituents of the adjacent polymer chains, *i.e.*, HPMC/SDS interaction occurred.[17] Such behavior could be explained by the fact that in semidilute conditions, at $c>c^*$, the hydrophobic substituents of the HPMC molecules were very close, expressing more hydrophobicity and hence, HPMC/SDS interaction could occur.

Interactions in binary mixtures of HPMC and Tween 20 with SDS, determined by conductometry, are presented in Fig. 4B. It could be observed that, at HPMC concentration below *c**, the nonlinearity region in conductometric curve is wider than for Tween 20/SDS system (Fig. 1B), implying that HPMC/SDS hydrophobic interaction occurs as well. However, when the HPMC concentration in the mixtures was higher than *c**, it seems that after the formation of mixed micelles, binding of SDS to hydrophobic sites of HPMC was disabled. Namely, Tween 20 has a highly branched, voluminous polar head and is thus expected that mixed micelles would be voluminous as well. Their presence in the neighborhood of the binding sites on the HPMC molecules, between neighboring polymer chains, probably resulted in steric hindrance and disabled the hydrophobic binding of SDS.

The addition of SDS to mixtures of HPMC and Pluronic F68 caused mixed micelle formation at HPMC concentration below and above *c**. Namely, the conductometric titration curves, presented in Fig. 4C, had exactly the same form as the one presented in Fig. 1C for the same Pluronic F68 concentration. After the mixed micelles had formed, further addition of SDS to the mixtures led to the formation of free SDS micelles only. As it can be seen, regardless of the HPMC concentration in the mixture, HPMC/SDS hydrophobic interaction failed. Such a behavior could be attributed to the shape of the formed Pluronic F68/SDS mixed micelles that sterically hindered hydrophobic SDS binding to the HPMC molecules.[24]

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Interactions of HPMC with nonionic surfactant/SDS mixed micelles

In order to examine the interactions of HPMC with nonionic surfactant/SDS mixtures, conductometric titrations of HPMC solutions at $c<c^*$ and $c>c^*$ with binary mixtures of the surfactants were performed. HPMC solutions were titrated with Triton X100/SDS, Tween 20/SDS and Pluronic F68/SDS mixtures at the mole ratios 1/1.7, 1/10.5 and 1/23.69 mol mol^{-1}, respectively. The nonionic surfactant/SDS mole ratios were chosen to include the amount of SDS molecules in the mixed micelles at the end of micellization (Fig. 2). Micellization of the nonionic surfactant/SDS mixtures in water were also determined, and the results are presented in Fig. 5.

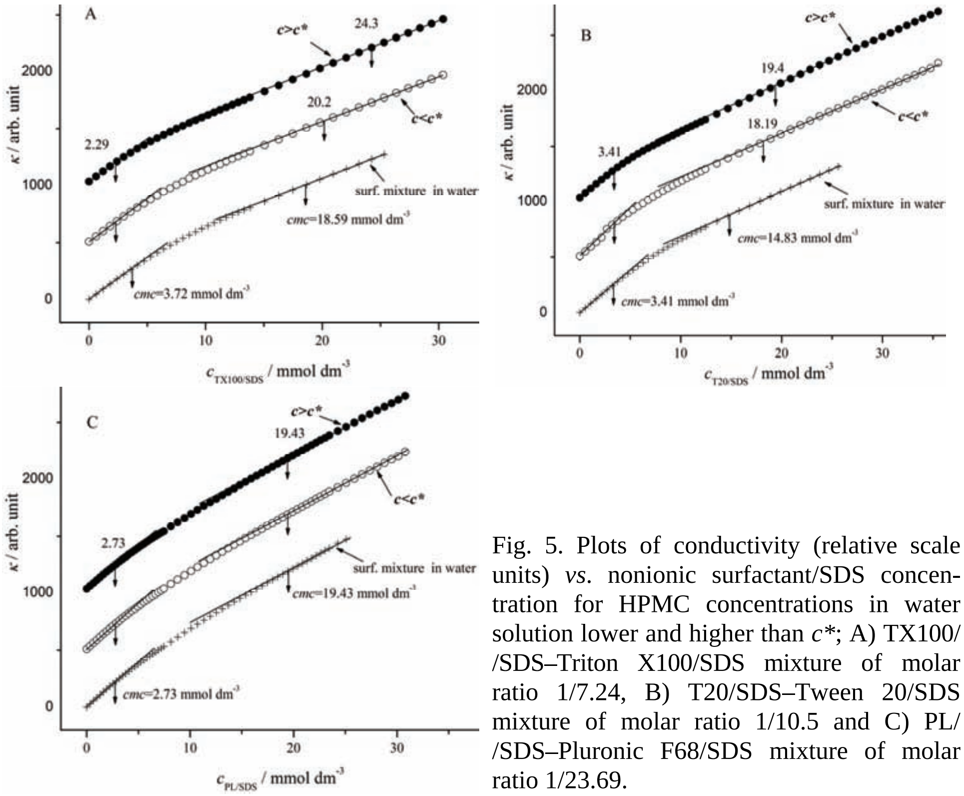

Fig. 5. Plots of conductivity (relative scale units) *vs*. nonionic surfactant/SDS concentration for HPMC concentrations in water solution lower and higher than c^*; A) TX100/ /SDS–Triton X100/SDS mixture of molar ratio 1/7.24, B) T20/SDS–Tween 20/SDS mixture of molar ratio 1/10.5 and C) PL/ /SDS–Pluronic F68/SDS mixture of molar ratio 1/23.69.

For all nonionic surfactant/SDS binary mixtures, the conductance *vs.* concentration curves showed two break points, *i.e.*, two *CMC* values. The existence of two break points for some surfactant mixtures was previously reported, which indicated the formation of two different kinds of mixed micellar aggregates, *i.e.* non-ideal behavior on mixing.[10,14] The first break point at low surfactant concentrations corresponded to mixed micelles with a high degree of ionization, shown by the slight change in the slope of the conductance–concentration curve. The

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second break point at higher surfactant concentration shows the existence of another type of micelle with a lower degree of ionization. Such a behavior is in agreement with the results presented in Fig. 2, indicating that the mixed micelles had the lowest molar content of SDS at the end of micellization.

Changes in the conductance of HPMC solutions at $c<c^*$ and $c>c^*$ with the addition of Triton X100/SDS binary mixtures showed two break points (Fig. 5A), which are related to the start and the end of the formation of HPMC/surfactant mixture interactions. The region of nonlinearity started at a mixture concentration of 2.29 mmol dm^{-3} (lower than the first *CMC*), indicating binding of surfactants molecules to the hydrophobic sites of polymer, which is more favorable than the formation of mixed micelles. This binding continues until saturation of all the available sites on the HPMC molecules, which is determined by the second break point (20.2 mmol dm^{-3} for $c<c^*$). Further addition of the surfactant mixture caused the formation of free micelles only, observed as the linear increase in conductance with the same slope as for the surfactant mixture in water after reaching second *CMC*. As expected, the interaction region is pronounced at HPMC concentrations higher than c^*.

The interaction of HPMC and Tween 20/SDS mixture was less pronounced (Fig. 5B). Namely, for both HPMC concentrations, the regions of nonlinearity in conductance–concentration titration curves were slightly wider compared to the region of the formation of mixed micelles. The micellization and/or interaction started at same concentration (3.41 mmol dm^{-3}) and it is possible that they occurred simultaneously. At both HPMC concentrations, the second break point, *i.e.*, the end of nonlinear region, was shifted toward higher concentrations of Tween 20/SDS mixtures, indicating that interactions occurred to a certain degree.

Concerning the Pluronic F68/SDS mixture, there was no interaction with HPMC, regardless of its concentration (Fig. 5C). Namely, the conductometric curves show two break points at the same concentrations as for the pure surfactant mixture in water. It is clear that formation of mixed Pluronic F68/SDS micelles was more favorable than its interaction with HPMC.

CONCLUSIONS

The conductometric titration method was a useful and relatively simple technique for investigations of nonionic/ionic surfactant mixed micellization and mixed micelles interactions with the nonionic polymer HPMC. The formations of mixed micelles of Triton X100, Tween 20 or Pluronic F68 with SDS were energetically more favorable than the formation of single surfactant micelles and the formation depended on the characteristics of the surfactant. The mixed micellar systems underwent significant changes in structural organization during aggregation and the concentration of the nonionic surfactant affected their structure, *i.e.*, the molar share of SDS molecules present in mixed micelles decreased with increasing concentration.

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In the HPMC/nonionic surfactant mixtures, the surfactant molecules were in the neighborhood of the HPMC hydrophobic sites and the introduction of SDS caused mixed micelle formation. After formation of the micelles, further addition of SDS could lead to interaction with HPMC depending on the HPMC concentration and on the size and shape of the formed mixed micelles. These parameters also affected the interaction of HPMC with nonionic surfactant/SDS mixed micelles.

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ИЗВОД

КОНДУКТОМЕТРИЈСКО ИСПИТИВАЊЕ СИСТЕМА ХИДРОКСИПРОПИЛМЕТИЛ--ЦЕЛУЛОЗА/НАТРИЈУМ-ДОДЕЦИЛСУЛФАТ/НЕЈОНСКИ СУРФАКТАНТ

ЛИДИЈА Б. ПЕТРОВИЋ, ВЕРИЦА Ј. СОВИЉ, ЈАДРАНКА Л. МИЛАНОВИЋ и ЈАРОСЛАВ М. КАТОНА

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Смеше сурфактаната се веома често користе у различитим формулацијама козметичих и фармацеутских производа јер делују синергистички, обебеђујући боља својства производа. Истовремено, присуство полимера у смеши са сурфактанатима може да доведе до молекулских интеракција, а самим тим и до промена стабилности и активности готовог производа. Из ових разлога веома је значајно испитати утицај интеракције појединих компонентата смеша сурфактаната на процесе формирања мицела и мешаних мицела, као и интеракције мешаних мицела са молекулима полимера. У раду је испитано формирање мешаних мицела нејонских сурфактаната, полисорбата 20 (Tween 20), полиоксиетиленоктилфенил етра (Triton X100) и полиоксиетилен–полиоксипропилен блок колполимера (Pluronic F68), и јонског сурфактанта, натријум-додецилсулфата, у води применом кондуктометријске титрације на 40 °C. Утврђено је да област формирања мицела зависи од својстава и концентрације нејонског сурфактанта. Формирање мешаних мицела у присуству нејонског полимера, хидроксипропилметил целулозе, и њихово везивање за хидрофобне центре на молекулима полимера је такође испитано. Анализа добијених резултата указује на присутво различитих интеракција у испитиваним системима, које су од пресудног значаја за њихову примену.

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