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Properties of poloxamer 407 and polysorbate mixed micelles: Influence of polysorbate hydrophobic chain

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ABSTRACT

In the present study, binary mixed micelles of poloxamer 407 and a homologous series of polysorbate surfactants (polysorbate 20, polysorbate 60, polysorbate 80, polysorbate 85) were investigated. Rubingh's model was applied to determine the physicochemical parameters of the poloxamer/polysorbate binary systems. The obtained negative values of the interaction parameter and excess Gibbs energy showed the existence of synergism. By comparing the values of the investigated parameters, and the values of micropolarity measurements, it was noticed that the inclusion of polysorbate surfactants with longer and more saturated hydrophobic chains leads to improved packing in the micellar interior and stronger interactions.

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Introduction

Knowledge of the properties of mixed micelles of nonionic surfactants is important because mixtures of these surface-active compounds, including poloxamers combined with polysorbates, are present in many pharmaceutical and cosmetic formulations [1–4].

It is also important to understand the factors underlying self-association in surfactant mixtures because of the known potential advantages of mixed micelles as compared to unicomponent aggregates [5–13]. Namely, it was noticed that mixed micelles commonly have different properties than unicomponent micelles, which are attributed to synergism in the mixed aggregates [14–16]. The synergism arises usually because of attractive enthalpic forces between different surfactants in the mixed micelles, thermodynamically stabilizing the mixed aggregates [14–16]. These enthalpic forces lead to a decrease in the critical micelle concentration (*cmc*) of surfactant mixtures with respect to the individual surfactants, i.e., the synergism can sufficiently lower the *cmc* value of a surfactant mixture below the *cmc* values of the individual surfactants [14–16]. In this way, a smaller amount of surfactant is needed for various industrial applications (solubilization of hydrophobic compounds in pharmaceutical formulations,

cosmetic products and food, oil remediation, synthesis of nano-sized materials), which is important from a safety, environmental, and economic standpoint.

Poloxamers are triblock copolymers composed of two polyoxyethylene (PEO) parts and one polyoxypropylene (PPO) moiety arranged in a basic PEO–PPO–PEO architecture. Their composition is usually presented with $(EO)_x-(PO)_y-(EO)_x$ formula because the triblock copolymers are available with different average numbers of ethylene oxide (EO) and propylene oxide (PO) units in the PEO and PPO chains, respectively [17,18]. Poloxamers are biocompatible compounds [18], investigated in pharmaceutical research area for controlled drug delivery [2–4,18] as well as for the synthesis of nanosized materials [19–21]. Among the triblock copolymers, poloxamer 407 (P407) is the most extensively used in pharmaceutical industry, although it has been investigated for use in other fields as well [20]. It is a hydrophilic polymer which can form spherical micelles in water solutions, i.e., polymeric micelles, with a PPO hydrophobic interior and a hydrophilic PEO mantle [22,23].

Polysorbates, also known as Tweens, are classic nonionic surfactants with 1–3 fatty acids attached to polyethoxylated sorbitan [24]. Owing to their nonionic nature, polysorbates are less toxic than most other conventional surfactants [25,26], and thus they have broad range of usages as detergents, solubilizers and emulsifiers, in food and pharmaceutical industries [24–27].

When a classic surfactant is added to the polymeric micelles, interactions with poloxamer usually occur [28–35], influencing the architecture of the aggregates and therefore their efficacy for

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various industrial purposes. This is why the interactions between poloxamer and classic surfactants have attracted great interest among researchers, particularly the influence of ionic surfactants on self-aggregation of the triblock copolymers [29–35]. There is, however, surprisingly little information on the interactions between poloxamers and classic nonionic surfactants given the extensive usage of these mixtures in pharmaceutical and cosmetic products, their potential application in drug delivery, and for other purposes. Only few studies using light scattering, small-angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) reported the investigation of poloxamer/classic nonionic surfactant mixed aggregates [13,28]. The formation of mixed micelles was noticed [13,28], in which the nonionic surfactant is inserted at the core-shell interface of the micelles of a triblock copolymer [13]. Yet, despite these informative studies, little is known about the extent and nature of interactions in poloxamer/polysorbate systems, and even less is known about the influence of variations in the structure of the nonionic surfactant's hydrophobic moieties on the degree and type of interactions with triblock copolymers.

Therefore, the aim of this study was to explore how the length and saturation of the hydrophobic part of polysorbate surfactants affects the interactions with the poloxamer and the thermodynamic stability of its micelles. To the best of our knowledge, we have for the first time determined and compared parameters related to the interactions between poloxamer 407 and a series of homologous polysorbate surfactants (Tween 20 (T20), Tween 60 (T60), Tween 80 (T80), and Tween 85 (T85)) having different alkyl tails (laurate, stearate, oleate, and three-oleate chains, respectively). The properties of the mixed systems are elucidated based on Clint's [38] and Rubingh's models [14,37–39], which are ubiquitous in this field.

Materials

Poloxamer 407 with a nominal molar mass of 12,935 g/mol and an average composition of (EO)₁₀₆-(PO)₆₁-(EO)₁₀₆ was donated by BASF Chemtrade GmbH, Germany. The sample was used as received. The polysorbate surfactants: 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). Pyrene was obtained from Aldrich (Germany). The degree of purity is >98%.

Methods

Surface tension measurements

Surface tension (γ) measurements were carried out on a Krüss Easy Dyne tensiometer (Germany) using the du Noüy ring method. Based on this method, aqueous solutions of P407/polysorbate surfactant mixtures and individual surfactants were measured. To obtain the critical micelle concentration of the individual surfactants and their mixtures, surface tension was monitored as a function of each surfactant or surfactant mixture concentration. The mole fraction of polysorbate surfactants in the surfactant mixtures (α_T) varied from 0.1 to 0.5. Temperature was kept constant at 298.15 ± 0.3 K. The measurements were repeated seven times. The relative standard uncertainty of the *cmc* values determination did not exceed 5%.

Fluorescence measurements

Fluorescence measurements for the determination of the critical micelle concentration values and for the micropolarity measurements were carried out using Agilent Cary Eclipse

Fluorescence Spectrophotometer. Pyrene was used as a fluorescence probe molecule in all measurements. The pyrene concentration in the surfactant water solutions was kept constant during the measurements (0.1 μM). Fluorescence emission spectrums of these solutions were obtained using an excitation wavelength of 339 nm. The intensities of the first (I_1) and third (I_3) vibrational bands of pyrene emission spectra were measured at 373 and 384 nm respectively.

For the *cmc* values determination, water solutions of individual surfactants and surfactant mixtures were investigated, whereby mole fraction of polysorbate surfactants in the surfactant mixtures varied from 0.1 to 0.5. The I_1/I_3 ratio was monitored as a function of individual surfactant or surfactant mixture concentration, at 298.15 ± 0.3 K. All measurements were repeated seven times. The relative standard uncertainty of the *cmc* values determination did not exceed 5%.

For the micropolarity investigations, the I_1/I_3 ratio was determined for each individual surfactant and surfactant mixture micellar solution, at the same concentration, well above the *cmc* values. Temperature was kept constant at 298.15 ± 0.3 K. The measurements were repeated seven times. The relative standard uncertainty of the I_1/I_3 ratio determination did not exceed 2.5%.

Theory

Clint's model

To investigate the presence of nonideality in the surfactant mixtures, the ideal critical micelle concentration of surfactant mixtures according to Clint (cmc_{12}^{id}) is usually calculated [36] using:

$$\frac{1}{cmc_{12}^{id}} = \frac{\alpha_1}{cmc_1} + \frac{\alpha_2}{cmc_2} \quad (1)$$

where cmc_1 and cmc_2 are the experimentally obtained values for the individual surfactants, and α_1 and α_2 represent the mole fractions of each surfactant in the surfactant mixture.

The ideal critical micelle concentration corresponds to the *cmc* of a surfactant mixture that forms mixed micelles having no interactions between different compounds [36]. Therefore, deviation of the experimentally obtained critical micelle concentration (cmc_{12}) values from the calculated cmc_{12}^{id} values indicates the presence of non-ideal behavior in surfactant mixtures. To quantify the deviation from ideality, Rubingh's model is usually applied.

Rubingh's model

Rubingh's model was developed within the framework of the pseudophase separation model and regular solution theory (RST). It is commonly applied to determine the physicochemical properties of various mixed micelles [32–35,40–44], including the characteristics of mixed aggregates of triblock copolymers and ionic amphiphiles [32–35]. Based on Rubingh's model, various parameters of mixed micelles can be obtained: mole fractions of the individual surfactants in mixed micelles, activity coefficients of the components of the mixed aggregates (f_1, f_2), the interaction parameter, which describes interactions between different surfactants in mixed micelles (β_{12}), and excess Gibbs energy (G^E) [14,37–39,45].

The mole fraction of the more hydrophobic surfactant (x_1) in mixed micelles is calculated according to the following equation:

$$1 = \frac{(x_1)^2 \ln(\alpha_1 cmc_{12} / cmc_1 x_1)}{(1 - x_1)^2 \ln((1 - \alpha_1) cmc_{12} / cmc_2 (1 - x_1))} \quad (2)$$

where x_1 is solved iteratively.

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