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AQUEOUS SOLUTION PROPERTIES OF ZETESOL SURFACTANT PREPARATIONS

Surface-active, optical and electrical properties of surfactant specimens ZETESOL ZN and ZETESOL MG water solution were investigated using various analysis methods (stalagmometry, turbidimetry, refractometry, conductometry). The quantitative characteristics of adsorption process such as the Langmuir's maximum adsorption, the constants of Shishkovsky's equation were calculated. It was determined that the specimens investigated have great surface activity on the frontier between surfactant specimens water solutions and air. The results of obtained by turbidimetric method show that the specimens are colloidal systems and their critical concentration of micelle formation are coequal. The admixture (laureth-3, phenoxyethanol, sulfates of metals) have the positive influence on the effect of aggregation in colloidal solutions of surfactant specimens. The specimen ZETESOL MG has greater effect on micelle formation than the specimen ZETESOL ZN because of larger quantitive constant in its composition. The characteristic curves "electro-conductivity – concentration of water solution of surfactant specimens" were carried out by conductometric method. The electrical properties of anionic specimens depend on the ionic qualitative composition of systems. It was established that electro-conductivity of ZETESOL MG water solutions is higher than that of ZETESOL ZN water solutions due to higher electrolyte ($MgSO_4$) concentration.

The investigations showed that the specimens ZETESOL group could be used in composition of hygienic detergents as foam-producing agents and stabilizers of foams.

Key words: anionic ethoxylated surfactant, surface activity, adsorption, micelle formation, refraction index, optical dense, conductivity.

Introduction. Surfactants play a major role in foaming, dispersion and decontamination processes, therefore they are widely used in hygienic detergent compositions. Anionic surfactants have superior foaming and washing power and are basic in detergents, but they have a strong irritating and defatting effect on skin. To reduce the negative effect of the anionic surfactants they are subjected to ethoxylation. This resulted in a large number of sulfaethoxylate based surfactant preparations (e.g. metal laureth sulfate), the properties of which are not well examined.

To understand and substantiate scientifically the functional action of surfactants it is important to know the basic relationship between the structure of a substance and the properties of its solutions, to realize the changes of these properties in the complex multi-component mixtures, e.g. modern detergents of personal hygiene [1]. That is why this research is of great importance.

The aim of the research was to study surfactant, optical and electrical properties of aqueous solutions of the surfactant preparations ZETESOL ZN and ZETESOL MG (made in Italy), the surfactant components being zinc or magnesium laureth sulfate with an average degree of ethoxylation equal to three. These surfactant preparations are used in the production of hygienic foaming detergents, but their properties require a detailed study to make a proper choice in the formulation of cosmetic products.

The surfactant preparations under investigation were viscous jelly-like systems; their composition is shown in Table 1.

Table 1

Surfactant preparations composition

Ingredient name	Ingredient content, %	
	ZETESOL ZN	ZETESOL MG
Metal laureth sulfate	25.00	50.00
Laureth-3	1.00	5.00
Metal sulfate	0.30	2.00
Phenoxyethanol	–	0.15
Water	73.70	42.85

The surfactant properties of preparation aqueous solutions were studied by stalagmometric methods, optical properties – by refractometric (light refraction) and turbidimetric (light scattering) methods and electrical properties – by conductimetric methods of analysis [2, 3]. Aqueous solutions of surfactant preparations were made using distilled water. Measurements were carried out at a temperature (22 ± 1)°C.

Main part. One of the most effective evaluations of the functional action of surfactants (including as part of hygienic detergents) is the use of criteria, which are the parameters and constants of the fundamental equations characterizing properties of surfactants at the interface "surfactant aqueous solution – air".

Fig. 1 shows surface tension isotherms of aqueous solutions of ZETESOL preparations in the concentration region $1.2 \cdot 10^{-5}$–$24.4 \cdot 10^{-5}$ mol/l.

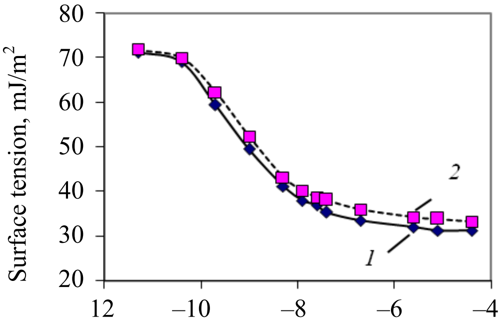

Fig. 1. Surface tension isotherms of aqueous solutions of ZETASOL ZN (*1*) and ZETASOL MG (*2*) preparations

Analysis of isotherms showed that for both of the preparations being studied there are three areas on the graph which differ in the nature of the concentration dependence of the surface tension. At concentrations up to $3.1 \cdot 10^{-5}$ mol/l surface tension is almost constant and equals to the surface tension at the interface "water – air". Consequently, in this area surfactant preparations act as surface-inactive substances, since the amount of surface-active anions in the surface layer of the liquid is negligible.

Increasing concentrations from $3.1 \cdot 10^{-5}$ to $1.2 \cdot 10^{-3}$ mol/l leads to a decrease in surface tension almost twice (from 69.98 to 36.10 mJ/m^2 in solutions of ZETESOL MG preparations and from 71.13 to 36.65 mJ/m^2 in solutions of ZETESOL ZN preparations). This testifies to the intense concentration of surfactant anions in the surface layer of the solution, therefore surfactant preparations exhibit significant surface activity. In the area of concentration $3.7 \cdot 10^{-3}$ up to $24.4 \cdot 10^{-3}$ mol/l system surface tension is practically constant, which indicates the formation of a saturated layer on the surface of the solution. It should also be noted that if concentrations of preparation solutions are similar, the surface tension is slightly lower when using the ZETESOL ZN preparation (an average of 0.5–1.5 mJ/m^2).

With the use of surface tension isotherms the main surface-active characteristics of the preparations have been calculated: surface activity (g), Shishkovsky equation constants (A and B), Langmuir limiting adsorption (a_∞) and the area occupied by the surfactant anion in the saturated surface layer of solution (S_0) [2]. The results are shown in Table 2.

Table 2 shows that the surface-active properties of the two preparations are similar. This is natural, since they are determined by the properties of the surface-active anion, which is the same for both preparations. Some of the differences are due to impurities present in the preparations, the impurities having little effect on the adsorption processes. As both preparations have a high surface activity, they can exhibit significant foaming properties.

Table 2

Surface-active characteristics of surfactant preparations

Characteristics	ZETESOL ZN	ZETESOL MG
g, J · l/mol · m^2	$3.35 \cdot 10^2$	$3.29 \cdot 10^2$
a_∞, mol/m^2	$5.40 \cdot 10^{-6}$	$5.26 \cdot 10^{-6}$
S_0, Å^2	30.7	31.6
B, J/m^2	$5.01 \cdot 10^{-3}$	$4.87 \cdot 10^{-3}$
A, l/mol	6686.6	6755.6

Refractive indexes were measured for the study of light refraction in aqueous solutions of ZETESOL preparations. The studies were made on the refractometer IRF 454B2M, the results are shown in Fig. 2.

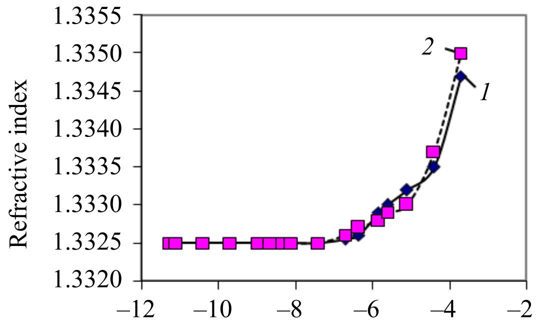

Fig. 2. The refractive index dependence on the concentration of surfactant preparations ZETESOL ZN (*1*) and ZETESOL MG (*2*)

It is obvious that in the region of low concentrations (for ZETESOL MG up to $6.1 \cdot 10^{-4}$ mol/l, for ZETESOL ZN up to $1.2 \cdot 10^{-3}$ mol/l) the refractive index is independent of the surfactant content in solution and equals to the refractive index of water at a temperature of 22°C. Since in the surfactant solutions with indicated concentrations the refraction does not change, they are considered to be true solutions. The refractive index in such solutions is determined by the molecular surfactant refraction, which is the sum of the atomic and bonds increments refractions.

Further increase in surfactant concentration results in the increase of the refractive index. This is due to the fact that the micelles are formed in the systems, and therefore in the total refractive system the refraction of surfactant ion bonds in the micelle is considered [3]. Thus, light refractive indexes in colloidal solutions of surfactant preparations ZETESOL MG and ZETESOL ZN are comparable at the same concentration.

The scattering of light in aqueous solutions of preparations based on ethoxylated zinc and magnesium laureth sulfates has been studied. Measurements of systems turbidity were performed on photoelectrocolorimeter CPK-3-01 “30M3” (cuvette width 3 cm, wave length 340 nm). The results obtained are shown in Fig. 3.

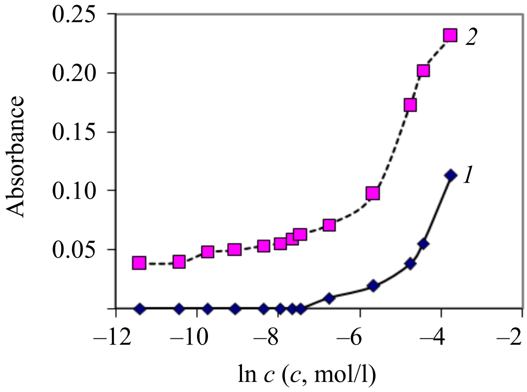

Fig. 3. Aqueous solutions absorbance of ZETESOL ZN (*1*) and ZETESOL MG (*2*) preparations

Turbidimetric analysis showed that the true solutions of ZETESOL ZN preparations do not scatter light (the absorbance is zero), while the absorbance of the true solutions of ZETESOL MG preparations is in the range of 0.038–0.050. This can be explained by the fact that the magnesium laureth sulfate preparation contains more ethoxylated alcohol (laureth-3) than ZETESOL ZN. Probably due to the limited solubility in water and different content, laureth-3 may be present in the system both in the molecular form and in the form of particles, that participate in the process of light scattering.

The increase in absorbance of the colloidal solutions of preparations is due to the growing number of micelles, increase of their volume and shape change. Thus, it is evident that in solutions of ZETESOL MG preparations the micelle formation proceeds more rapidly than in solutions of ZETESOL ZN preparations, despite the fact that the micelles are formed from the same laureth sulfate anion $CH_3–(CH_2)_{11}–O–(CH_2CH_2O)_3–SO_3^-$. Nevertheless the absorbance value is higher in ZETESOL MG systems if the surfactant content in solutions of two preparations is the same. In our opinion, this is due to a higher amount of ethoxylated alcohol (laureth-3): alcohol molecules adsorbed on the micelles surface, reduce the electrostatic repulsion forces between the negatively charged micelles (electrostatic stabilization factor) that promotes aggregating process [4]. Phenoxyethanol present in ZETESOL MG preparation in an amount 0.15% behaves similarly. The micelle formation process was also influenced by the presence of electrolytes. It is known [5] that electrolytes reduce the hydration of the surfactant ions and thereby increase their tendency to association.

Comparison of experimental data of stalagmometric, turbidimetric and refractometric analyses allowed to quantify the critical micelle formation concentration (CMC) in aqueous solutions of surfactant preparations; they were practically similar and amounted to $1.22 \cdot 10^{-3}$ mol/l for ZETESOL MG and $1.16 \cdot 10^{-3}$ mol/l for ZETESOL ZN.

An important characteristic of ionic surfactants is electric conductivity of their solutions. Aqueous solutions resistivity of preparations with concentrations 0.005–20.000 g/l was measured on the Conductometer EC 215 (Germany) at 22°C, pH control of solutions was performed using a pH-meter-millivoltmeter HI-8314. The experimental data obtained are presented in Fig. 4 and 5.

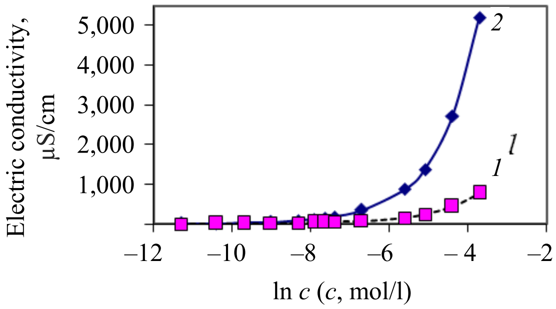

Fig. 4. Electric conductivity dependence of aqueous solutions on the concentrations of surfactant preparations ZETESOL ZN (*1*) and ZETESOL MG (*2*)

Fig. 4 shows that the increase of concentration in true surfactant solutions results in the negligible increase of electric conductivity (the range being 13–122 μS/m) if ZETESOL MG preparations are used. The range of electric conductivity for ZETESOL ZN preparations is 4–18 μS/m. The electrical properties of these systems are determined by the number and electrophoretic mobility of ions $CH_3–(CH_2)_{11}–O–(CH_2CH_2O)_3–SO_3^-$, Zn^{+2}, Mg^{+2} and SO_4^{-2}.

Due to the fact that according to reference data, the equivalent conductivity of magnesium and zinc cations are close in their limit values, differences in the electric conductivity of the two preparations with the same surfactant concentrations are associated, in our opinion, with the presence of different amounts of electrolytes – magnesium and zinc sulphates (Table 1).

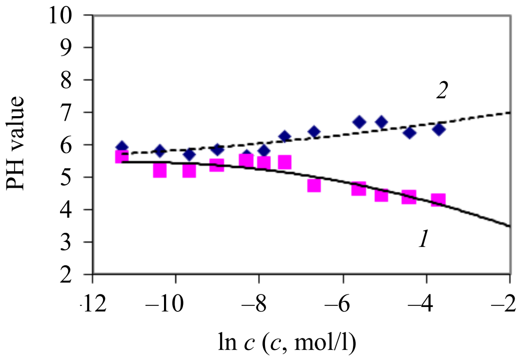

Fig. 5. pH aqueous solutions dependence of ZETESOL ZN (*1*) and ZETESOL MG (*2*) preparations on the surfactant concentration

In the range of surfactant concentrations corresponding to true solutions, the studied PH systems are close in their numerical values (Fig. 5).

The CMC having been reached, the electric conductivity of both surfactant solutions increases sharply. This is due to the appearance of micelles, the increase of their dimensions, and hence the charge determining their mobility in an electric field.

In colloidal solutions the preparation ZETESOL MG behaves as a stronger electrolyte in comparison with the preparation ZETESOL ZN. Regular pH changes in the micelle solutions of preparations show the difference in the ionic composition of the systems under investigation.

Conclusion. Thus, the study of the aqueous solutions properties of ZETESOL preparations showed: surface-active properties of surfactant preparations are similar, since they are determined mainly by the nature of the surfactant anion; the scattering of light is more intense in colloidal solutions of the preparation ZETESOL MG, due to the quantitative predominance of the impurities; the electric conductivity of colloidal solutions of ZETESOL MG preparation is 5 times higher than the electric conductivity of ZETESOL ZN solutions, that is directly dependent on the amount of metal sulfate in the surfactant preparation.

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