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The influence of the structure of selected Brij and Tween homologues on the thermodynamic stability of their binary mixed micelles

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ABSTRACT

In order to construct micelles with desirable characteristics and predictable behaviour, insights in micellization mechanisms and factors leading to micelle stabilization are necessary.

In this study, Brij S10, Brij S20, Tween 20, Tween 80 and their binary systems were examined. Spectrofluorimetry was used in order to obtain experimental values of critical micelle concentrations from which thermodynamic parameters were calculated.

The aim of the study was to determine the nature of the excess Gibbs energy in examined systems. Analysis of the function $\beta = f(T)$, allowed us to define how variations in surfactants' structure affect the thermodynamic stabilization of binary systems.

Results show that the difference in the length of hydrophobic segments in mixed micelles is responsible for the additional stabilization of Brij S10/Tween 20 and Brij S20/Tween 20 binary systems. In comparison to them, mixed micelles containing alkyl chains of the same length have lower excess entropy values. Introduction of olefin bond in surfactant's alkyl chain (Tween 80) destabilizes the binary system and reduces its excess entropy values. Elongation of hydrophilic segments results in a favourable enthalpic and an unfavourable entropic contribution to the excess Gibbs energy.

1. Introduction

Understanding of the micellization process is necessary in order to expand the application area of surfactants. In some cases, surfactant molecules, when combined in solutions, build mixed micelles that are thermodynamically more stable than single-component micelles of individual surfactants. Such binary systems are characterized with lower critical micelle concentrations (*cmc*) than pure solutions of surfactants [1–6]. Changes that lead to the stabilization of a mixed micelle need to be explored in order to construct new types of mixed micelles, predict their behaviour and facilitate their safe application industry-wide [7,8].

Combining different surfactant molecules as building units of a mixed micelle allows the optimization of the micelle's characteristics. This way many features of micelles as drug transporters can be improved: their solubilization capacities and their stability in the organism can be increased, their possible adverse effects can be eliminated, the bioavailability of drugs transported by micelles can be enhanced, targeted release of drugs in tissues can be achieved, drug efflux from targeted cells can be prevented, etc. [9–15]. Understanding of the nature of mixed micelles can also prompt their implementation in other fields of industry.

Subjects of this research are binary mixed micelles built of either Brij S10 or Brij S20 and Tween 20 or Tween 80 non-ionic surfactants. Brij surfactants have been researched as possible constituents of different drug carrying systems since they have been shown to modify the bioavailability of certain drugs by modifying their absorption and efflux [16–20]. The difference in the structure is most likely responsible for variations in behaviour of different Brij molecules in biological systems, hence research aimed at explaining this dependence can be of scientific value. Brij molecules have linear polyoxyethylene chains representing their polar heads and linear alkyl chains as hydrophobic tails (Fig. 1). Two representatives of this group of surfactants will be compared in this paper: Brij S10 and Brij S20.

Polysorbates (Tweens) are a class of non-ionic surfactants that have a wide medical, commercial and research application due to their high solubilizing capacity, stabilizing potential and adequate biocompatibility [9,10,21–25]. Although it is possible for them to undergo certain degradation processes, Tweens are perceived as stable and nontoxic molecules [26,27]. They are made of polyethylenglycolated sorbitol, representing the polar head of the molecule, esterified with a fatty acid. This fatty acid represents the point of distinction between individual Tweens (Fig. 1).

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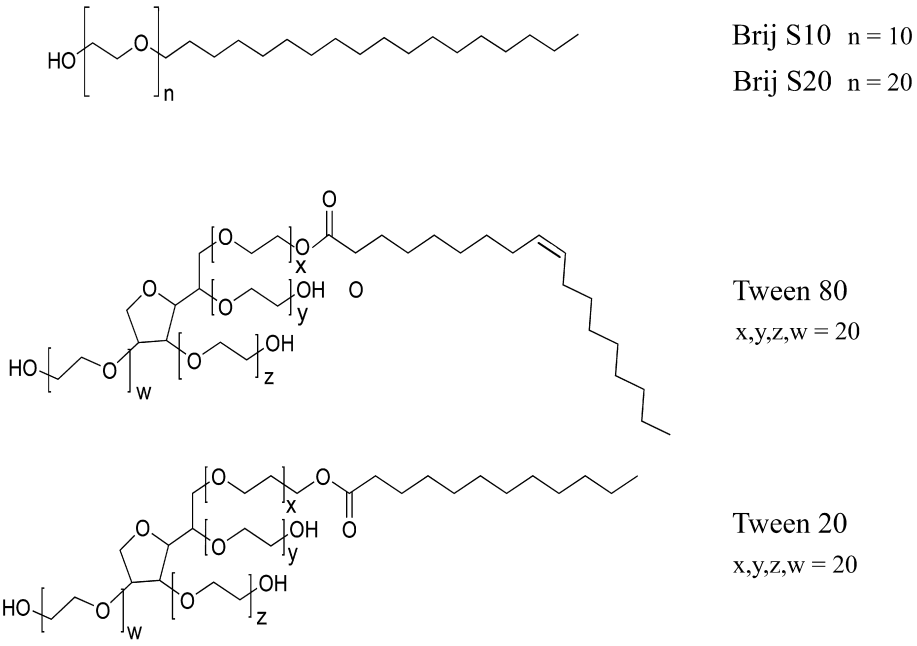

Fig. 1. Structures of the surfactants investigated.

One of the aims of this study is to determine if the excess Gibbs energy in examined systems is solely of the enthalpic nature or does the excess entropy contribute to it. Regular solution theory (RST) is widely established approach for thermodynamic characterization and composition determination of surfactant mixtures. Since RST describes binary systems in which the excess Gibbs energy is solely of the enthalpic nature (the excess entropy is null), the applicability of RST on selected binary mixtures will be assessed [2,28]. The possible existence of an entropic input will be examined by observing the influence of temperature variations on thermodynamic parameters. Investigation of binary mixtures built of monomers with various lengths of hydrophobic and hydrophilic segments, will allow us to define how molecular structure affects the stability of a micelle. Also, we will examine if the degree of saturation of surfactant's hydrophobic tail has influence on the micellization process.

2. Materials and metods

2.1. Materials

Polysorbate 20 (polyoxyethylene (20) sorbitan monolaurate) and Polysorbate 80 (polyoxyethylene (20) sorbitan monooleate) were obtained from J.T. Baker (Holland). Brij S10 and Brij S20 (polyethylene glycol octadecyl ethers) were purchased from Sigma Aldrich (Germany). Chemical purities were assessed using chromatography (HPLC system Agilent 1100 Series), and for all of them the degree of mass fraction purity was higher than 0.99 (Table 1). No additional purification of the surfactants was conducted. Pyrene, which was used as a probe molecule in spectrofluorimetric measurements, was obtained from Sigma Aldrich, and was used as received without pre-treatment. Investigated solutions were prepared by dissolving accurately weighed quantities of surfactants in requisite volumes of deionized water saturated with pyrene. Conductivity of deionized water was measured using Boeco CT-600 conductivity meter, and the measured conductivity was less than 1 $\mu S \cdot cm^{-1}$ at 298.15 K (the error of determination did not exceed 1%). Freshly prepared solutions were used for all measurements.

2.2. Methods (spectrofluorimetric measurements)

In this study, critical micelle concentrations of pure surfactants and of their binary mixtures were obtained using Agilent Cary Eclipse fluorescence spectrophotometer equipped with a Peltier thermostatted cell holder. Measurements were conducted at following temperatures: 273.15 K, 283.15 K, 293.15 K, 303.15 K and 313.15 K. Pyrene was used as a probe molecule since it is highly sensitive to changes in the hydrophobicity of the environment [29–32]. Concentration of pyrene in all analysed solutions was 0.6 μM.

Pyrene was excited at a wavelength of 334 nm and fluorescence emission spectrums of investigated solutions were obtained. The intensities of the first (I_1, 373 nm) and the third (I_3, 384 nm) vibrational band of pyrene emission spectrum were measured. I_3/I_1 values were calculated and analysed as a function of the total

Table 1
Provenance and purity of the materials used.

Compound	Provenance	Mass fraction purity	Purity analysis method
Brij S10 (polyethylene (10) glycol octadecyl ether)	Sigma Aldrich	>0.990	HPLC – reverse phase
Brij S20 (polyethylene (20) glycol octadecyl ether)	Sigma Aldrich	>0.990	HPLC – reverse phase
Tween 20 (polyoxyethylene (20) sorbitan monolaurate)	J.T. Baker	>0.990	HPLC – reverse phase
Tween 80 (polyoxyethylene (20) sorbitan monooleate)	J.T. Baker	>0.990	HPLC – reverse phase
Pyrene	Sigma Aldrich	>0.980	–
Water	Doubly distilled and deionized		