



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.

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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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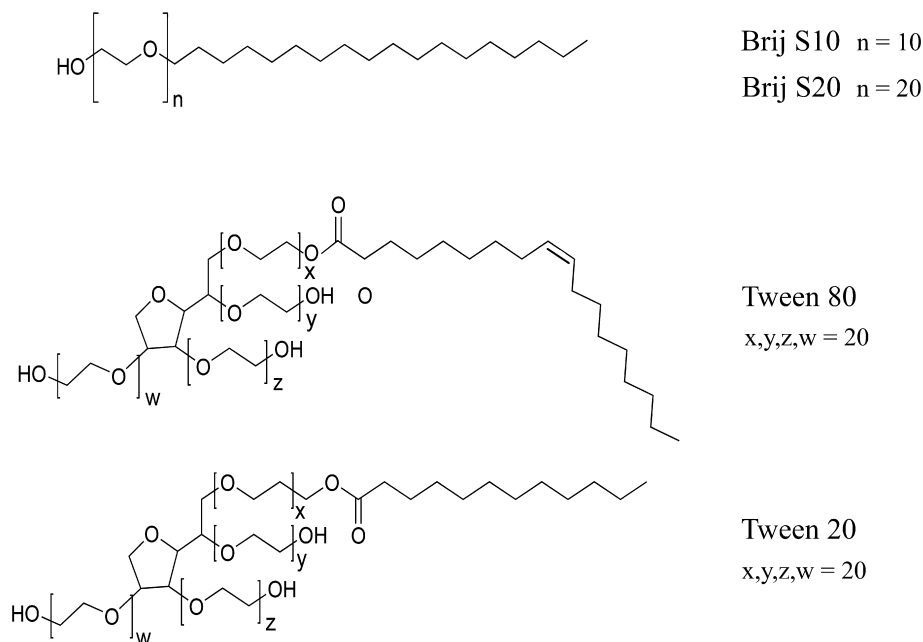


Fig. 1. Structures of the surfactants investigated.

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 methods

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 $1 \mu\text{S}\cdot\text{cm}^{-1}$ 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 $0.6 \mu\text{M}$.

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		

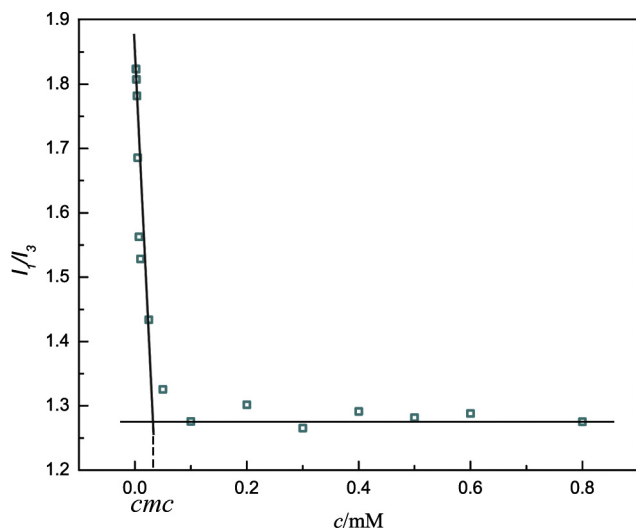


Fig. 2. Determination of the critical micelle concentration from the intersection point of two different tangents in plane $I_1/I_3 - c_T$ (example Tween 20, measurements are conducted on 283.15 K).

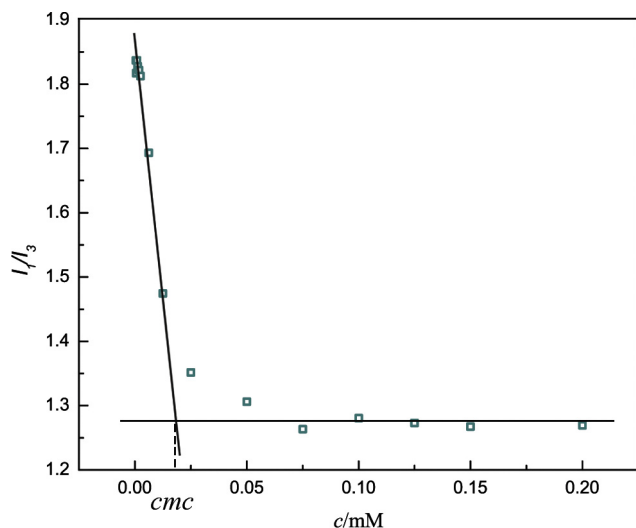


Fig. 3. Determination of the critical micelle concentration from the intersection point of two different tangents in plane $I_1/I_3 - c_T$ (example Brij S10 - Tween 20 ($\alpha = 0.2$), measurements are conducted on $T = 283.15$ K).

concentration of surfactants c_T (Figs. 2 and 3). Negative slope of the function $I_1/I_3 = f(c_T)$ corresponds to the rise in hydrophobicity of the system, while the horizontal part of the function points to the existence of micelles. The intersection point of two tangents dragged from these two parts of the function $I_1/I_3 = f(c_T)$ was taken as an experimental cmc value of the analysed solution [29,33]. All measurements were repeated seven times. The error of described method for the determination of cmc did not exceed 5% ($error = (S_x/\bar{x})100$, S_x - standard deviation of \bar{x}).

3. Theory

Binary mixed micelles in aqueous solutions can be treated as a separate pseudo-phase. This pseudo-phase is a result of mixing two separate phases, each containing pure micelles of different surfactants (i, j) [34]. In the moment when mixed micelles start to form, the total concentration of the surfactants equals critical micelle concentration cmc_{ij} . In the state of equilibrium between

mixed micelle pseudo-phase and monomers from aqueous solution, the following relation exists:

$$\chi_i^{mM} = \frac{\alpha_i cmc_{ij}}{f_i^{mM} cmc_i}, \quad (1)$$

where χ_i^{mM} represents the mole fraction of the surfactant i in a mixed micelle, α_i represents the mole fraction of the surfactant i in a binary mixture of surfactants, f_i^{mM} is the activity coefficient of the surfactant i in a mixed micelle and cmc_i is its critical micelle concentration of surfactant i in a single-component aqueous solution [1,2,8]. In a binary mixed micelle:

$$\chi_i^{mM} + \chi_j^{mM} = 1. \quad (2)$$

In binary mixed micelle, the average energies of intermolecular interactions which exist between different building units do not differ from the average energies existing in single-component micelles. The enthalpy of mixing is zero, and the ideal Gibbs energy of mixing is a result of change in the entropy of the system. In ideal mixtures, the activity coefficients are: $f_i^{mM} = f_j^{mM} = 1$, and for calculation of ideal cmc values of surfactant mixtures Clint's equation can be applied [35,36]:

$$\frac{1}{cmc_{ij}} = \frac{\alpha_i}{cmc_i} + \frac{\alpha_j}{cmc_j}. \quad (3)$$

The Gibbs energy of formation of real binary mixed micelles includes the excess Gibbs energy. According to RST, the excess Gibbs energy is solely of enthalpic nature [2].

The molar Gibbs energy of mixing ($\Delta_{mix}G_{ij}$) is defined as a sum of ideal molar Gibbs energy of mixing ($\Delta_{mix}G_{ij}^{id}$) and excess molar Gibbs energy (G_{ij}^E) [35]:

$$\Delta_{mix}G_{ij} = \Delta_{mix}G_{ij}^{id} + G_{ij}^E \quad (4)$$

Regular solution theory excludes the existence of entropic influence on excess Gibbs energy ($S^E = 0$), since it approaches surfactant molecules as rigid structures [2]. The correlation between the excess Gibbs energy (G_{ij}^E) and β interaction parameter (β_{ij}) can be made [5,8]:

$$G_{ij}^E = RT\beta_{ij}(\chi_i^{mM} - (\chi_i^{mM})^2). \quad (5)$$

If the process of mixed micelle formation is more spontaneous than the formation of an ideal mixed micelle, it will be characterized with negative values of $G_{ij}^E/G_{ij}^E < 0$, and analogous to the Eq. (4): $\Delta_{mix}G_{ij} < \Delta_{mix}G_{ij}^{id}$. In these cases, β interaction parameter will at A_{ij} so have negative values ($\beta_{ij} < 0$), which is consistent with the Eq. (5). On the other hand, if the micellization process is less spontaneous than the formation of an ideal micelle, excess Gibbs energy will have positive values ($G_{ij}^E > 0$; $\Delta_{mix}G_{ij} < \Delta_{mix}G_{ij}^{id}$), as will interaction parameter ($\beta_{ij} < 0$) [2,8,35].

Describing the stability of binary mixtures, Porter developed a model independent equation (equation that does not assume $S^E = 0$) [37]:

$$G_{ij}^E = H_{ij}^E = A_{ij}(\chi_i^{mM} - (\chi_i^{mM})^2), \quad (6)$$

where H_{ij}^E represents the excess enthalpy of the micellization process and represents coefficient of interaction in Porter's expression. Hoffmann and Pössnecker utilized this empirical equation to describe mixed micelle formation and to circumvent the shortcomings of RST concerning the excess entropy. Comparison of Eq. (6) with the RST relation Eq. (5) gives:

$$A_{ij} = RT\beta_{ij}. \quad (7)$$

Coefficient of activity (f_i^{mM}) in binary mixed micelle pseudo-phase is related to the excess Gibbs energy with the following partial derivative:

$$(\partial G_{ij}^E / \partial n_i)_{p,T,n_j} = RT \ln f_i^{\text{mM}}, \quad (8)$$

where n_i and n_j represent the number of moles of surfactants i and j in the binary pseudo-phase, respectively.

Introduction of Eq. (5) (RST relation for the excess Gibbs energy) in partial derivative above results in expressions for the activity coefficients ($f_i^{\text{mM}}, f_j^{\text{mM}}$) in the binary mixed micelle pseudo-phase [1,2]:

$$\ln f_i^{\text{mM}} = \beta_{ij} (1 - x_i^{\text{mM}})^2, \quad (9)$$

$$\ln f_j^{\text{mM}} = \beta_{ij} (1 - x_j^{\text{mM}})^2. \quad (10)$$

From the Eqs. (1), (9) and (10) the expression is derived that allows determination of molar fraction of surfactant i in binary mixture (x_i^{mM}) from obtained cmc values of pure surfactants (cmc_i, cmc_j) and of their binary mixture (cmc_{ij}) [2,8]:

$$1 = \frac{(1 - x_i^{\text{mM}})^2 \ln [(1 - \alpha_i) cmc_{ij}] / (cmc_j (1 - x_i^{\text{mM}}))}{(x_i^{\text{mM}})^2 \ln [(\alpha_i cmc_{ij}) / (cmc_i x_i^{\text{mM}})]}. \quad (11)$$

Table 2
Definitions of calculated thermodynamic parameters of binary mixed micelles.

Symbol	Name	Equation	Unit
x_i	Mole fraction of the more hydrophobic component in a binary mixed micelle [1,2]	$1 = \frac{(1 - x_i^{\text{mM}})^2 \ln [(1 - \alpha_i) cmc_{ij}] / (cmc_j (1 - x_i^{\text{mM}}))}{(x_i^{\text{mM}})^2 \ln [(\alpha_i cmc_{ij}) / (cmc_i x_i^{\text{mM}})]}$	–
x_j	Mole fraction of the less hydrophobic component in a binary mixed micelle [1,2]	$x_j^{\text{mM}} = 1 - x_i^{\text{mM}}$	–
β	Interaction parameter according to Rubingh [1,2]	$\beta_{ij} = \ln (cmc_{ij} \alpha_i / cmc_i x_i) / (1 - x_i)^2$	–
f_i	Activity coefficient of the more hydrophobic component in a binary mixed micelle [1,2]	$f_i^{\text{mM}} = \exp [\beta_{ij} (1 - x_i^{\text{mM}})^2]$	–
f_j	Activity coefficient of the less hydrophobic component in a binary mixed micelle [1,2]	$f_j^{\text{mM}} = \exp [\beta_{ij} (1 - x_j^{\text{mM}})^2]$	–
A_{ij}	Interaction parameter according to Porter [5,8]	$A_{ij} = RT \beta_{ij}$	J·mol ⁻¹
G^E	Excess Gibbs energy of binary mixed micelle formation [37]	$G_{ij}^E = A_{ij} (x_i^{\text{mM}} - (x_i^{\text{mM}})^2)$	J·mol ⁻¹
S^E/R	Quotient of excess entropy divided by universal gas constant [35]	$-\frac{S^E}{R} = x_i^{\text{mM}} x_j^{\text{mM}} (\beta_{ij} + T \frac{\partial \beta_{ij}}{\partial T}) + T \frac{\partial (x_i^{\text{mM}} x_j^{\text{mM}})}{\partial T} \beta_{ij}$	–

α_i – mole fraction of the more hydrophobic component in the binary mixed micelle, cmc_{ij} – experimentally obtained critical micelle concentration of the binary mixed micelle, cmc_i, cmc_j – critical micelle concentrations of single-component micelles.

Table 3
Thermodynamic parameters of binary mixed micelles of Brij S10 and Tween 20: α_i – mole fraction of Brij S10 in the binary mixture, cmc_{ij} – experimentally obtained critical micelle concentration of the binary mixed micelle, x_i, x_j – mole fractions of Brij S10 and Tween 20 in the binary mixed micelle, respectively, β_{ij} – interaction parameter according to Rubingh, f_i, f_j – activity coefficients of Brij S10 and Tween 20 in the binary mixed micelle, respectively, A_{ij} – interaction parameter according to Porter, G^E – the excess Gibbs energy of binary mixed micelle formation. Measurements were conducted at following temperatures: 273.15 K, 283.15 K, 293.15 K, 303.15 K, 313.15 K; and at $p_a = 1.00 \times 10^5$ Pa.

T/K	$cmc_{ij}/\text{mmol}\cdot\text{kg}^{-3}$	x_i	x_j	β_{ij}	f_i	f_j	$A_{ij}/\text{J}\cdot\text{mol}^{-1}$	$G^E/\text{J}\cdot\text{mol}^{-1}$	$x_i x_j$
$\alpha_i = 0.2$									
273.15	0.015	0.157	0.844	0.590	1.521	1.015	1339.100	176.772	0.132
283.15	0.019	0.400	0.601	-1.329	0.619	0.809	-3127.951	-750.395	0.240
293.15	0.022	0.377	0.624	-1.790	0.499	0.776	-4363.050	-1024.216	0.235
303.15	0.038	0.381	0.619	-1.481	0.567	0.806	-3733.797	-880.930	0.236
313.15	0.042	0.378	0.622	-2.912	0.324	0.660	-7582.329	-1782.542	0.235
$\alpha_i = 0.4$									
273.15	0.012	0.439	0.561	-0.463	0.864	0.915	-1052.024	-259.091	0.246
283.15	0.017	0.552	0.448	-0.922	0.831	0.755	-2169.838	-536.524	0.247
293.15	0.022	0.507	0.493	-1.146	0.757	0.745	-2794.183	-698.413	0.250
303.15	0.030	0.520	0.480	-1.802	0.660	0.615	-4542.116	-1133.766	0.250
313.15	0.039	0.477	0.523	-2.744	0.472	0.536	-7144.230	-1782.146	0.249
$\alpha_i = 0.6$									
273.15	0.017	0.730	0.271	1.046	1.080	1.745	2376.217	468.898	0.197
283.15	0.018	0.743	0.257	-0.116	0.992	0.938	-272.886	-52.121	0.191
293.15	0.025	0.667	0.334	-0.458	0.950	0.816	-1116.710	-248.220	0.222
303.15	0.033	0.651	0.349	-1.105	0.874	0.626	-2784.186	-632.564	0.227
313.15	0.037	0.559	0.441	-2.896	0.570	0.404	-7539.444	-1858.349	0.246
$\alpha_i = 0.8$									
273.15	0.018	0.468	0.532	3.226	2.489	2.030	7327.047	1824.445	0.249
283.15	0.022	0.547	0.454	3.791	2.181	3.102	8924.491	2211.826	0.248
293.15	0.030	0.560	0.440	3.126	1.832	2.664	7618.283	1877.236	0.246
303.15	0.037	0.847	0.153	-0.320	0.993	0.794	-807.748	-104.509	0.129
313.15	0.045	0.671	0.329	-2.479	0.765	0.327	-6455.158	-1424.371	0.221

Brij S10 (cmc_i) values: 0.013 mmol·kg⁻³ ($T = 273.15$ K), 0.015 mmol·kg⁻³ ($T = 283.15$ K), 0.023 mmol·kg⁻³ ($T = 293.15$ K), 0.035 mmol·kg⁻³ ($T = 303.15$ K), 0.069 mmol·kg⁻³ ($T = 313.15$ K). Tween 20 (cmc_j) values: 0.014 mmol·kg⁻³ ($T = 273.15$ K), 0.031 mmol·kg⁻³ ($T = 283.15$ K), 0.036 mmol·kg⁻³ ($T = 293.15$ K), 0.061 mmol·kg⁻³ ($T = 303.15$ K), 0.083 mmol·kg⁻³ ($T = 313.15$ K).

Standard uncertainties u , are: $u(T) = \pm 0.10$ K, $u(p_a) = \pm 0.002$ MPa, $u(x_i) = \pm 0.01$, $u(cmc_i) = \pm 0.003$ mmol·kg⁻³, $u(cmc_j) = \pm 0.002$ mmol·kg⁻³, $u(cmc_{ij}) = \pm 0.003$ mmol·kg⁻³, $u(x_j) = \pm 0.004$, $u(x_j) = \pm 0.003$, $u(\beta_{ij}) = \pm 0.071$, $u(f_i) = \pm 0.072$, $u(f_j) = \pm 0.071$, $u(A_{ij}) = \pm 5.422$ J·mol⁻¹, $u(G^E) = \pm 7.041$ J·mol⁻¹.

Table 4

Thermodynamic parameters of binary mixed micelles of Brij S10 and Tween 80: α_i – mole fraction of Brij S10 in the binary mixture, cmc_{ij} – experimentally obtained critical micelle concentration of the binary mixed micelle, x_i, x_j – mole fractions of Brij S10 and Tween 80 in the binary mixed micelle, respectively, β_{ij} – interaction parameter according to Rubingh, f_i, f_j – activity coefficients of Brij S10 and Tween 80 in the binary mixed micelle, respectively, A_{ij} – interaction parameter according to Porter, G^E – the excess Gibbs energy of binary mixed micelle formation. Measurements were conducted at following temperatures: 273.15 K, 283.15 K, 293.15 K, 303.15 K, 313.15 K; and at $p_a = 1.00 \times 10^5$ Pa.

T/K	$cmc_{ij}/\text{mmol}\cdot\text{kg}^{-3}$	x_i	x_j	β_{ij}	f_i	f_j	$A_{ij}/\text{J}\cdot\text{mol}^{-1}$	$G^E/\text{J}\cdot\text{mol}^{-1}$	$x_i x_j$
$\alpha_i = 0.2$									
273.15	0.008	0.359	0.641	-2.515	0.356	0.723	-5710.919	-1314.834	0.230
283.15	0.010	0.346	0.654	-2.182	0.393	0.770	-5136.607	-1162.174	0.226
293.15	0.018	0.323	0.677	-1.665	0.466	0.841	-4057.128	-887.033	0.219
303.15	0.023	0.320	0.680	-1.919	0.412	0.821	-4836.335	-1052.908	0.218
313.15	0.031	0.301	0.699	-2.482	0.298	0.798	-6463.000	-1360.323	0.210
$\alpha_i = 0.4$									
273.15	0.009	0.459	0.541	-1.671	0.613	0.703	-3795.962	-942.609	0.248
283.15	0.011	0.455	0.545	-1.632	0.616	0.714	-3841.880	-952.621	0.248
293.15	0.016	0.451	0.549	-1.556	0.626	0.729	-3792.965	-939.134	0.248
303.15	0.023	0.435	0.565	-1.578	0.604	0.742	-3977.400	-977.545	0.246
313.15	0.036	0.384	0.616	-1.626	0.540	0.787	-4233.128	-1001.615	0.237
$\alpha_i = 0.6$									
273.15	0.009	0.566	0.434	-1.808	0.712	0.560	-4106.663	-1008.560	0.246
283.15	0.012	0.578	0.422	-1.086	0.824	0.696	-2556.222	-623.623	0.244
293.15	0.019	0.576	0.424	-1.038	0.829	0.709	-2530.801	-618.236	0.244
303.15	0.026	0.555	0.445	-1.167	0.794	0.698	-2942.545	-726.703	0.247
313.15	0.040	0.495	0.505	-1.430	0.694	0.705	-3724.205	-930.943	0.250
$\alpha_i = 0.8$									
273.15	0.013	0.802	0.198	-0.151	0.994	0.907	-343.783	-54.674	0.159
283.15	0.017	0.871	0.129	0.606	1.010	1.584	1426.269	160.042	0.112
293.15	0.025	0.852	0.148	0.438	1.010	1.374	1067.795	134.645	0.126
303.15	0.036	0.807	0.193	0.160	1.006	1.109	402.202	62.742	0.156
313.15	0.051	0.659	0.342	-0.906	0.900	0.675	-2357.638	-530.180	0.225

Brij S10 (cmc_i) values: 0.013 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 273.15$ K), 0.015 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 283.15$ K), 0.023 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 293.15$ K), 0.035 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 303.15$ K), 0.069 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 313.15$ K). Tween 80 (cmc_j) values: 0.014 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 273.15$ K), 0.016 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 283.15$ K), 0.025 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 293.15$ K), 0.033 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 303.15$ K), 0.045 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 313.15$ K).

Standard uncertainties u , are: $u(T) = \pm 0.10$ K, $u(p_a) = \pm 0.002$ MPa, $u(\alpha_i) = \pm 0.01$, $u(cmc_i) = \pm 0.003$ $\text{mmol}\cdot\text{kg}^{-3}$, $u(cmc_j) = \pm 0.003$ $\text{mmol}\cdot\text{kg}^{-3}$, $u(cmc_{ij}) = \pm 0.003$ $\text{mmol}\cdot\text{kg}^{-3}$, $u(x_i) = \pm 0.004$, $u(x_j) = \pm 0.004$, $u(\beta_{ij}) = \pm 0.082$, $u(f_i) = \pm 0.083$, $u(f_j) = \pm 0.082$, $u(A_{ij}) = \pm 7.324$ $\text{J}\cdot\text{mol}^{-1}$, $u(G^E) = \pm 8.242$ $\text{J}\cdot\text{mol}^{-1}$.

Table 5

Thermodynamic parameters of binary mixed micelles of Brij S20 and Tween 20. α_i – mole fraction of Brij S20 in the binary mixture, cmc_{ij} – experimentally obtained critical micelle concentration of the binary mixed micelle, x_i, x_j – mole fractions of Brij S20 and Tween 20 in the binary mixed micelle, respectively, β_{ij} – interaction parameter according to Rubingh, f_i, f_j – activity coefficients of Brij S20 and Tween 20 in the binary mixed micelle, respectively, A_{ij} – interaction parameter according to Porter, G^E – the excess Gibbs energy of binary mixed micelle formation. Measurements were conducted at following temperatures: 273.15 K, 283.15 K, 293.15 K, 303.15 K, 313.15 K; and at $p_a = 1.00 \times 10^5$ Pa.

T/K	$cmc_{ij}/\text{mmol}\cdot\text{kg}^{-3}$	x_i	x_j	β_{ij}	f_i	f_j	$A_{ij}/\text{J}\cdot\text{mol}^{-1}$	$G^E/\text{J}\cdot\text{mol}^{-1}$	$x_i x_j$
$\alpha_i = 0.2$									
273.15	0.013	0.256	0.744	0.094	1.054	1.006	213.781	40.686	0.190
283.15	0.019	0.402	0.598	-1.000	0.699	0.851	-2353.765	-565.836	0.240
293.15	0.024	0.384	0.616	-0.877	0.717	0.878	-2137.576	-505.829	0.237
303.15	0.033	0.407	0.593	-1.857	0.520	0.735	-4681.863	-1129.711	0.241
313.15	0.041	0.433	0.567	-1.891	0.544	0.702	-4924.038	-1208.707	0.245
$\alpha_i = 0.4$									
273.15	0.010	0.492	0.508	-0.728	0.829	0.838	-1653.799	-413.354	0.250
283.15	0.014	0.553	0.448	-1.686	0.713	0.598	-3968.745	-981.247	0.247
293.15	0.015	0.538	0.462	-2.041	0.647	0.554	-4974.176	-1236.361	0.249
303.15	0.026	0.531	0.469	-2.133	0.626	0.548	-5376.664	-1338.966	0.249
313.15	0.032	0.554	0.446	-2.175	0.649	0.512	-5661.912	-1398.722	0.247
$\alpha_i = 0.6$									
273.15	0.011	0.678	0.322	-0.068	0.993	0.970	-153.513	-33.503	0.218
283.15	0.016	0.729	0.271	-0.460	0.967	0.783	-1081.994	-213.956	0.198
293.15	0.020	0.710	0.291	-0.539	0.956	0.763	-1313.088	-270.640	0.206
303.15	0.032	0.678	0.322	-0.907	0.910	0.659	-2286.952	-499.197	0.218
313.15	0.038	0.708	0.292	-0.915	0.925	0.632	-2382.691	-492.588	0.207
$\alpha_i = 0.8$									
273.15	0.011	0.893	0.107	0.475	1.005	1.460	1078.366	102.954	0.095
283.15	0.015	0.879	0.121	-0.259	0.996	0.816	-608.922	-64.903	0.107
293.15	0.018	0.844	0.156	-0.601	0.985	0.653	-1464.030	-192.861	0.132
303.15	0.031	0.818	0.182	-0.861	0.972	0.563	-2169.237	-323.085	0.149
313.15	0.034	0.814	0.186	-1.260	0.957	0.441	-3281.341	-497.632	0.152

Brij S20 (cmc_i) values: 0.010 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 273.15$ K), 0.014 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 283.15$ K), 0.018 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 293.15$ K), 0.031 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 303.15$ K), 0.035 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 313.15$ K). Tween 20 (cmc_j) values: 0.014 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 273.15$ K), 0.031 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 283.15$ K), 0.036 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 293.15$ K), 0.061 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 303.15$ K), 0.083 $\text{mmol}\cdot\text{kg}^{-3}$ ($T = 313.15$ K).

Standard uncertainties u , are: $u(T) = \pm 0.10$ K, $u(p_a) = \pm 0.002$ MPa, $u(\alpha_i) = \pm 0.01$, $u(cmc_i) = \pm 0.003$ $\text{mmol}\cdot\text{kg}^{-3}$, $u(cmc_j) = \pm 0.002$ $\text{mmol}\cdot\text{kg}^{-3}$, $u(cmc_{ij}) = \pm 0.003$ $\text{mmol}\cdot\text{kg}^{-3}$, $u(x_i) = \pm 0.004$, $u(x_j) = \pm 0.003$, $u(\beta_{ij}) = \pm 0.073$, $u(f_i) = \pm 0.075$, $u(f_j) = \pm 0.074$, $u(A_{ij}) = \pm 5.944$ $\text{J}\cdot\text{mol}^{-1}$, $u(G^E) = \pm 6.981$ $\text{J}\cdot\text{mol}^{-1}$.

4. Results and discussion

In order to investigate the influence of temperature on the excess Gibbs energy, thermodynamic parameters (Table 2) were acquired in the temperature range from 273.15 K to 313.15 K. According to RST, considering the assumption that $S^E = 0$, temperature variations should not result in the change of excess Gibbs energy. If we try to isolate solely the influence of temperature on the micellization process, with respect to RST, we should get a relation [5]:

$$(\partial G_{ij}^E / \partial T)_{p, x_i^{mm}} = 0. \quad (12)$$

Table 6
Thermodynamic parameters of binary mixed micelles of Brij S20 and Tween 80. α_i – mole fraction of Brij S20 in the binary mixture, cmc_{ij} – experimentally obtained critical micelle concentration of the binary mixed micelle, x_i, x_j – mole fractions of Brij S20 and Tween 80 in the binary mixed micelle, respectively, β_{ij} – interaction parameter according to Rubingh, f_i, f_j – activity coefficients of Brij S20 and Tween 80 in the binary mixed micelle, respectively, A_{ij} – interaction parameter according to Porter, G^E – the excess Gibbs energy of binary mixed micelle formation. Measurements were conducted at following temperatures: 273.15 K, 283.15 K, 293.15 K, 303.15 K, 313.15 K; and at $p_a = 1.00 \times 10^5$ Pa.

T/K	$cmc_{ij}/\text{mmol} \cdot \text{kg}^{-3}$	x_i	x_j	β_{ij}	f_i	f_j	$A_{ij}/\text{J} \cdot \text{mol}^{-1}$	$G^E/\text{J} \cdot \text{mol}^{-1}$	$x_i x_j$
$\alpha_i = 0.2$									
273.15	0.009	0.358	0.642	-1.564	0.525	0.819	-3550.960	-815.937	0.230
283.15	0.011	0.343	0.657	-1.843	0.452	0.805	-4338.390	-978.069	0.225
293.15	0.019	0.329	0.671	-1.007	0.635	0.897	-2455.224	-542.013	0.221
303.15	0.033	0.206	0.794	0.033	1.021	1.001	83.065	13.582	0.164
313.15	0.055	0.132	0.868	1.155	2.388	1.020	3008.532	344.927	0.115
$\alpha_i = 0.4$									
273.15	0.008	0.493	0.507	-1.556	0.670	0.685	-3533.445	-883.193	0.250
283.15	0.011	0.462	0.538	-1.219	0.703	0.771	-2870.018	-713.360	0.249
293.15	0.019	0.484	0.516	-0.392	0.901	0.912	-955.043	-238.519	0.250
303.15	0.034	0.407	0.593	0.144	1.052	1.024	362.537	87.499	0.241
313.15	0.053	0.406	0.594	1.155	1.502	1.210	3006.004	725.053	0.241
$\alpha_i = 0.6$									
273.15	0.008	0.611	0.389	-1.386	0.811	0.596	-3148.358	-748.019	0.238
283.15	0.010	0.581	0.419	-1.481	0.771	0.607	-3487.231	-848.984	0.243
293.15	0.018	0.647	0.353	-0.432	0.948	0.834	-1052.528	-240.264	0.228
303.15	0.031	0.603	0.397	-0.201	0.969	0.930	-505.451	-120.959	0.239
313.15	0.038	0.657	0.343	0.011	1.001	1.005	29.867	6.727	0.225
$\alpha_i = 0.8$									
273.15	0.008	0.718	0.282	-1.846	0.864	0.386	-4193.050	-848.443	0.202
283.15	0.011	0.726	0.274	-1.260	0.910	0.514	-2966.919	-589.789	0.199
293.15	0.016	0.775	0.225	-0.873	0.957	0.592	-2127.956	-371.296	0.174
303.15	0.031	0.797	0.203	-0.130	0.995	0.921	-327.276	-53.028	0.162
313.15	0.040	0.908	0.092	0.815	1.007	1.958	2122.183	177.279	0.084

Brij S20 (cmc_i) values: 0.010 mmol·kg⁻³ (T = 273.15 K), 0.014 mmol·kg⁻³ (T = 283.15 K), 0.018 mmol·kg⁻³ (T = 293.15 K), 0.031 mmol·kg⁻³ (T = 303.15 K), 0.035 mmol·kg⁻³ (T = 313.15 K). Tween 80 (cmc_j) values: 0.014 mmol·kg⁻³ (T = 273.15 K), 0.016 mmol·kg⁻³ (T = 283.15 K), 0.025 mmol·kg⁻³ (T = 293.15 K), 0.033 mmol·kg⁻³ (T = 303.15 K), 0.045 mmol·kg⁻³ (T = 313.15 K).

Standard uncertainties u , are: $u(T) = \pm 0.10$ K, $u(p_a) = \pm 0.002$ MPa, $u(\alpha_i) = \pm 0.01$, $u(cmc_i) = \pm 0.003$ mmol·g⁻³, $u(cmc_j) = \pm 0.003$ mmol·kg⁻³, $u(x_i) = \pm 0.004$, $u(x_j) = \pm 0.004$, $u(\beta_{ij}) = \pm 0.084$, $u(f_i) = \pm 0.084$, $u(f_j) = \pm 0.085$, $u(A_{ij}) = \pm 7.873$ J·mol⁻¹, $u(G^E) = \pm 9.250$ J·mol⁻¹.

Table 7
Excess entropy values of investigated binary systems: α_i – mole fraction of more hydrophobic surfactant in the binary mixture (Brij), S^E/R – quotient of excess entropy divided by universal gas constant. Measurements were conducted at following temperatures: 273.15 K, 283.15 K, 293.15 K, 303.15 K, 313.15 K; and at $p_a = 1.00 \times 10^5$ Pa.

T/K	S^E/R (BS10 – T20)				T/K	S^E/R (BS10 – T80)			
	$\alpha_i = 0.2$	$\alpha_i = 0.4$	$\alpha_i = 0.6$	$\alpha_i = 0.8$		$\alpha_i = 0.2$	$\alpha_i = 0.4$	$\alpha_i = 0.6$	$\alpha_i = 0.8$
273.15	0.765	3.799	4.203	9.753	273.15	-5.661	1.013	-5.574	-3.064
283.15	5.145	4.089	4.862	9.952	283.15	-3.516	1.189	-3.724	-2.782
293.15	5.295	4.340	6.056	10.441	293.15	-1.275	1.351	-1.681	-0.922
303.15	5.426	4.555	6.796	4.992	303.15	1.067	1.600	0.564	3.007
313.15	5.865	4.917	8.739	18.336	313.15	3.445	1.840	3.070	16.539
T/K	S^E/R (BS20 – T20)				T/K	S^E/R (BS20 – T80)			
	$\alpha_i = 0.2$	$\alpha_i = 0.4$	$\alpha_i = 0.6$	$\alpha_i = 0.8$		$\alpha_i = 0.2$	$\alpha_i = 0.4$	$\alpha_i = 0.6$	$\alpha_i = 0.8$
273.15	2.465	2.961	1.290	0.822	273.15	-3.473	-4.254	-2.342	-4.553
283.15	3.839	3.266	1.286	1.366	283.15	-4.371	-4.514	-2.562	-4.343
293.15	3.841	3.473	1.401	1.915	293.15	-5.167	-4.893	-2.690	-3.838
303.15	4.601	3.604	1.609	2.357	303.15	-3.586	-4.981	-2.952	-3.253
313.15	4.829	3.686	1.569	2.716	313.15	-0.503	-5.244	-2.877	-1.066

Standard uncertainties u , are: $u(T) = \pm 0.10$ K, $u(p_a) = \pm 0.002$ MPa, $u(\alpha_i) = \pm 0.01$, $u(S^E/R) = \pm 0.082$ J·mol⁻¹.

This implies that, analogous to Porter's function Eq. (6), the differential of A_{ij} over temperature should also equal zero [5,37]. Calculated results that are presented in Tables 3–6 indicate that the assumption $S^E = 0$ is not suitable for describing investigated binary systems, since G_{ij}^E (β_{ij}) varies with the temperature.

Since surfactant molecules cannot be regarded as rigid objects, conformational analysis of micelle's building units needs to be considered. Formation of a mixed micelle may lead to a change in the number of possible monomer conformations (in comparison to the number of possible conformations in pure micelles). Also, changes in the structure of mixed micelles can lead to the difference in the degree of their hydration. Both effects can be observed as excess

entropy. Taking into an account that $\partial\beta_{ij}/\partial T \neq 0$ and $\partial(x_i^{mM}x_j^{mM})/\partial T \neq 0$ the excess entropy can be calculated using the relation [35]:

$$-\frac{S^E}{R} = x_i^{mM}x_j^{mM} \left(\beta_{ij} + T \frac{\partial\beta}{\partial T} \right) + T \frac{\partial(x_i^{mM}x_j^{mM})}{\partial T} \beta_{ij}. \quad (13)$$

Calculated S^E/R values for every analysed binary system are presented in Table 7 ($S^E/R \neq 0$). Obtained dependences $\beta_{ij} = f(T)$ for every analysed binary system in investigated temperature range can be fitted with linear functions or with polynomial functions of the second order (Fig. 4). Dependences $x_i x_j = f(T)$ in investigated temperature range were also fitted with either linear functions or polynomial functions of the second order (Fig. 5).

Molecular structures of analysed surfactants are presented in Fig. 1. Tween 20 and Tween 80 are homologous esters of fatty acids. They have typical surfactant structure with polar heads portrayed by polyethyleneglycolated sorbitol and hydrophobic tails represented by lauric acid (containing 12 C atoms) in Tween 20 and oleic acid (containing 18 C atoms) in Tween 80. This difference in the length of hydrophobic chains and the presence of the 9-cis double bond in Tween 80 are responsible for divergence in their mixing behaviour in aqueous solutions.

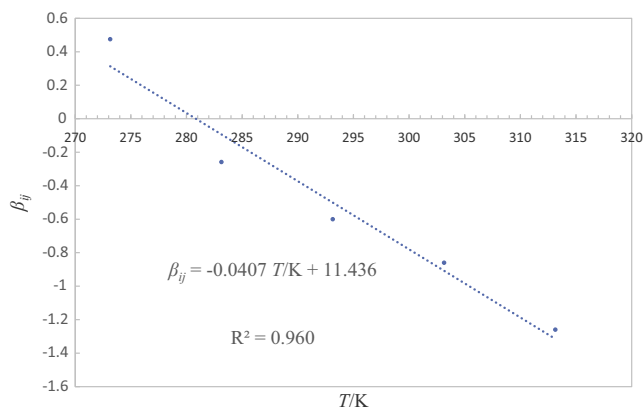


Fig. 4. Changes of the values of the interaction parameter β_{ij} as a function of temperature (example Brij S20 – Tween 20 ($\alpha = 0.8$)). The dependence $\beta_{ij} = f(T)$ in temperature range from 273.15 K to 313.15 K is fitted with the linear function.

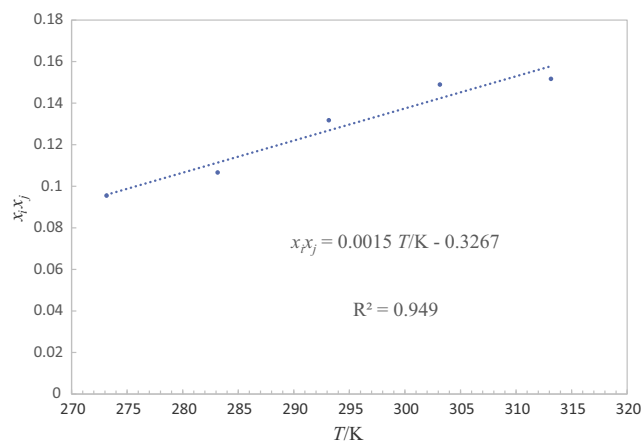


Fig. 5. Changes of the $x_i x_j$ values as a function of temperature (example Brij S20 – Tween 20 ($\alpha = 0.8$)). The dependence $x_i x_j = f(T)$ in temperature range from 273.15 K to 313.15 K is fitted with the linear function.

Both, Brij S10 and Brij S20 have their polar heads made of a single linear polyethyleneglycolated chain and their hydrophobic tails are represented by an 18 C atoms long alkyl chain. They are distinguished one from another by the length of the polar chain, i.e. Brij S10 has hydrophilic segment built of approximately 10 oxyethylene units, while Brij S20 has approximately 20 oxyethylene units in its structure.

4.1. Single-component micelles

All investigated surfactants in pure aqueous solutions form spherical single-component micelles. Their alkyl chains presumably assume elongated conformations and are radially arranged forming the micelle's hydrophobic core. Elongated conformation of alkyl tails of surfactants is, considering the enthalpy of the system, the most desirable conformation having the least gauche interactions. The most stable arrangement of surfactants with linear alkyl chains is the one having their molecular axes parallel to each other. In spherical micelles, since parallel orientation is not attainable, the radial allocation of alkyl tails is most plausible. This geometry of micelles imposes an existence of free spaces on the surface of the micelle's core [38–42]. These spaces can be filled with polyoxyethylene chains originating from polar heads. Considering the entropy of the system, this model of a micelle is the most stable one. Alternative means of filling these cavities are either with water molecules or with alkyl chains assuming folded conformations.

Filling the gaps with folded alkyl chains is possible only on higher temperatures, since higher energy levels of molecules are necessary in order to overpower gauche interactions. In this case, polar heads cannot completely screen the surface of the hydrophobic core which leads to its partial hydration and an unfavourable enthalpic contribution to the energy of the system. Molecules of water engaged in hydration process lose their freedom of movement, which is followed by an entropy decline [38].

Filling the gaps with molecules of water will have similar effects. Obtained *cmc* values reflect described changes that follow different arrangements of monomers in a micelle. With the increase in temperature, the values of the *cmc* of pure surfactants rise.

Polar chains may also contribute to the observed rise in *cmc* values in high temperatures. Polyoxyethylene chains predominantly assume the conformation described with the lowest free energy and the highest values of the dipole moment (C–C bonds have *cis*, and C–O bonds have *trans* conformation). As the temperature of the system rises, other conformations of polar chains appear, having a lower dipole moment, and therefore engaging in lesser hydrogen bonds [43]. Formation of hydrogen bonds is energetically favourable ($\Delta H < 0$), despite the decrease in freedom of movement of engaged water molecules. Therefore, on higher temperatures the micelles are stabilized with hydrogen bonds to a lesser extent and *cmc* values rise.

4.2. Binary mixed micelles

In this study four binary systems were analysed: Brij S10/Tween 20, Brij S20/Tween 20, Brij S10/Tween 80 and Brij S20/Tween 80. Calculated thermodynamic parameters and excess entropy values of investigated binary mixtures are presented in Tables 3–7. Higher excess entropy values of binary mixtures containing Tween 20, may be explained with the difference in the length of hydrophobic chains of monomers building the micelle. Presented results indicate that the saturation of alkyl chains and the voluminosity of surfactants' polar segments also influence the stability of their binary systems.

Brij surfactants are more hydrophobic components in investigated mixed micelles. It can be assumed that Brij monomers firstly form aggregates in which (during the process of mixed micelle formation) less hydrophobic Tween molecules get incorporated. Polar heads of Brij molecules are linear and they themselves are not covering the surface of the hydrophobic core efficiently. The result is its high hydration. The hydration of the hydrophobic core decreases as voluminous polar heads of Tween get introduced into the micelle. This provides the additional stabilization of the mixed micelle, *i.e.* a lesser extent of core's hydration is beneficial from both, the enthalpic and the entropic point of view.

4.2.1. Influence of the hydrophobic chain length

Analogous to the described model of pure micelles, on lower temperatures fiords that emerge between elongated monomers are predominately filled with segments of polar chains. However, on high enough temperatures, a certain number of alkyl chains assume folded conformation in order to fill in the fiords [38]. In Brij/Tween 20 mixed micelles, Tween 20 molecules which have shorter hydrocarbon chains are much more likely to take on Brij's part in performing this function. The difference in length of hydrophobic tails determines if the shorter tails will also have to assume folded conformations or not [38]. If the difference is not significant, shorter alkyl chains should take folded conformations in order to fill the gaps adequately. Since the difference of 6 methylene units most probably allows the prevalence of elongated conformation of Tween 20 molecules [38], an alternative model of mixed micelles emerges.

This alternative model of Brij S10/Tween 20 and Brij S20/Tween 20 mixed micelles presumes that both, Tween's and Brij's alkyl chains have elongated conformation and are radially arranged. Protruding terminal parts of Brij's alkyl tails will most likely assume globular conformation in the very centre of the hydrophobic core. This arrangement allows more solid and uniform structure of the micelle's interior (Fig. 6) [38,44]. The region of higher

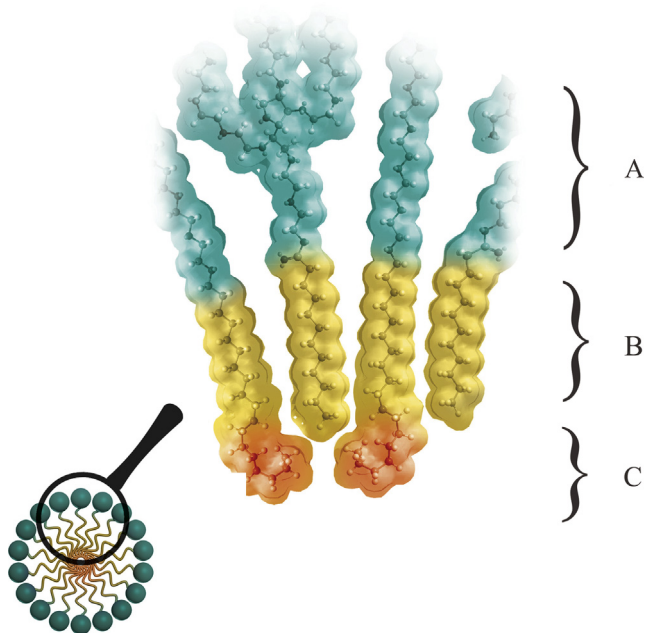


Fig. 6. The schematic diagram of a Brij S10 – Tween 20 mixed micelle. A: Micelle's surface is built of polyoxyethylene chains that are interacting with each other and with water molecules. B: The outer region of mixed micelle's core is made of radially arranged elongated alkyl chains of monomers. This region is characterized with low entropy values. C: In the central region of mixed micelle's core, globular forms appear. This region is characterized with high disorder.

disorder that is formed in the micelle's center contributes to the entropy of the system ($S^E > 0$). Calculated results presented in Table 7 confirm the hypothesis that the formation of mixed micelle containing Tween 20 is followed by positive change in entropy of the system.

In Brij S10/Tween 80 and Brij S20/Tween 80 mixed micelles all participants have hydrophobic tails of the same length. The insertion of voluminous polar heads of Tween 80 may lead to more efficient covering of the hydrophobic area. However, filling the fiords on the surface of the hydrophobic core with folded alkyl chains is still required on high temperatures.

With respect to the second model of mixed micelles presented in this research, in mixed micelles containing Tween 80, the central area of the micelle's core (characterized with high conformational freedom) is left out (Fig. 7) [38,44]. As a result of this, entropy of Brij S10/Tween 80 and Brij S20/Tween 80 systems has lower values than the entropy of systems containing Tween 20 (Table 7).

4.2.2. Influence of the hydrophobic chain saturation

Results obtained for Brij S20/Tween 80 systems show that the interaction parameter rises in the temperature range from 283.15 K to 313.15 K ($\alpha = 0.2, \alpha = 0.6$) and in range from 273.15 K to 313.15 K ($\alpha = 0.4, \alpha = 0.8$) (Fig. 7). The situation is similar in Brij S10/Tween 80 binary systems where an initial increase in β parameter (and G^E) can be observed in the temperature range from 273.15 K to 293.15 K ($\alpha = 0.2, \alpha = 0.4, \alpha = 0.6$) and in range from 273.15 K to 283.15 K ($\alpha = 0.8$). A positive change in β interaction parameter that follows the temperature rise in mixed micelles containing Tween 80 can be explained by Tween 80's less favourable enthalpic and entropic influence on the excess Gibbs energy. The olefin bond present in Tween 80's hydrophobic tail is responsible for its rigidity. Therefore, the stabilization expected with the temperature rise, by means of higher conformational freedom of alkyl chains, is restricted. Gaps on the surface of the micelle's hydrophobic core are less likely to be filled with Tween 80's folded alkyl chains themselves, leaving them to be filled with polar segments, hydrated by water molecules (negative enthalpic and entropic effects) or padded with Brij's alkyl chains (Fig. 8) [8,44].

4.2.3. Influence of the polar chain length

Polar chains in single-component micelles are mostly surrounded by other polar chains. They are interacting with each other via dipol-dipol interactions and by forming numerous hydrogen bonds. Polar chains of Brij molecules are longer than those of Tween molecules, hence in mixed micelles Brij's terminal

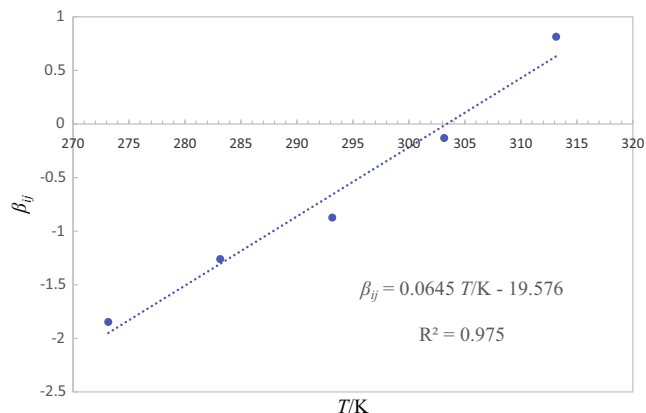


Fig. 7. Changes of the values of the interaction parameter β_{ij} as a function of temperature (example Brij S20 – Tween 80 ($\alpha = 0.8$)). The dependence $\beta_{ij} = f(T)$ in temperature range from 273.15 K to 313.15 K is fitted with the linear function.

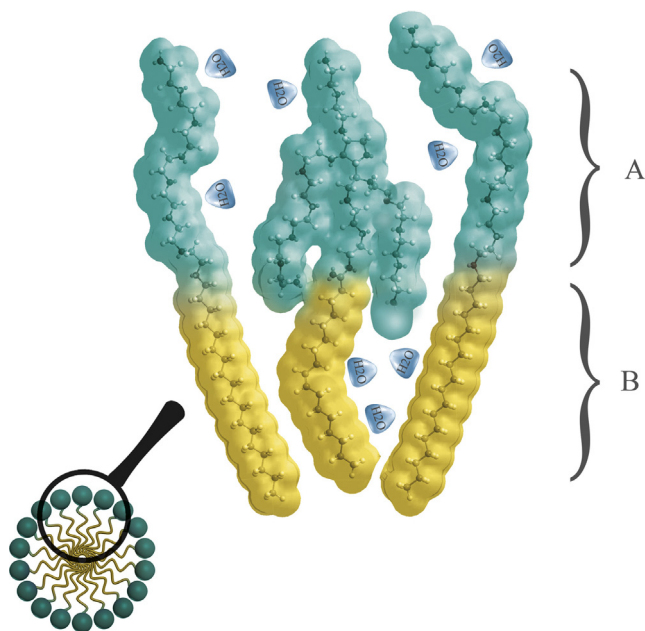


Fig. 8. The schematic diagram of a Brij S10 – Tween 80 mixed micelle. All alkyl chains have the same length. 9-cis olefin bond in Tween 80 molecules is responsible for its rigid structure. The result is higher hydration of the micelle's core.

segments become emerged into the bulk solution forming hydrogen bonds with water [35]. This loss of freedom of movement of water molecules is observable as an entropy decrease.

Since Brij S20 has a longer polyoxyethylene chain than Brij S10, hydrogen bonds are more numerous in its micelles. Formation of Brij S20/Tween binary mixed micelles is followed with a greater

decrease in freedom of water molecules (Fig. 9). Therefore, the altogether entropy of these binary mixtures is lower than the entropy of mixtures containing Brij S10. This conclusion is in compliance with obtained results, i.e. calculated S^E values for Brij S20/Tween systems are lower than S^E values for Brij S10/Tween systems (Table 7). The effect is most noticeable in Brij S20/Tween 80 systems in which the stabilization in the micelle's hydrophobic core is left out (as well as its positive entropic contribution) and subsequently S^E has negative values.

5. Conclusions

Regular solution theory cannot be applied on investigated binary mixtures without certain corrections regarding the existence of the excess entropy. Changes in the values of the β interaction parameter for analysed binary systems can be described as a function of temperature. This is a conformation of both entropic and enthalpic nature of excess Gibbs energy of micellization. The difference in length of the hydrophobic chains in mixed micelles (present in Brij S10/Tween 20 and Brij S20/Tween 20 micelles) is responsible for their additional stabilization. In comparison to them, systems built of monomers with alkyl chains of the same length have lower excess entropy values. Since longer polyoxyethylene chains engage in more hydrogen bonds with solvent molecules, elongation of polar segments results in favourable enthalpic contribution that opposes an unfavourable entropic contribution. Olefin bond present in Tween 80 molecules is responsible for an increase in the area of hydrophobic surface of a micelle's core that needs to be hydrated. This effect reduces both enthalpic and entropic input in excess Gibbs energy.

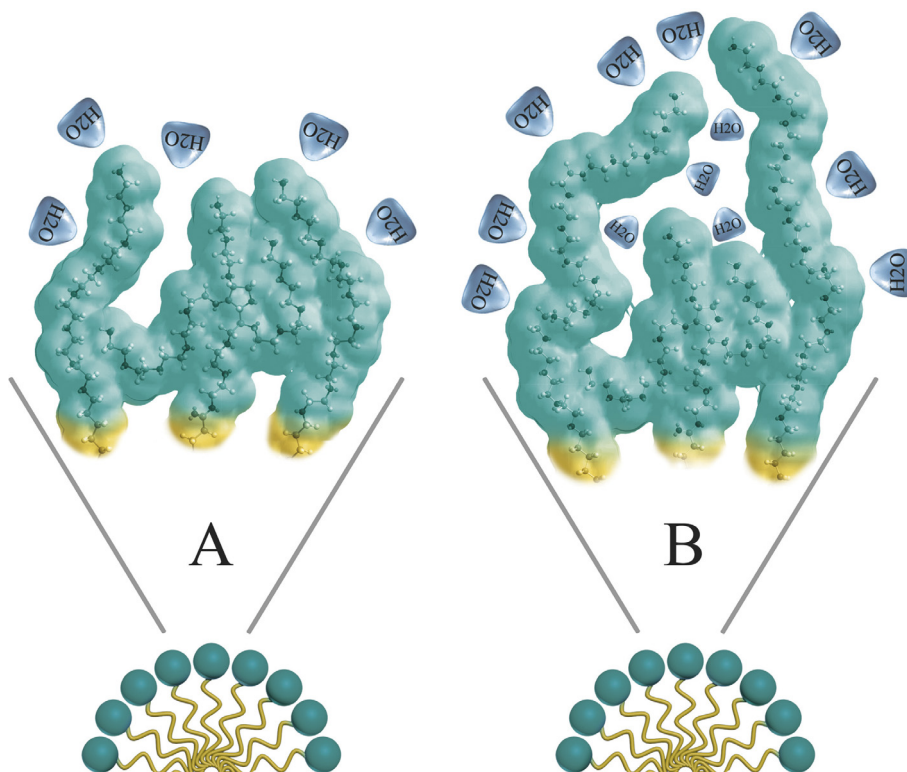


Fig. 9. A: The schematic diagram of a mixed micelle made of Brij S10 and Tween molecule. Terminal segments of polar chains engage in hydrogen bonds with water molecules. B: The schematic diagram of a mixed micelle made of Brij S20 and Tween molecule. Terminal segments of Brij S20 are protruding into the solution which results in more interactions with water molecules.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2017.01.020>.

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