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COLLOID-CHEMICAL PROPERTIES OF SURFACTANT TECHNICAL SPECIMENS USED IN COSMETICS INDUSTRY

The surface-active and colloid-chemical properties of surfactant technical specimens Genapol LRO, Texapon K12G, TWEEN 20, TWEEN 80 and Cremophor A25 have been studied using different methods of analysis. The surface activity, adsorption, micelle formation and solubilization quantitative characteristics have been determined; hydrophilic-lipophilic balance has been calculated. It has been shown that the usage of the investigated specimens in cosmetic compositions is related to with their surface-active and colloid-chemical properties determining their function in cosmetics (stabilizer, emulsifier, solubilizer and others).

Introduction. Nowadays the production and consumption of cosmetics in the Republic of Belarus is developing intensively due to a desire to be beautiful and healthy. The increase in the production and consumption is also connected with the growth of income per head. Cosmetics are different dispersed systems the main components of which are surface-active substances (surfactants, SAS). They determine such application properties of cosmetics as washing and foaming ability, consistency, stability upon storage, etc. [1]. Surfactants are used in cosmetics industry as technical specimens which are in themselves mixtures of individual substances. The main part of these specimens are anionic and non-ionogenic surfactants.

The aim of the research was to study surface and colloid-chemical properties of surfactant technical specimens and their aqueous solutions to provide their scientifically based usage in developing compositions of different cosmetic products. Surface-active properties of individual surfactants as well as those of their aqueous solutions have been investigated [2]. The surfactant specimens used nowadays are not properly studied. They have specific properties related to the adsorption of dissimilar surfactant molecules and ions [3].

Materials and Methods. The following surfactant technical specimens were used during the research: Genapol LRO – a mixture of sodium dioxy-laurylsulphate and dioxy-myristilsulphate; Texapon

K12G – sodium laurylsulphate; TWEEN 20 – polyoxyethylene (20) sorbitanmonolaurate; TWEEN 80 – polyoxyethylene (20) sorbitanmonooleate; Cremophor A25 – a mixture of polyethylene glycol cetyl and stearyl ether (the average degree of oxyethylation – 25). The main surfactant specimen parameters are shown in Table 1.

Different methods were used to examine the properties of surfactant specimens and their aqueous solutions, such as: stalagmometric, refractometric, turbidimetric, viscosimetric, photocalorimetric and calorimetric.

Main part. The specimen surface properties were studied by using stalagmometric method [4]. The surface tension of the specimen aqueous solutions in the concentration zone 0.02–50.000 g/l (temperature $(20 \pm 1)^\circ\text{C}$) has been determined. Surface tension isotherms are shown in Fig. 1.

The following parameters have been calculated on the basis of the surface tension isotherms: specimen surface activity (g); limiting adsorption at the interface “specimen aqueous solution – air” (a_∞); one surfactant molecule area in the solution surface layer (S); Shishkovsky equation constants (A and B) [5].

Hydrophilic-lipophilic balance (HLB) values for all the investigated specimens have been calculated by the Davis method [6]. The results are shown in Table 2.

Table 1

Main surfactant specimen parameters

Parameter	Parameter values for surfactant specimens				
	Genapol LRO	Texapon K12G	TWEEN 20	TWEEN 80	Cremophor A25
Surfactant concentration, %	69.5	97.9	98.5	98.2	99.5
Appearance	viscous liquid with a pearl shade	porcelain colour granules	light-yellow viscous oily liquid	light-yellow viscous oily liquid	tiny white flakes
Surfactant molar mass, g/mole	384*	288	1,226*	1,308*	1,356*

* Averaged values

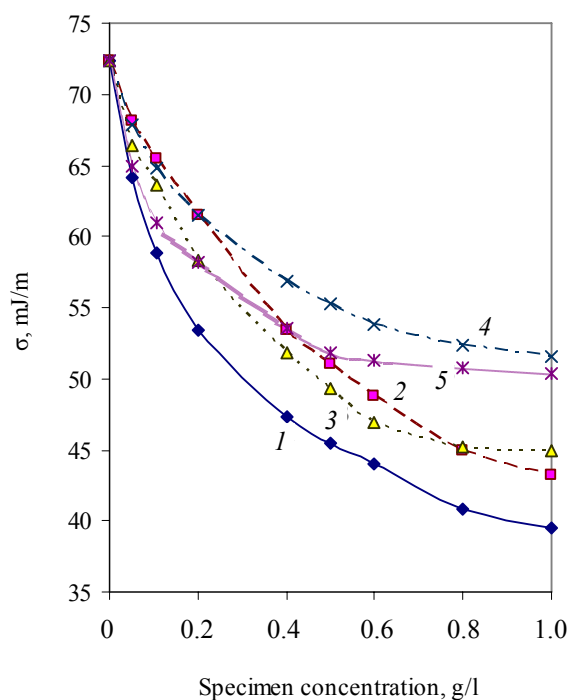


Fig. 1. Surface tension dependence on the surfactant specimen concentration in an aqueous solution: 1 – Genapol LRO; 2 – Texapon K12G; 3 – TWEEN 20; 4 – TWEEN 80; 5 – Cremophor A25

It has been determined that Cremophor A25 specimen has the highest activity at the interface “specimen aqueous solution – air”. The molecules of this surfactant specimen have a long hydrocarbon radical (C_{16-18}) and a considerable polar area (25 etoxygroups). Nevertheless, the influence of the lipophilic molecules prevails thus providing their more intensive expulsion from the polar medium. This is affirmed by the minimal numerical value of Shishkovsky equation constant B in comparison with all the other tested surfactants. In case of the surface layer saturation, the surface tension is still large ($\sigma = 50.2$ mJ/m). It depends on the molecule cross section area of the surface-active substance and complies with the minimal limiting adsorption. In this case due to the large number of etoxygroups and their surface layer orientation, the surfactant molecule area in the saturated surface

layer is maximum in comparison with all the other tested specimens.

Comparison of the surface-active properties of the TWEEN specimens detected their similarity. The molecules of these surfactants have the same polar area, but nonpolar molecule areas differ by the number of carbon atoms (C_{11} for TWEEN 20 and C_{17} for TWEEN 80). Besides, a nonpolar area of TWEEN 80 contains a double bond. According to Langmur’s conception concerning the structure of the surface layer at the interface “solution – gas”, in case of the limiting adsorption nonpolar hydrocarbon radicals are practically vertically transformed into the air phase. That is why the obtained numerical values of a_{∞} and S_0 are similar.

The surface activity of the oxyethylated Genapol LRO specimen is 2.5 times higher than that of the nonoxyethylated Texapon K12G specimen. It means that the surface properties are mainly influenced by the nonpolar surfactant molecules in the composition of Genapol LRO specimen.

Nonpolar surfactant molecules in the composition of Texapon K12G specimen are two $-CH_2-$ groups longer than those in the composition of Genapol LRO specimen. The degree of oxyethylation of the surfactant molecules (equal to 2) practically doesn’t affect the surface activity.

Micelle-forming ability of the surfactants contained in the composition of the tested specimens was determined by the micelle formation critical concentration (MCC) in aqueous solutions and by the micelle formation heat [8]. Table 3 shows the MCC of the technical specimens determined by different methods.

It has been determined that TWEEN 20 has the highest potential to micelle formation while Genapol LRO – the lowest.

It should be noted that MCC values determined by different methods are different. Lower values were obtained by using viscosimetric method. This is probably due to the fact that aggregates consisting of two, three and more surfactant molecules (not micelles yet) move slower during the process than single molecules thus resulting in the increase of viscosity.

Table 2

Surface characteristics of surfactant specimens

Specimen and HLB value	Parameter values					
	A , l/mole	$B \cdot 10^3$, J/m	g , J m/mole	σ , mJ/m	$a_{\infty} \cdot 10^6$, mole/m	S_0 , (\AA) ²
Genapol LRO (HLB = 13.8)	7,540	11.67	0.088	30.5	4.8	35
Texapon K12G (HLB = 40.0)	2,413	13.26	0.032	32.1	5.4	31
TWEEN 20 (HLB = 16.7)	1,608	9.70	0.156	39.7	4.0	42
TWEEN 80 (HLB = 15.0)	1,524	9.25	0.141	45.2	3.8	44
Cremophor A25 (HLB = 9.1)	3,594	6.90	0.248	50.2	2.8	59

The highest MCC value for all surfactant specimens was obtained by refractometric method. The specific feature of this method is in the little change of the refraction coefficient during micelle formation. The micelle size is much smaller than the wavelength of light and when light comes through the solution the refraction index averages, for this reason micelles manifest themselves better if their concentration in the investigated system is higher.

The heat effect of micelle formation was calculated proceeding from the calorimetric measurements of the dilution heat of surfactant specimen colloid solutions. Heat measurement was carried out on the laboratory calorimetric installation [8].

The process of micelle formation is endothermic. The calculated values of the micelle formation heat amount approximately to 10 kJ/mole. The heat effect is rather small, but the obtained result coordinates well with the published data for the non-ionic surfactants which are similar by their nature to the investigated specimens [9]. Small values of the heat effects during micelle formation [9] are due to the fact that water molecules form ordered structures (polymolecular complexes) around hydrocarbon chains of nonionic surfactants. For this reason the micelle formation process is preceded by the process of destruction of these complexes.

Cosmetic products often contain dyes which impart them attractive appearance. Not all of them are water-soluble but they are able to solubilization in micellar systems. It is known [7] that surfactants the HLB value of which is in the interval 15–18 have a solubilizing effect. For this reason the solubilization of the dye cerasine red (4-(2-hydroxy-naphthyl-1-azo)-azobenzene) in the aqueous solutions of the TWEEN 20 and TWEEN 80 specimens has been studied.

The concentration of the investigated aqueous surfactant solutions was in the interval 0.005–25.000 g/l under the temperature $(20 \pm 1)^\circ\text{C}$. The dye batch with a constant mass (5.0–10.0 g) was added into each solution. To provide contact between solubilizer particles and the surfactant specimen micelles the systems were shaken from time to time in a mechanical shaker. To study the dye solubilization process the photocalorimetric method was used [7].

Fig. 2 shows optical density dependences of the systems “water – dye – surfactant” on the surfactant content and the time of shaking.

The obtained data indicate that the state of the chemical equilibrium (equilibrium between the dye content in the true solution, in the micelles and in the solid phase wherein the optical density is nearly constant) in the studied systems is reached within 12 h at concentrations in the interval 0.005–5.000 g/l and within 16 h at concentrations 5.000–25.000 g/l (for both specimens of the TWEEN specimen).

To estimate quantitatively the solubilizing action of the surfactant specimens towards the dye cerasine red a calibration diagram has been graphed. The diagram demonstrated optical density dependence of the true solutions in benzene on their concentration. The diagram helped to determine solubilizing ability which indicated the mass of the dye dissolved in the unit volume of a system.

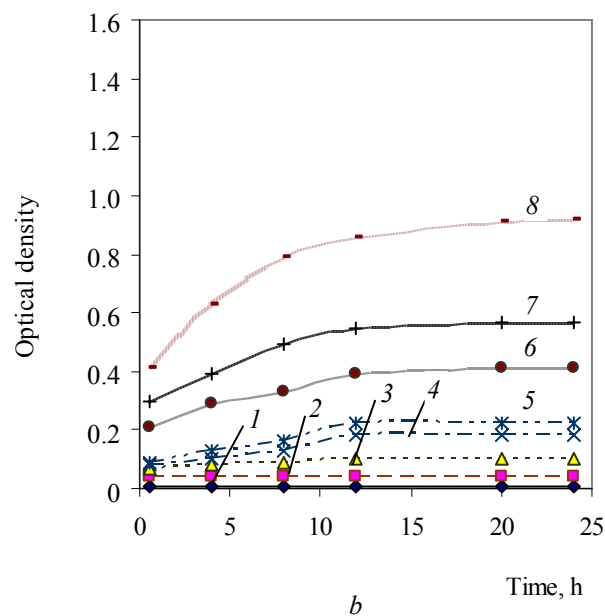
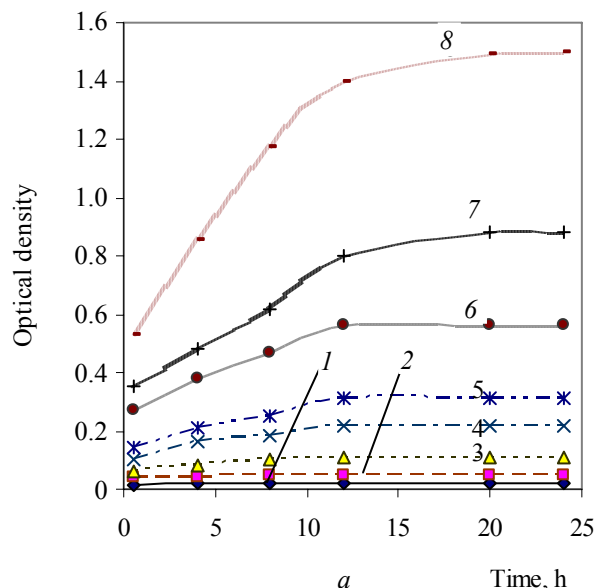


Fig. 2. Optical density dependences of the systems “water – dye – surfactant specimen” on the surfactant content and the time of shaking.

Surfactant specimens:

a – TWEEN 80; *b* – TWEEN 20

Surfactant content, g/l: 1 – 0.005; 2 – 0.01; 3 – 0.1; 4 – 0.5; 5 – 1.0; 6 – 5.0; 7 – 10.0; 8 – 25.0

Table 3

Surfactant specimens MCC value

Method of determination	MCC value for surfactant specimens, mole/l				
	Genapol LRO	Texapon K12G	TWEEN 20	TWEEN 80	Cremophor A25
Refractometric	$2.10 \cdot 10^{-2}$	$1.7 \cdot 10^{-2}$	$1.41 \cdot 10^{-3}$	$2.00 \cdot 10^{-3}$	$2.2 \cdot 10^{-3}$
Turbidimetric	$2.04 \cdot 10^{-2}$	$1.6 \cdot 10^{-2}$	$1.18 \cdot 10^{-3}$	$1.79 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$
Viscosimetric	$1.48 \cdot 10^{-2}$	$1.3 \cdot 10^{-2}$	–	–	$2.0 \cdot 10^{-3}$
Conductometric	$1.95 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	–	–	–
Stalagmometric	$1.90 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	$1.02 \cdot 10^{-3}$	$1.55 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$

Solubilizing ability dependences on the concentrations of the surfactant specimen aqueous solutions (In c , g/l) are shown in the hystogram (Fig. 3).

It has been determined that in true solutions of the surfactant specimens the dye dissolves but little, while in water it doesn't dissolve at all. In solutions the concentrations of which are higher than the MCC, the dye solubility increases steeply which is due to the solubilization process. The solubilizing ability of the TWEEN 80 specimen is higher (approximately 1.5–1.7 times depending on the concentrations) than that of the TWEEN 20 specimen. The obtained data can be explained.

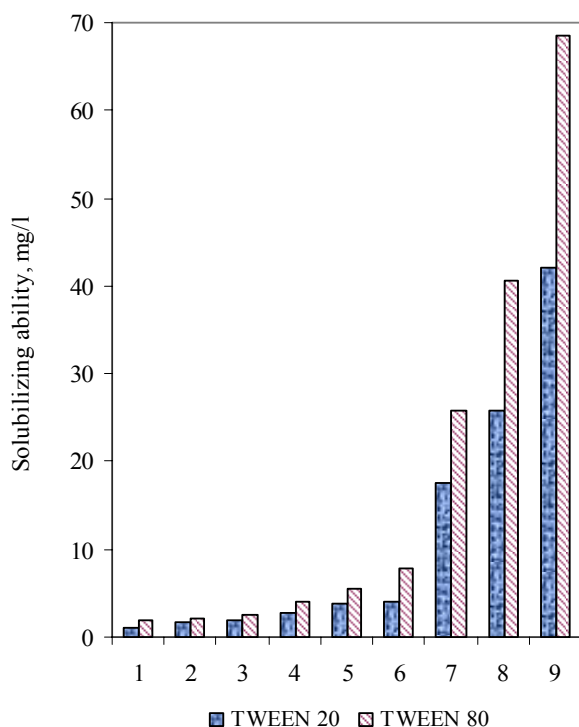


Fig. 3. Surfactants solubilizing ability depending on their concentration

It is a well known fact that the solubilization process depends on many factors, the size and the number of micelles are among them. The mean micelle diameters in colloid solutions of (the TWEEN specimen) with concentrations 5.0–

25.0 g/l have been determined using the turbidimetric method (Rayleigh method). It has been ascertained that the size of the micelles formed by polyoxyethylene(20) sorbitan monolaurate molecules is 2.5–6.8 nm, while that of the micelles consisting of polyoxyethylene(20) sorbitan monooleate molecules is 3.4–7.5 nm. This is quite logical since the latter has a larger chain length of the nonpolar hydrocarbon radical.

According to the micelle formation theory [9], the micelle form depends on the surfactant solution concentration. The micelle forms are spherical in case their concentrations are close to MCC. And they have more complex structure when their concentrations are tens or hundreds of times higher than those of MCC. So, in the above mentioned structures the micelle form of surfactants is close to the spherical one. The micelles of the TWEEN 80 specimen have a large size (if the solution concentration is the same). This factor explains high solubilizing ability of this specimen, i.e. the ability to retain nonpolar dye molecules within micelle hydrocarbon nuclei.

The obtained data are used to estimate foam-forming and emulsifying abilities of the investigated surfactant technical specimens [10, 11].

Conclusion. The surface-active and colloid-chemical properties of the surfactant technical specimens and their aqueous solutions have been studied. This helped to determine the criteria for the evaluation of their functional operation in cosmetic compositions.

It has been ascertained that the specimen Cremophor A25 is more preferable in the emulsion systems (creams, beauty milk, etc.) because it provides oil phase emulsification being at the same time a good stabilizer at the interface of two liquids. This is due to its high surface activity and low HLB.

The specimens Genapol LRO and Texapon K12G are more advanced as foam boosters and are good foam stabilizers. The surface-active properties of the surfactants which are in the composition of the above mentioned specimens exhibit themselves at the interface “specimen aqueous solution – air”, that is why it is reasonable to use them in the hygienic detergent composition.

The specimens TWEEN 20 and TWEEN 80 exhibit high solubilizing ability towards water-insoluble dye cerasine red and can be used in the composition of coloured cosmetics.

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