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TREATMENT OF TEXTILE MATERIALS IN BINARY MIXTURES OF SURFACTANTS

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1. Introduction

Surfactants are used in various technological processes of the treatment of textile materials in the compositions with more or less complex structure. An important feature of such compositions is the weakening or strengthening of their properties in comparison with the properties of individual components, resulting respectively in antagonistic or synergistic interaction of components in the mixture. Combined use of surfactants in the mixture allows regulating the necessary properties of multicomponent systems and their changing in the required direction. Despite the large experimental data the combination of surfactants is carries out empirically, as until now the accurate criteria have not found for prediction of the behavior of surfactants in mixtures with sufficient definition due to a variety of surfactants, their chemical structure and different physical and chemical properties.

2. The approach

The study of surface properties of binary surfactants mixtures of different nature is useful for theoretical understanding of adsorption and determination of the main components of this complicated process. In turn this will allow deliberately choosing of surfactants in the mixtures which effectively reduce the interfacial energy and improve adsorption properties. Adsorption of surfactant on fibers causes their modification *in situ* and regulates their surface and capillary properties.

The widespread approach for study of the adsorption of binary mixtures surfactant at the interface solution of surfactants – air bases on the pseudo-phase model [1] and the theory of the regular solutions [2]. The basis of this method is the proposition that the partial entropies of components in the mixed micelle equal to partial entropies of components of the ideal micelle, and the enthalpy of mixing is different from zero. The use of models of Rubingh - Rosen [1,3,4] allows determining of the composition of mixed micelles, the nature and strength of intermolecular interactions, identifying the deviations of behaviour of solutions from ideality. The parameter β^m of the intermolecular interaction is a measure of deviation from ideality of the solution. According to the [1,3] the criterion of the synergism of micelle formation will be the fulfillment of two conditions:

1) $\beta^m < 0$,
2) $\left|\ln\frac{C_1}{C_2}\right| < \left|\beta^m\right|$.

Thus the purpose of the work is to study the process of micelle formation in binary mixtures of cationic surfactant with anionic and nonionic surfactants and the research of influence of treatment by solutions of these surfactants on the properties of synthetic textile materials.

3. The research objects and methodologies

As objects of research the surfactant produced in Ukraine were chosen: cationic Barvamid 2K, anionic Sulfonol NP-3 and nonionic surfactant Stearoks 920 [5]. Sulfonol NP-3 is the sodium alkylbenzene sulfonate on the basis of α-olefins of thermal cracking of paraffins with carbon chain C_8-C_{12}.

$$C_nH_{2n+1}C_6H_4SO_3Na$$

Stearoks 920 is a mixture of ethoxylated esters of stearic acid with 9 and 20 mol ethoxylation level.

$$C_{17}H_{35}COO(C_2H_4O)_9H$$

$$C_{17}H_{35}COO(C_2H_4O)_{20}H$$

Cationic surfactant Barvamid 2K is the product of the reaction of ß-oxyethylethylenediamine with higher fatty acids C_{12}-C_{14} of coconut oil.

$$\left[HO-CH_2-CH_2-\underset{\displaystyle O=C-R}{\underset{|}{N}}-CH_2-CH_2-NH-CH_2-CH_2-OH\right]\cdot CH_3COOH \qquad R = C_{12} - C_{14}$$

The surface tension of the surfactant solution was determined at different temperatures using the maximum pressure in the bubble, then appropriate isotherms were drawn and the composition of mixed micelles and intermolecular interaction parameter were calculated on the basis of theory of the regular solutions.

Polyester and polyamide fabric were treated by solutions of individual surfactants and their mixtures and capillarity and hygroscopicity of the treated samples were determined.

4. Results and discussion

Examples of surface tension isotherms at 20^0C is shown in Fig. 1. The lowest value of surface tension has been observed in the mixture of cationic and anionic surfactants at the molar concentration of Barvamid 2K of 80%. This mixture has shown the synergistic properties relative to critical micelle concentration (CMC) and surface tension, although the synergistic effect is slightly expressed. With increasing temperature CMC of individual surfactant and mixtures at W = 20% and W = 33,33% increases at the temperature range from 15°C to 25°C and CMC of the studied mixtures decreases at 30°C (Fig. 2). In mixtures of cationic and nonionic surfactants the synergistic effect is strongly expressed relative to CMC.

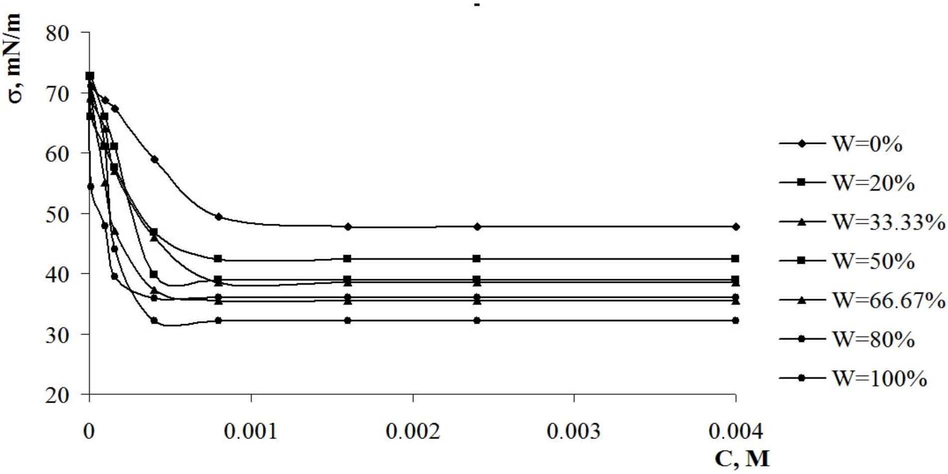

Figure 1. Isotherms of surface tension of surfactants Barvamid 2K and Sulfonol NP-3 and their mixtures at the molar concentration of Barvamid 2K (W, %) in mixtures

The mechanism of interaction and nature of intermolecular associates depend on the nature of surfactants and their ratio in mixture. The intermolecular interaction in the binary mixtures of cationic and anionic surfactants is caused primarily by electrostatic attraction of oppositely charged surfactants ions and hydrophobic interaction of nonpolar hydrocarbon radicals and the formation of hydrogen bonds. Thus, the synergistic effect is observed since the molar concentration of Barvamid 2K more than 50% in the mixtures with Sulfonol NP-3. When surfactants are mixed at their stoichiometric ratio we can observe the turbidity and sediment formation due to the formation of insoluble complexes of intermolecular hydrophobic nature resulting from electrostatic interaction of oppositely charged surface-active ions.

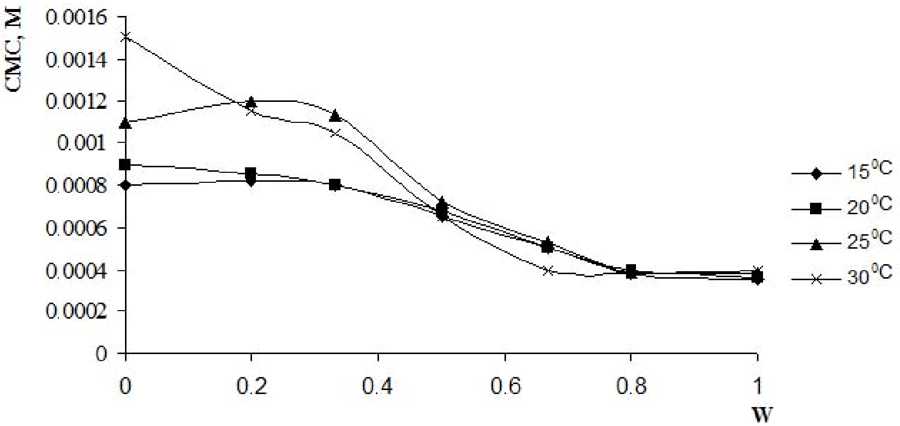

Figure 2. Dependence of CMC of mixtures of Barvamid 2K and Sulfonol NP-3 on the molar concentration of Barvamid 2K (W) in mixtures at the different temperatures

To assess and analyze the process of intermolecular interactions in solutions of surfactants the theory of regular solutions was used and the molar composition of the micelles X_1 (molar proportion of 1 component Barvamid 2K in the mixtures) was calculated by the formula (1) and parameter of interaction in mixed micelles β^m was calculated by the formula (2). $C`_{12}$ is CMC calculated by the formula (3), α – the molar concentration of the surfactant 1 in the solution, C_1 and C_2 – CMC of the individual surfactants (1 – Barvamid 2K), C_{12} – experimental CMC of mixed system.

$$\frac{X_1^2 \ln\left(\frac{C_{12}\alpha}{C_1 X_1}\right)}{(1 - X_1)^2 \ln\left[\frac{C_{12}(1-\alpha)}{C_2(1 - X_1)}\right]} = 1 \qquad (1)$$

$$\beta^m = \frac{\ln\left(\frac{C_{12}\alpha}{C_1 X_1}\right)}{(1 - X_1)^2} \qquad (2)$$

$$\frac{1}{C^{`}_{12}} = \frac{\alpha}{C_1} + \frac{1-\alpha}{C_2} \qquad (3)$$

Calculation of the micelles and interaction parameters has shown that the micelles Barvamid 2 K – Sulfonol NP-3 enriched with a strong surfactant Barvamid 2K already at its molar concentration in mixtures W = 33.3% and more (Table 1). The negative value of interaction at molar concentration Barvamid 2K more than 66.7% indicates the existence of excessive attraction between the components of the mixture in micelles. This synergism at the micelle formation can depend on steric factor associated with the utility of package of surfactant molecules in mixed micelles. Thus, a small difference between the CMC of individual surfactants, as well as the formation of micelles of optimal composition influence on the synergism in mixtures of surfactants.

Table 1. The composition of mixed micelles and intermolecular interaction parameter

α	0.2	0.333	0.5	0.667	0.8
Barvamid 2K + Sulfonol NP-3					
C_{12}, M	0.00085	0.0008	0.00068	0.0005	0.0004
X_1	0.306	0.619	0.937	0.921	0.892
β^m	0.903	1.167	2.037	0.998	-0.251
$C`_{12}$, M	0.000692	0.000602	0.000514	0.00045	0.000409
Barvamid 2K + Stearoks 920					
C_{12}, M	0.00016	0.00015	0.00012	0.0001	0.000355
X_1	0.404	0.457	0.513	0.557	0.800
β^m	-4.254	-4.044	-4.739	-5.609	-0.296
$C`_{12}$, M	0.000414	0.000403	0.000391	0.000380	0.000371

Polyester and polyamide fabrics were treated in solutions of individual surfactants and their mixtures with total concentration from $1\cdot10^{-5}$ to $4\cdot10^{-3}$ M for 1 hour at the temperature of 20^0C. Then the adsorption of surfactants on the fibres and the height of capillary rise of solution of $K_2Cr_2O_7$ for 60 minutes were determined. Some results of this study are shown in Table 2 and indicate that treatment of fabrics by surfactant solutions enhances their hydrophilicity, resulting in improving their wettability by aqueous solutions and a considerably increases capillarity due to the presence of adsorbed surfactants on the surface of materials [5]. The data in Table 2 correspond to the treatment of polyester fabrics: 1 – untreated sample, 2 – treatment by Barvamid 2K, 3 – Stearoks 920, 4 – Sulfonol NP-3, 5 – mixture of 80% Barvamid 2K and 20% Sulfonol NP-3, 6 – mixture of 66.7% Barvamid 2K and 33.3% Stearoks 920 at the total concentration in solution $4\cdot10^{-4}$ and $1.6\cdot10^{-3}$ M. Height of liquid rise in the textile material treated by mixtures №5 and №6 is higher in comparison with other samples, which indicates an increase of capillary properties and confirms the demonstration of synergism at the application of mixtures of this compositions. After treatment by surfactants the surface electrical resistance of synthetic fabrics has decreased from $1.92 \cdot 10^{12}$ to 10^9-10^{10} Ω due to the presence of surfactants on the fibres, which shows the increase of their antistatic properties.

Table 2. The height of capillary rise of solution of $K_2Cr_2O_7$ on the polyester fabrics

№	$C = 4 \cdot 10^{-4}$ M			$C = 1.6 \cdot 10^{-3}$ M		
	2 min.	10 min.	60 min.	2 min.	10 min.	60 min.
1	4	14	25	-	-	-
2	63	119	170	70	123	179
3	69	134	217	83	151	244
4	64	137	205	72	140	229
5	84	144	238	85	152	242
6	74	140	220	89	160	262

5. Conclusion

Study has shown that mixtures of surfactants have high surface activity, wetting ability, low CMC and synergistic effect, enabling their use in compositions for the treatment of textile materials in various technological processes. Adsorption of surfactants molecules on the surface of synthetic fibres leads to a change in their hydrophilicity, resulting in improving their capillarity, hygroscopicity, antistatic properties, and in general positively impacts on the higenic characteristics of materials and comfort of clothing.

6. Acknowledgment

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7. References

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