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SOLUBILIZING CAPACITY OF ETYLTRIMETHYLAMMONIUM BROMIDE IN RELATION TO ETHYL OLEATE IN THE AQUEOUS DISPERSION MEDIUM

SUMMARY. The paper studies the surface properties of the two- and three-component colloid systems based on cationic surface-active agents (surfactants) of cetyltrimethylammonium bromide (STAB), and ester of unsaturated fatty acid ethyl oleate (EO) in the aqueous dispersion medium and the solubilizing capacity of the STAB micelles in relation to EO. The methods applied include the refractometric method and the method of maximum bubble pressure (Rebinder's method). The critical micelle concentrations (CCM) of STAB in the three-component colloid system are determined. The increase in the CCM value is registered in the STAB dispersion with ethyl oleate. The synergistic effect of ethyl oleate within STAB in the concentration corresponding to CCM is registered. It is stated that the size of micelles in the three-component colloid system containing EO – CTAB-H_2O is 3.5 and 10 times as much as the size of STAB micelles; that is likely to be due to structuring the three-component colloid systems and solubilizing EO with STAB micelles. The micelle formation in the three-component colloid system is registered in the molar ratio of 4 ethyl oleate to 1 STAB. The high solubilizing capacity of the cationic STAB surfactant in relation to EO is determined, which provides the opportunity to use the water-lipid emulsion stabilized colloidal system as a substrate for peroxidation.

KEY WORDS. Cetyltrimethylammonium bromide, solubilization, peroxidation.

Introduction. The solubilizing capacity is one of the most typical properties of micelle-forming surfactant solutions opening new prospects for their use, that is discussed in a number of works [1-6]. They are used as a medium for chemical reactions, purification of effluents and surface waters from oil and petrochemicals, and the cloud point extraction. It is stated that the water-lipid kinetic model for anti-oxidant testing is effective, and the lipid oxidation rate is 100-1,000 times as much as it is in the benzene chloride solution. [7-8]. The results obtained can be explained by forming ultramicroheterogenous systems with an effective phase interface, which provides a successful contact of the agents, having different solubility in the organic and aqueous phases.

The purpose of the this paper is to study the properties of two- and three-component colloidal systems and the solubilizing capacity of cationic surfactants by cetyltrimethylammonium bromide (STAB) in relation to ethyl oleate (EO).

The experiment. The investigation has been carried out with the application of physicochemical methods and mathematical processing of the experimental data.

Ethyl oleate was prepared by esterification from pure oleic acid, GOST 104-75 (Russian National Standard), applying the known technique [9]: it underwent vacuum distillation, the fraction with the boiling point of 160-164°C at 1 mm of mercury was collected. Cetyltrimethylammonium bromide (STAB) was twice re-precipitated from the ethanol solution by ethyl ether. Absolute ethyl alcohol was prepared by the technique described in [9]. The solutions and water-lipid colloidal systems were prepared using double-distilled water.

The target of our research included two- and three-component colloidal systems of the following compositions: STAB - H_2O, EO - STAB - H_2O.

The critical concentration for the micelle formation (CCM) in the systems under investigation, adsorption, surface reactivity, and a micelle size were determined by the maximum bubble pressure method using the Rebinder apparatus. The ethyl oleate solubilization in the STAB solution was determined by the refractometric method using the IRF-454 B2M apparatus thermostatically-controlled at 23±0.2°C. The volume of solubilized EO at saturation was plotted by the technique described by S.S. Vojutsky in [10-11]. The volume of solubilized EO at any degree of saturation was calculated; the micelle solubilization capacity (MSC) of cetyltrimethylammonium bromide in relation to ethyl oleate was evaluated by the additivity rule for the specific refraction.

The method of substrate saturation has no effect on the accuracy of the refractometric determination of solubilized hydrocarbon [6]; thus, in this work the agitation was carried out by slow circular motions during 30-40 minutes, and when the equilibrium was attained, the refraction index of the aqueous phase was determined.

The value of the hydrophilic-lipophilic balance (HLB) for the STAB molecules was determined by the Davies method [12].

Results and discussion. The value of the surface tension allows estimating the critical concentration for the micelle formation, since it is known [13] that the micelle-forming surfactants show their high solubilization capacity in the concentration corresponding to CCM.

To achieve this, the surface tension and the surface activity of the cetyltrimethylammonium bromide solution with the concentration in the range from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-2}$ mol / L were determined by the above-described technique. The typical isotherm curves of the surface tension are presented in Fig. 1.

It has been stated that in the STAB – H_2O two-component colloidal system, CCM corresponds to the surfactant concentration equal to $(1.0 \pm 0.1) \cdot 10^{-3}$ mol / L, which corresponds to the data published. Further in our investigation, the STAB solution with the final concentration $1 \cdot 10^{-3}$ mol / L in the sample corresponding to CCM was used.

Then, the value of the hydrophilic-lipophilic balance (HLB) for cetyltrimethylammonium bromide molecules was determined by the Davies method and it is equal to 16.4. The high value of HLB for STAB molecules and their full dissolving in the aquatic dispersive medium, forming clear solutions, indicate strong emulsifying and solubilizing properties of this surfactant.

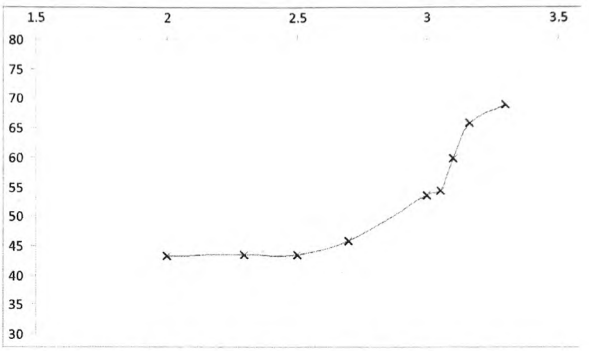

Fig.1 The surface tension isotherm for the aqueous solutions with the concentration in the range: $1 - 5 \cdot 10^{-4} - 4 \cdot 10^{-3}$ mol / L, STAB

M.V. Poteshnova et al. [6] specify that STAB displays a high solubilization capacity in relation to toluene, and its solubilization capacity (MSC) is 1.38 mol / mol of the surfactant. Thus, the role of solubilization in the EO dispersion formation in the micelle STAB solution is of interest. For this purpose, the refractometric method was used to study the refraction index for the STAB solution with the final concentration $1 \cdot 10^{-3}$ mol / L in the sample, the absolute EO, and the three-component colloidal system of the following composition:

EO ($7 \cdot 10^{-4}$ — $3.6 \cdot 10^{-1}$ mol / L) — STAB ($1 \cdot 10^{-3}$ mol / L) — H_2O.

The typical dependence of the refraction index on the EO volume is presented in Fig.2.

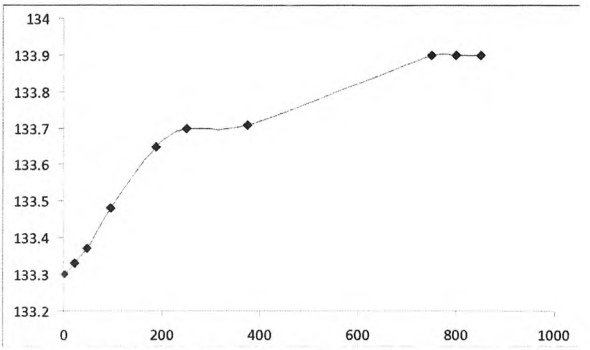

Fig. 2. Dependence of the STAB solution refraction index with the final concentration of $1 \cdot 10^{-3}$ mol / L in a sample on the EO concentration

The dependence is complex, with two explicit plateaus, which indicate the saturation phase reached. The volumes of EO solubilized by STAB micelles were calculated by the above-described technique, they were 63.1 and 331 mcL, respectively;

and the values of STAB micelle solubilization capacity were 3.6 and 18.5 mole / mole of surfactant.

The results obtained demonstrate that with the increase in the EO concentration the efficiency of EO molecule incorporation into STAB micelle improves gradually from 4:1 to 19:1 of EO molecule per STAB molecule, i.e. the micelle cross-linking is observed, and their size is likely to increase.

Further, to determine the micelle size in the three-component colloidal system of EO ($2•10^{-3}$ — $9•10^{-3}$ mol/L) — STAB ($1•10^{-3}$ mol/L) — H_2O, the values of the surface tension, maximum adsorption, the surface area occupied by a molecule, and CCM were determined by the Rebinder method. It is stated that the surface tension of the STAB colloidal system with EO is 1.5 times as little, that indicates the synergistic effect of EO. The three-component system CCM is 4 times as much, i.e. this colloidal system has lower surface activity and, therefore, weaker capacity for the micelle formation. These results correspond to the observation: the ultramicroheterogenous systems of EO, the stabilized STAB with low aggregative stability, which is due to the hydrophobic nature of EO molecules, are formed.

The molecular ratio of the components, at which the micelle-forming process is observed, is n(STAB) : n(EO) : $n(H_2O)$ = 1 : 4 : 55,500, i.e. the three-component colloidal system micelles are formed in the molecular ratio of 1 STAB to 4 EO.

The micelle size was determined by the technique [10]. It is stated that, while solubilizing at various saturation, with the increase in the EO concentration, the micelle size increases from 7.3 to 20.8 nm, which confirms our assumptions about the cross-linking and incorporation of EO molecules into STAB micelles.

The results obtained indicate a high solubilization capacity of STAB micelles in relation to EO, which provides reasons to use water-lipid stabilized substrates as nanoreactors for free-radical oxidation reactions. The stability of water-lipid colloidal system is additionally maintained by means of continuous stirring.

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