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**RESEARCH OF THE COLLOIDAL, CHEMICAL AND  
TECHNOLOGICAL PROPERTIES OF THE BINARY MIXTURES OF  
SURFACTANTS**

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**Introduction**

Influence of mixtures of the substances on various physical and chemical processes in binary systems, in particular a micelleformation, causes a great interest in scientists and their research is one of the perspective directions in colloidal chemistry [1, 2]. Formation of micelles in solutions of the substances comes owing to formation of associates from molecules of surfactants in narrow area of concentration which is called as the critical concentration of a micelleformation. Determination of the critical micelle concentration (CMC), the mixed micelles and adsorption layers at different phases within the distribution plays an important role in modeling the structure and properties of these system, and also in the description of various colloidal and chemical processes (adsorption, wetting, solubilization, micellar catalysis and other properties). For binary mixtures of ionic and nonionic surfactants are characterized by explicit effects of intermolecular interactions, which are accompanied by the formation of intermolecular aggregates, complexes of different nature in solutions [2, 3].

To control of the processes at the interface between the two phases a mixture of surfactants having different surface activity are usually used. The study of surface phenomena of binary mixtures of surfactants is relevant for the purpose of theoretical studies, and applied aspect, as it allows purposefully choosing and combining the mixtures of surfactants that reduces the surface energy between phase, which mainly determines the effectiveness of the

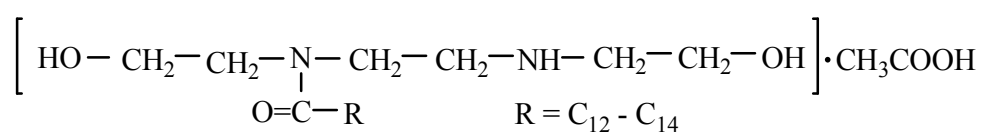
practical use of mixtures of different types of surfactants in many industrial processes (finishing and dyeing textile materials, water purification, etc.) [4].

Most of the tracks are associated with the effect of surfactant is a complex mixture composing of two or more surfactants. Effectiveness of their use is affected by many factors, including the multi-operational properties (homogeneity, viscosity, transparency). Components of the mixtures of surfactant interact with each other and affect on their characteristics, resulting in increase of surface activity, wetting, foaming, washing capacity and others.

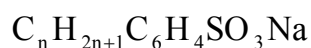
### Research methodology

In the research the following surfactants are used [5]:

1. Barvamid 2K (TU U 24.1-32257423-118-2005) – a surfactants of the cationic nature, this product is obtained during interaction  $\beta$ -oxyethylethylenediamin and higher fatty acids of the fraction  $C_{10} - C_{13}$  or  $C_{16} - C_{20}$  with subsequent neutralization with acetic acid. The process of obtaining of product consists of two stages. Formula of Barvamid 2K is follows:



2. Sulfonol NP-3 (TU U 24.6-20257936-022:2006) – is an anionic surfactant, sodium alkylbenzosulfonat based on  $\alpha$ -olefins of thermal cracking of paraffins with content of 8 – 12 carbon atoms in radical. The formula is shown below:



Research is performed on the fabric from white polyamide and polyester fibre with size 5 cm  $\times$  30 cm. Some of them were processed in mixtures of surfactants at different concentrations and temperatures, then the samples were used for the measurement of capillary properties. The other part was treated with a mixture of pollutants based on soot and oil.

After processing the fabrics were pressed, dried at room temperature and then placed in an drying room and then samples withstand in air for three days.

Uniformly polluted fabrics were used to determine the degree of removal of pollutions.

Wash of the polluted fabrics was carried out at temperatures of 15, 20, 25 and 30°C in mixtures of surfactants Barvamid 2K (component A) and Sulfonol NP-3 (component B). The molar ratio of components A, B (%) in the initial solution: 0-100, 20-80, 50-50, 80-20, 100-0.

After washing the samples were dried at room temperature, and then withstand in the drying oven for 30 minutes.

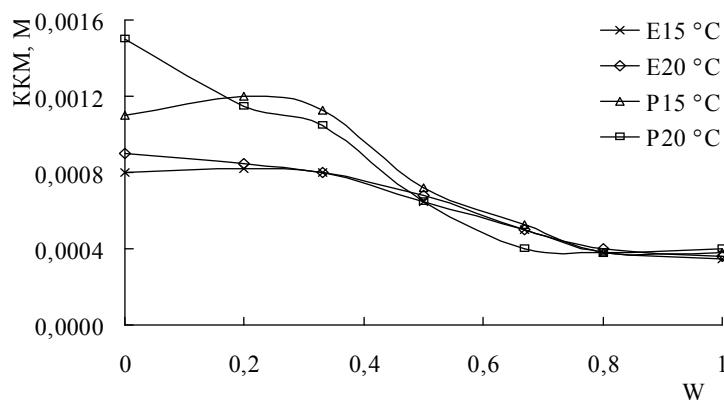
The surface tension was determined using the method of maximum bubble pressure [6]. The maximum pressure for each surfactant mixture was determined when the avulsion of air bubbles blown into the liquid through the capillary. To determine the ability of foam height of the column of foam and its stability the method of measurement and calculations was carried out according to GOST 22567.1-77.

The technique of the determination of the capillarity consists in measuring the height solution of potassium dichromate on the basis of fabrics at intervals from 0 to 60 minutes. This indicator was determined according to the methodology and the requirements of GOST 29104.11-91.

The washing ability of the mixtures of surfactants was determined with help of the optical method that is based on measuring the reflection coefficients from the initial, polluted and processed in the researched solution samples of fabrics. For measurements of reflection coefficients the photometer universal objective was used. Assessment of the degree of washing of the solution of surfactant mixtures was performed at different rates [7].

### **Results of the research and discussion**

Researched isotherms of the surface tension of solutions of individual surfactants and their mixtures are typical as solutions of the micelle formation surfactant: with increasing of the concentration of surfactant the surface tension decreases and then takes a constant value or decreases slightly, indicating the achievement of the critical micelle concentration.



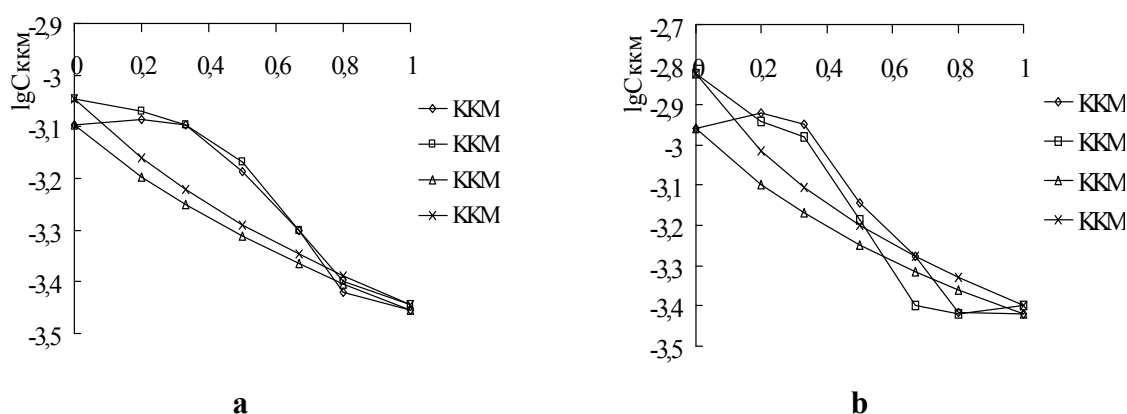
**Fig. 1. Dependence of critical micelle concentration (CMC) on a molar share (W) of Barvamid 2K in a mixtures with Sulfonol NP-3: E15 °C, E20 °C – experimentally defined values, P15 °C, P20 °C – calculated values**

Analysis of the graphs in Fig. 1 indicates that a mixtures of cationic surfactants with anionic surfactants in micelle formation and adsorption on the interfacial surface solution / air are conducted themselves imperfect and their values are deviated from the additive values. Depending on the ratio of the components in the solution there are antagonistic and synergistic effects. Thus, a synergistic effect occurs, since the molar proportion Barvamid 2K is more than 50% in a mixture with Sulfonol NP-3. Antagonism is observed in the values of critical micelle concentration up to molar ratio of surfactant in solution as 1:1. When mixed surfactants are at their stoichiometric ratio the turbidity and sedimentation are observed, which is associated with the formation of insoluble intermolecular complexes of hydrophobic nature resulting from electrostatic interaction of oppositely charged surfactant ions.

To evaluate and analyze the process of intermolecular interactions in solutions of surfactants the theory of the regular solutions and model of the pseudophase division are used [3, 6], according to which the molar composition of micelles  $X_1$  (molar fraction of component 1 – Barvamid 2K mixed with Sulfonol NP-3) and the interaction parameter in mixed micelles ( $\beta$ ) were determined.  $\beta$  is determined experimentally on the basis of values of critical micelle concentration and is used to interpret properties of the system.

Calculation of the micelles and interaction parameters showed that micelles of Barvamid 2 K – Sulfonol NP-3 are enriched by the stronger surfactants (Barvamid 2K) already at molar fraction of cationic surfactant  $W = 33,3\%$  or more. The negative value of the interaction parameter with mole fraction Barvamid 2K more than  $66,7\%$  shows the excess attraction between the

components of the mixture in the micelle. In this case there is synergistic effect at micelle formation, which can depend on steric factor associated with the utility package of the surfactant molecules in mixed micelles. Thus, the synergism in mixtures of surfactants depends on a small difference between the critical micelle concentration of individual surfactants, and the possibility of the formation of micelles of optimal composition. For presentation Fig. 2 shows the plots of experimental ( $KKM_E$ ) and calculated ( $KKM_P$ ) critical micelle concentration values at different temperatures.



**Fig. 2. The dependence of experimental ( $KKM_E$ ) and calculated ( $KKM_P$ ) values of critical micelle concentration on composition of solution of a mixtures of Barvamid 2K - Sulfonol NP-3: a – at temperatures of 15 °C and 20 °C, b – at temperatures of 25 °C and 30 °C**

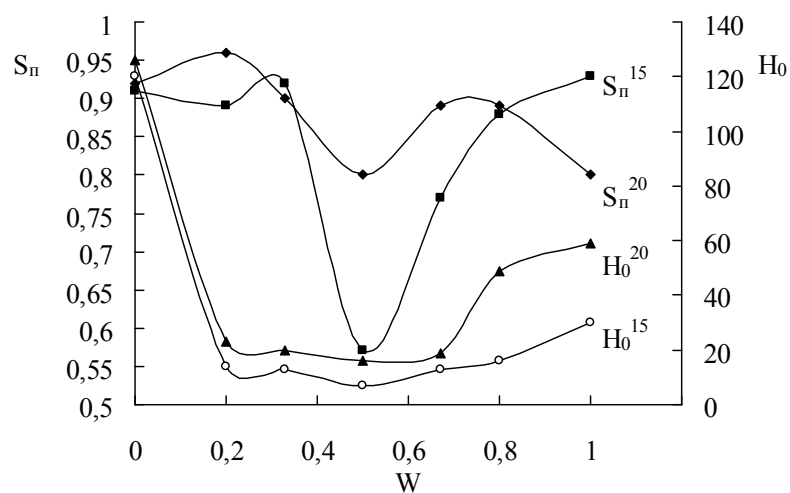
If we compare the critical micelle concentration mixtures of the studied surfactants with critical micelle concentration of the ideal mixed micelles, we can conclude that the experimentally determined critical micelle concentration of surfactant mixtures are larger than the calculated values of critical micelle concentration, that there is a positive deviation from ideal behavior. But in mixtures with molar content of Barvamid 2K is more than 80% the synergistic effect of the micelle formation is confirmed.

For the calculation the line of the surface tension isotherms at  $\sigma = \text{const}$  was performed and the points of intersection of this line with the surface tension isotherms concentration of solutions of individual surfactants and mixtures were determined at which of the selected value of the surface tension. The obtained values are inserted into the equation and then molar fraction Barvamid 2K in mixed adsorption layers  $X_1^\sigma$  and parameter interaction in layers were determined. Three sections were selected: 55 mN/m, 50 mN/m and 45 mN/m.

According to calculations, the adsorption layer of Barvamid 2K – Sulfonol NP-3 is highly enriched by cationic surfactant (Barvamid 2K). Interaction parameters at 15 °C and 20 °C are positive and change their sign to negative with increasing the temperature up to 25 °C and increasing the molar fraction of Barvamid 2K in a mixture of 80% or higher, and the negative interaction parameters is negative at 30 °C that indicates weakly pronounced synergistic effect in mixtures of surfactants. With increasing of the content of Barvamid 2K in a solution of a mixture of surfactants the intensity of intermolecular interaction increases.

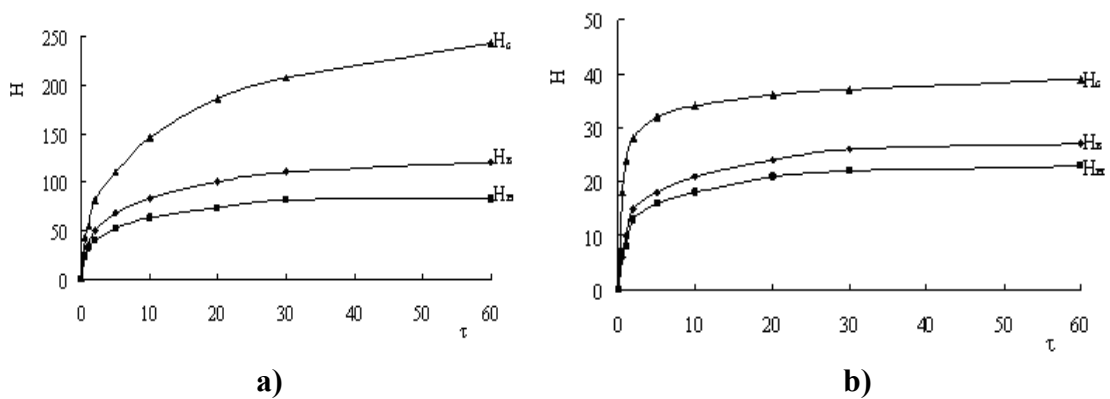
For a general assessment of the ability of foaming the graph of the dependence of height and foam stability on molar fraction Barvamid 2K mixed with Sulfonol NP-3 with a total concentration of surfactant in solution 0,004 M presents in Fig. 3.

Thus, all researched surfactant mixtures show the antagonistic properties in the study of high of foaming. The greatest antagonism in the study of foam stability is observed at molar content of Barvamid 2K 50% in the mixture with Sulfonol NP-3, that is associated with the formation of a complex salt with surfactant ions that is poorly soluble in water. The decrease of temperature to 15 °C leads to increase of phenomenon of antagonism in foaming.



**Fig. 3. Dependence of height and stability of foam on a molar fraction of Barvamid 2K in a mixtures:  $S_{n15}$ ,  $S_{n20}$  – stability of foam respectively at 15 °C and 20 °C;  $H_{015}$ ,  $H_{020}$  – height of formation of foam respectively at 15 °C and 20 °C**

Capillarity of polyester and polyamide textiles was determined before and after treatment with solutions of mixtures of surfactants. Fig. 4 shows the experimental results after treatment with a solution of surfactant with total concentration of 0,004 M at molar content Barvamid 2K 80% in the mixtures with Sulfanol NP-3 for polyester fibers (a) and nylon fibers (b). Fixation of the height of solution of potassium dichromate is performed at baseline and at such intervals in minutes: 0,5; 1; 2; 3; 5; 10; 20; 30.



**Fig. 4. Dependence of height of lifting of wettable substance on polyester fibers (a) and nylon fibers (b) that were previously processed in a mixtures of surfactants:**

**H – the height of lifting of liquid; indexes: H – the original sample, B - the sample processed in water, C – the sample processed in a mixtures of surfactants**

The curves in Fig. 4 have a characteristic form for capillar - porous textile material. The height of lifting of liquid of fabrics which were treated with a mixture of surfactants at the following molar composition: 80% Barvamid 2K and 20% Sulfanol NP-3 is much higher than original and processed in water samples.

The capillarity of polyester materials processed in the mixtures of surfactants at a temperature of 20°C is shown in Table 1 (W – molar content of Barvamid2K in a mixtures, %).

According to the abovementioned data we can conclude the synergistic mixture of surfactant relative to the components. There is a tendency to increase the speed and the height of liquid with increasing concentration in solution. The maximum value of the height of liquid is observed at the molar content of Barvamid 2K in a mixture of 20%.

**Table 1. Capillarity of polyester materials processed in the mixtures of surfactants at a temperature of 20 °C**

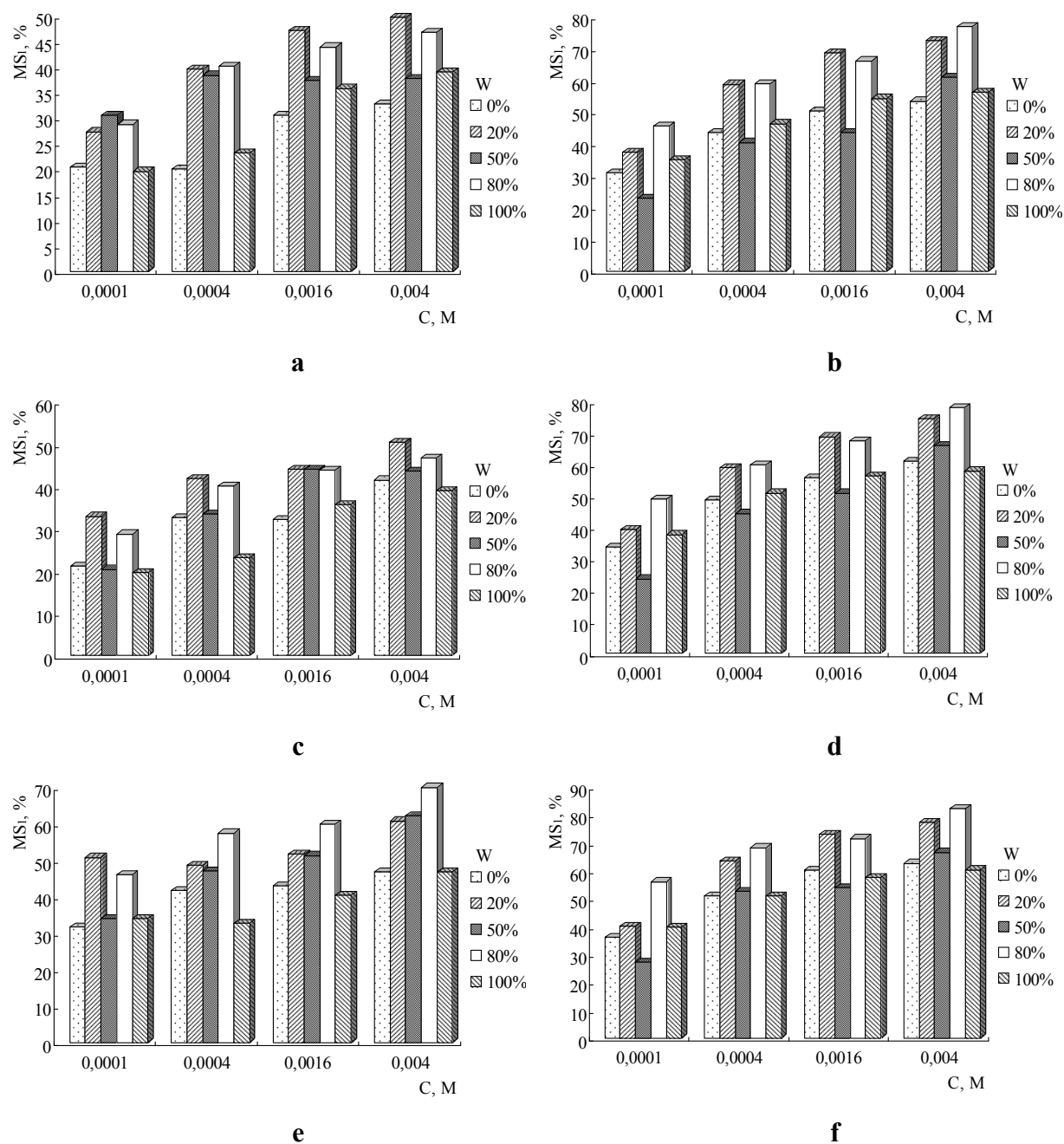
W, %	Concentration, M	Time after contacting the sample with a wetting liquid, seconds								
		0	0,5	1	2	5	10	20	30	60
0	0,0001	0	30	43	58	85	112	140	156	173
	0,0004	0	38	51	64	100	137	160	182	205
	0,0016	0	43	58	72	107	140	180	200	229
	0,004	0	40	54	75	112	146	185	205	241
20	0,0001	0	44	58	76	108	135	167	182	223
	0,0004	0	47	60	82	119	154	193	215	253
	0,0016	0	48	63	84	120	154	194	216	255
	0,004	0	50	64	85	121	155	196	214	255
50	0,0001	0	30	43	61	85	112	147	165	202
	0,0004	0	42	56	78	135	161	192	208	238
	0,0016	0	41	58	79	103	150	192	214	248
	0,004	0	39	58	80	115	148	193	213	250
80	0,0001	0	28	36	51	96	112	131	158	167
	0,0004	0	44	59	84	111	144	178	201	238
	0,0016	0	34	50	75	130	152	181	203	242
	0,004	0	44	55	82	111	146	186	208	243
100	0,0001	0	31	50	61	94	113	140	156	167
	0,0004	0	32	48	63	90	121	148	160	170
	0,0016	0	36	52	70	100	123	153	163	179
	0,004	0	34	50	66	96	120	145	160	181

As shown in Table 1 the capillary properties increase with increasing the temperature of pretreatment of samples.

Washing ability is a complex index it is determined by the degree of reflection of soiled fabric after washing in the solution. Washing ability can be expressed by the ratio of reflectance of the washed white material to unpolluted material (%). Washing ability depends on surface active washing substance, its ability to emulsify the fat and oil, temperature, pH and other parameters [8, 9].

In the experiment we used an optical method which consists in measurement of reflectance of polluted and original samples. Fig. 6 shows an assessment of the degree of washing ability of the mixture depending on the

concentration and molar content of Barvamid 2K (W) in the mixture for polyester and polyamide fibres.



**Fig. 5. Evaluation of washing the mixture of surfactants for materials: (a) polyester fabrics, (b) polyamide fabrics at a temperature 20°C; (c) polyester fabrics, (d) polyamide fabrics at a temperature 25°C; (e) polyester fabrics, (f) polyamide fabrics at a temperature 30°C**

Fig. 5 clearly demonstrates the synergistic actions of washing of the mixture relatively to the individual components of the mixture. The most

important action for the degree of washing of polyester fabrics fibres is revealed in the mixture of surfactant at the molar contents of Barvamid 2K 20% and 80%. Action of the mixture at a washing contents cationic and anionic surfactant 1:1 decreases with increasing concentration and it is explained by the formation of soluble complex salt, which has a brown color and partly settles on the fabric.

The difference between the values of washing ability of the fibres mainly causes by differences in the structures of textile materials.

With increasing the temperature up to 25°C (Fig. 5c) the washing ability has increased by an average of 5% and a maximum of 25% in the mixture of 2K Barvamid with molar contents of 80% and at a concentration of 0,0016 M.

Fig. 5d shows the significant increase of washing ability for a mixture of surfactant with molar contents of Barvamid 2K 20% and 80%, which confirms the synergism of mixture relative to its components. As the temperature increases the washing performance, but a significant increase of washing ability is observed for fabrics with polyester fibers.

### **Conclusion**

Therefore, study on the model of pseudophase division of surfactant mixtures showed the synergistic effect in the mixtures with molar fraction of Barvamid 2K of 80% or higher, resulting in lower critical concentration of micelleformation and surface tension of the solution compared with the corresponding values of individual surfactants. The behavior of surfactant mixtures is determined by the behavior of a stronger surfactant which replaces the less active component of mixture (Sulfonol NP-3) in the micelles and adsorption layers.

When processing of textile materials nylon polyester fibers in the researched range of temperatures and concentrations the synergistic effect is observed in the surfactant mixture with molar content of Barvamid 2K 20% and 80%.

Research indicates a synergistic effect of the mixtures of cationic and anionic surfactant relatively to the study of critical micelle concentration of components, capillarity, washing action, and antagonism of foaming. According to research the mixture of surfactants can be used as an active component in detergents for textile and other manufacturing finishing processes [10, 11].

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