

Abrasive Treatment of Iron, Copper and Aluminum Alloys in Aqueous Binary Solutions of Polyalkylene Glycol-Sodium Alkyl Sulfate

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ABSTRACT: The results of studies of dispersing, surfactant, rheological and conductometric properties of aqueous solutions of polyalkylene glycols (PAG), sodium dodecyl sulfate (DDSNa) and aqueous binary solutions (WBS) PAG - DDSNa are presented. The synergism of the dispersing properties of the FBG components was found, the value of which is determined by the molecular weight (Mwt.) of the polymer, the concentration of the surfactant, and the nature of the alloys. The symbaticity of changes in dispersive, surface-active, rheological properties and electrical conductivity of WBS was established, which is explained by the formation of intermolecular complexes IMC PAG - DDSNa.

The lack of synergism in the dispersing action of PAG20 - DDSNa WBS components is explained by a change in the conformation of PAG20 macromolecules during the formation of IMC with DDSNa, which complicates optimal contact with metal surface cations. The weak synergism of the dispersing properties of the WBS components during the dispersion of an aluminum alloy is explained by the competitive adsorption of lauryl sulfate ion on a freshly formed positively charged surface.

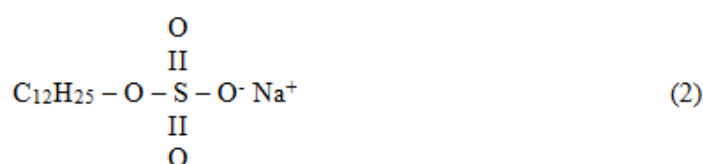
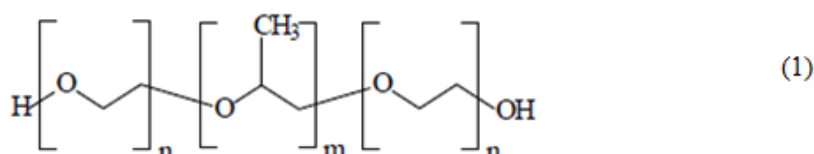
KEYWORDS: abrasive processing, metal, dispersion medium, polymer, surfactant, intermolecular complex, synergism.

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I. INTRODUCTION

The efficiency of using in the processes of abrasive processing of metals of aqueous solutions of binary compositions polymer - surfactant and oligomer - surfactant is shown in [1-3]. It is of interest to carry out complex studies of dispersion media based on aqueous binary solutions of PAG - DDSNa, in which both components belong to the class of surfactants: PAG is a high molecular weight nonionic surfactant, and DDSNa is an anionic surfactant [4-5]. The used chemical compounds have the following structure: PAG (1) and DDSNa (2):



II. MATERIALS AND RESEARCH METHODS

The dispersing properties of aqueous solutions of PAG35 (Mwt. = $35 \cdot 10^3$), PAG20 (Mwt. = $20 \cdot 10^3$), PAG8 (Mwt. = $8 \cdot 10^3$), DDSNa and WBS PAG - DDSNa were studied by the gravimetric method with abrasive dispersion of discs made of iron alloys (St. 45), copper (bronze BrAZh9, brass L59) and aluminum alloy (D16T) on a friction machine [6] at a load of 0,1 mPa and a linear velocity of 0,12 m/s. Gray cast iron was used as a lap and silicon carbide (KZM20) was used as an abrasive. The dispersing effect of the components of the dispersion medium was determined by the increase in the removal ΔQ^C , i.e. by the difference between the amount of metal removal in solution (Q^S) and in water (Q^W): $\Delta Q^C = Q^S - Q^W$ [2]. Visual inspection of the samples shows that after the experiments, the surface of the discs becomes dull, of the corresponding color, and the absence of scratches and burns on it indicates the normal course of the microcutting process.

The rheological properties of the solutions were investigated by the falling ball method (viscometer Lovis 2000M Anton PAAR, Austria) at a temperature of 20 °C.

The surface tension of the solutions was determined by the modified Wilhelmy method (platinum plate) [7] at $T = 20$ °C.

Investigation of the specific electrical conductivity of aqueous solutions of PAG, DDSNa and their binary solutions carried out by conductometry (MPC227, METTLER TOLEDO).

III. RESEARCH RESULTS AND DISCUSSION

3.1. DISPERSING PROPERTIES

The results of studying the concentration dependence of the dispersing properties of PAG20 and PAG35 polyalkylene glycols during abrasive grinding of metal alloys are shown in Fig. 1 and Fig. 2.

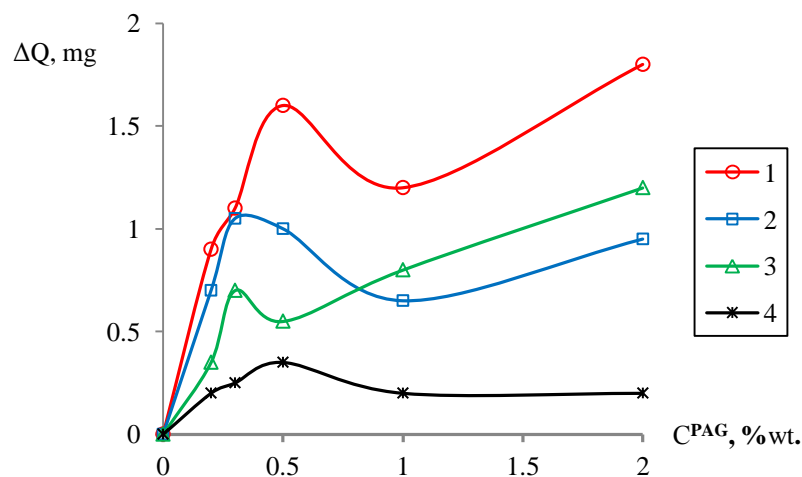


Fig. 1. Dependence of the increase in removal ΔQ during abrasive processing of bronze BrAZh9 (1), aluminum alloy D16T (2), brass L59 (3) and St. 45 (4) on the concentration of the polymer PAG20

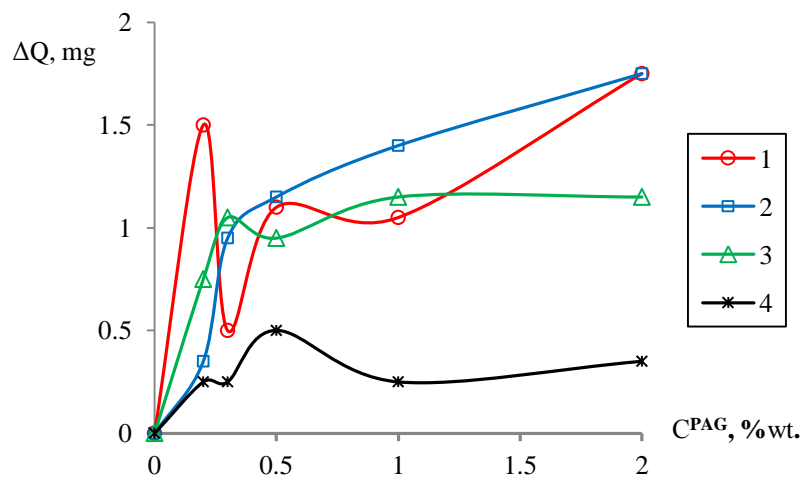


Fig. 2. Dependence of the increase in removal ΔQ during abrasive processing of bronze BrAZh9 (1), aluminum alloy D16T (2), brass L59 (3) and St. 45 (4) on the concentration of the polymer PAG35

Comparative analysis of those shown in Fig. 1 and Fig. 2 of the results shows significant differences in the concentration dependences of the dispersing action (ΔQ^C) of PAG20 and PAG35, which are significantly influenced by both the nature of the alloy and the Mwt. of the polymers. The nature of the concentration curves of the ΔQ dependence can be explained by counter processes that occur in the microcutting zone in accordance with the Rebinder effect [6, 8]. In the range of concentrations 0.2-0.5%wt. clear maxima of ΔQ values are observed, which indicates the classical version of the Rebinder effect in aqueous solutions of PAG, which are nonionic surfactants [4]. The differences in the character of the ΔQ concentration curves are largely due to the rheological properties of the solutions, which are determined by the Mwt. of the polymers.

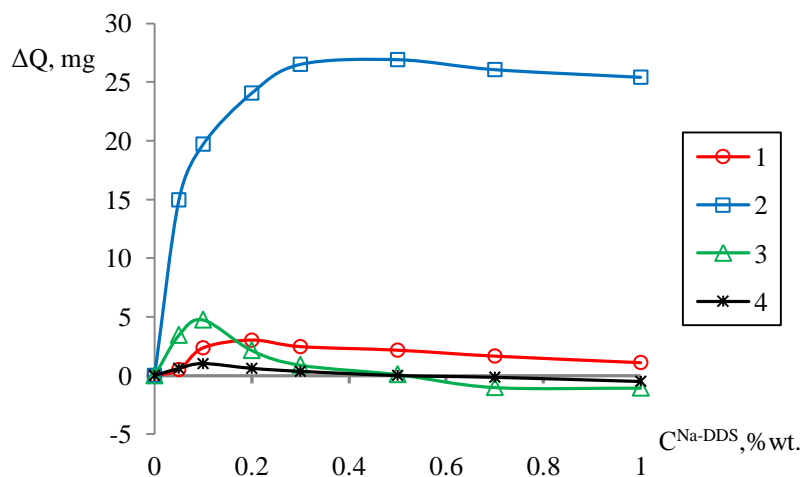


Fig. 3. Dependence of the increase in removal ΔQ on the concentration of DDSNa during abrasive processing of bronze BrAZh9 (1), aluminum alloy D16T (2), brass L59 (3) and St. 45 (4)

From the analysis of the concentration dependences of the dispersing properties of aqueous solutions of DDSNa, shown in Fig. 3, it follows that the values of ΔQ are significantly affected by the surfactant concentration and the nature of the alloy. For iron and copper alloys, an extreme dependence of the ΔQ values on the surfactant content is observed, and the maxima lie in the range of 0.1-0.2 %wt., which is optimal for the implementation of the Rebinder effect. When the D16T aluminum alloy is dispersed, high values of ΔQ are observed even at a DDSNa concentration of 0.05 %wt.

The results of studying the concentration dependences of the dispersing properties of WBS PAG20 - DDSNa and PAG35 - DDSNa are shown in Fig. 4-7. The concentration of PAG in BS is 2%wt. and was selected taking into account the results on the increase in the removal of ΔQ^{PAG} in aqueous solutions of PAG20

and PAG35, which makes it possible to determine the values of ΔQ^{BS} and compare them with the additive sum of ΔQ^C values of ΔQ^C in solutions of DDSNa and PAG, i.e. to establish the presence of synergism or antagonism of the dispersing action of WBS components [1-3].

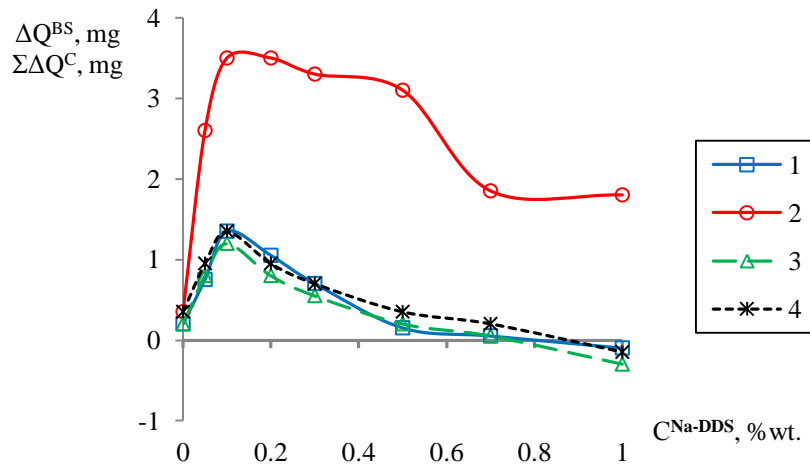


Fig. 4. Dependence of the increase in removal ΔQ of St. 45 on the concentration of DDSNa in WBS PAG20 - DDSNa (1), PAG35 - DDSNa (2) and calculated values of the additive sum $\Sigma\Delta Q^C$ for solutions of PAG20 (3) and PAG35 (4)

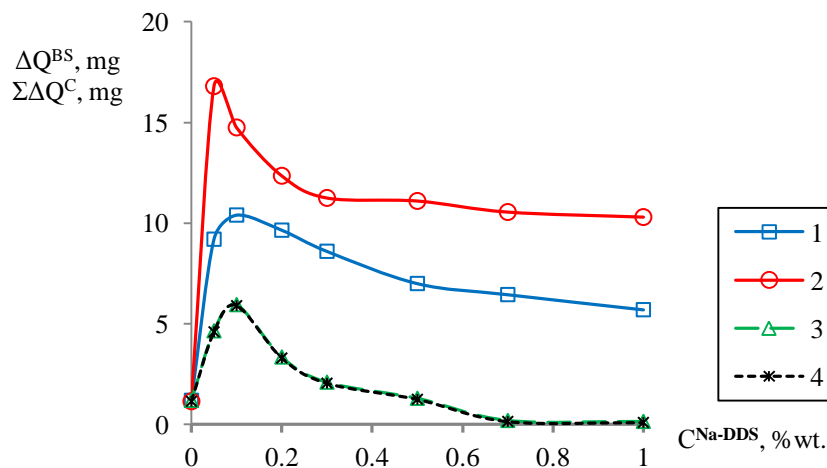


Fig. 5. Dependence of the increase in removal ΔQ of brass L59 on the concentration of DDSNa in WBS PAG20 - DDSNa (1), PAG35 - DDSNa (2) and calculated values of the additive sum $\Sigma\Delta Q^C$ for solutions of PAG20 (3) and PAG35 (4)

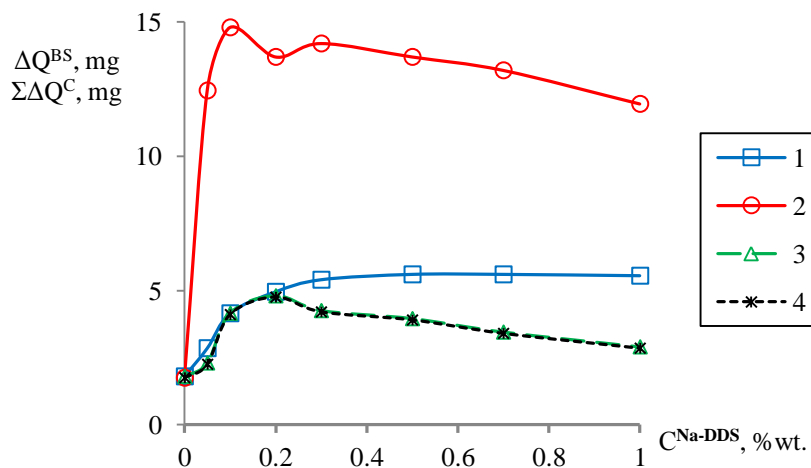


Fig. 6. Dependence of the increase in removal ΔQ of bronze BrAZh9 on the concentration of DDSNa in WBS PAG20 - DDSNa (1), PAG35 - DDSNa (2) and calculated values of the additive sum $\Sigma \Delta Q^C$ for solutions of PAG20 (3) and PAG35 (4)

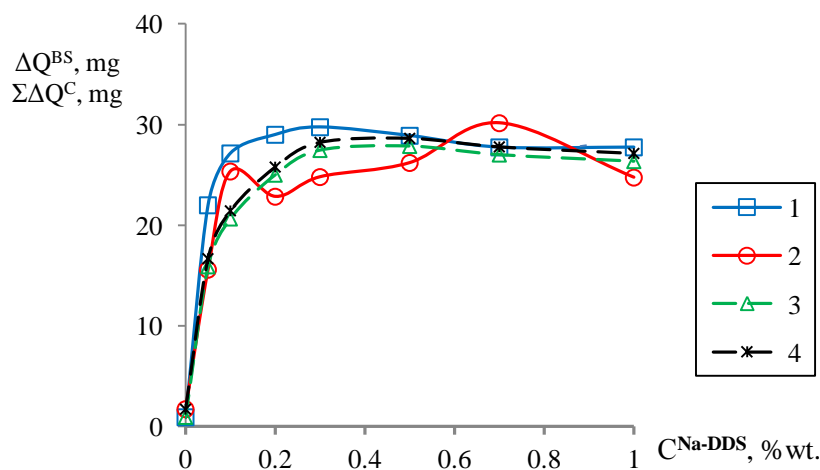


Fig. 7. Dependence of the increase in removal ΔQ of the D16T aluminum alloy on the concentration of DDSNa in WBS PAG20 - DDSNa (1), PAG35 - DDSNa (2) and calculated values of the additive sum $\Sigma \Delta Q^C$ for solutions of PAG20 (3) and PAG35 (4)

As shown in Fig. 4-7 results, depending on the nature of the alloys, Mwt. PAG and surfactant concentration, synergism is observed, i.e. mutual reinforcement of the dispersing action of the WBS components ($\Delta Q^{BS} > \Sigma \Delta Q^C$) or antagonism ($\Delta Q^{BS} < \Sigma \Delta Q^C$).

Analysis of the data shown in Fig. 4 of the results shows that during abrasive treatment of St. 45 in WBS PAG20 - DDSNa, there is a slight synergism in the dispersing action of the components. However, when St.45 is dispersed in WBS PAG35 - DDSNa, the increase in ΔQ^{BS} is almost 3 times higher than the values of $\Sigma \Delta Q^C$ (Fig. 4, curves 3 and 4), which indicates an abnormally high synergism of the action of the components, which can be explained by the formation of IMC PAG35 - DDSNa.

Comparison of the concentration dependences of the dispersing properties of WBS PAG20 - DDSNa and PAG35 - DDSNa during abrasive processing of copper alloys shows (Fig. 5 and Fig. 6) that in the range of DDSNa concentrations 0.1-0.2 %wt. the increase in ΔQ^{BS} is 2-3 times higher than the values of $\Sigma \Delta Q^C$. Considering that bronze and brass differ not only in microhardness, but also in a package of alloying impurities, it can be argued that the synergism of the dispersing action of WBS components is the result of the interaction of IMC PAG - DDSNa with copper cations Cu^{2+} .

During abrasive processing of aluminum alloy D16T in BS PAG - DDSNa in the range of concentrations of 0.1-0.2%wt. the ΔQ^{BS} values are 15-20% higher than the $\Sigma \Delta Q^C$ values, which indicates a

noticeable synergism of the dispersing action of the WBS components (Fig. 7). However, when the surfactant concentration is higher than 0.35% wt. the curves ΔQ^{BS} and $\Sigma \Delta Q^C$ practically converge, which indicates the absence of synergism in the action of the components. It is important to note that on the curve of the dependence of ΔQ^{BS} on the surfactant concentration during the dispersion of D16T (Fig. 7, curve 1) there is no maximum in the range of 0.1–0.2 %wt, in which the Rebinder effect is realized [8]. Considering that the values of ΔQ^{DDSNa} for D16T exceed the values of ΔQ^{DDSNa} for copper and iron alloys by 5-10 times (Fig. 4-6), the strong dispersing effect of surfactants is probably due to the high penetrating properties of DDSNa molecules into the microcutting zone of the D16T alloy. Apparently, in this case, the main role is played by the electrostatic interaction of the freshly formed surface of the aluminum alloy and lauryl sulfate ion, since the aluminum surface is positively charged [10]. In this case, it can be assumed that the nature of the concentration dependences of the dispersing action of WBS PAG - DDSNa during the dispersion of the D16T alloy is the result of competitive adsorption on the freshly formed surface of DDSNa molecules, DDSNa micelles, and IMC PAG-DDSNa.

Summarizing the results obtained, it can be assumed that the dispersing effect of WBS PAG - DDSNa is determined by the possibility of formation of IMC PAG - DDSNa, the stereochemistry of which causes strong synergism during abrasive processing of iron and copper alloys, and weak synergism during the dispersion of D16T indicates the prevailing role of competitive adsorption of components on freshly formed aluminum alloy surface.

3.2. SURFACTANT AND RHEOLOGICAL PROPERTIES

As is known [9], the maximum dispersing effect of technological compositions is realized with an optimal combination of wetting and penetrating properties, which are determined by surface tension and viscosity. The results of measuring the surface tension γ_g of WBS PAG - DDSNa and PEG - DDSNa depending on the concentration of the components, i.e. isotherms of surface tension are shown in Fig. 8.

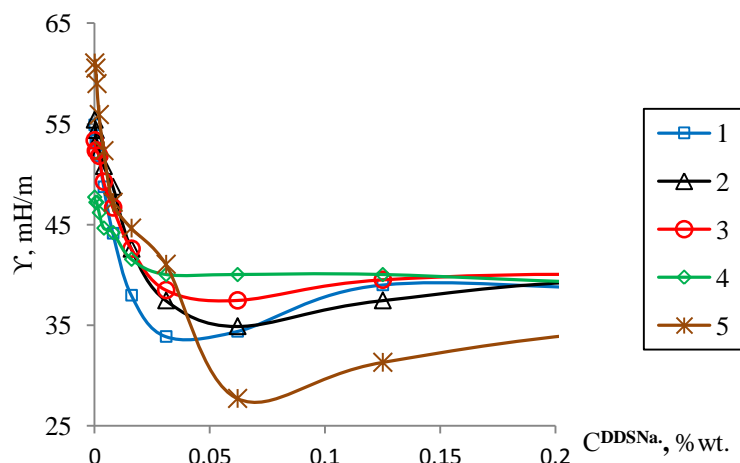


Fig. 8. Dependence of the surface tension γ of WBS PAG35 - DDSNa (1), PAG20 - DDSNa (2), PAG8 - DDSNa (3), PAG1.65 - DDSNa (4), PEG6000 - DDSNa (5) on Mwt. PAG and surfactant concentration

The character of isotherms is significantly influenced by WBS (Fig. 8, curves 1-5) Mwt. PAG, which indicates the possibility of the formation of IMC PAG - DDSNa, the stereochemistry and strength of which is determined by the interaction of PAG macromolecules of different Mwt. with DDSNa. This is evidenced by the presence of a small minimum on the WBS isotherms in the region of 0.03-0.04 %wt, the depth of which decreases to zero with a decrease in Mwt. PAG from $35 \cdot 10^3$ to $1.65 \cdot 10^3$. The possibility of the formation of IMC was shown in binary solutions of lysine-DDSNa [11], on the isotherms of which there is a small minimum in the concentration range, which is 3 times less than the CMC of DDSNa itself. By analogy with binary solutions of Triton-DDSNa [12], the formation of IMC PAG - DDSNa is possible by the mechanism of coordination of methylene oxide blocks of PAG around sodium lauryl sulfate cations. Comparative analysis of the effect of polyethyleneglycol (PEG6000) on the decrease in γ_g values in the micellar concentration range (Fig. 8, curve 5) shows that DDSNa in WBS forms IMC mainly with ethyleneoxide PAG blocks.

The possibility of the formation of IMC in the WBS polymer - surfactant is confirmed by studies in which a nonmonotonic and synergistic change in viscosity was found with an increase in the concentration of surfactants, including anionic ones [1-3]. Taking these results into account, we studied the dependence of the

dynamic viscosity of WBS PAG - DDSNa on the surfactant concentration and Mwt. of the polymer, the results of which are shown in Fig. 9.

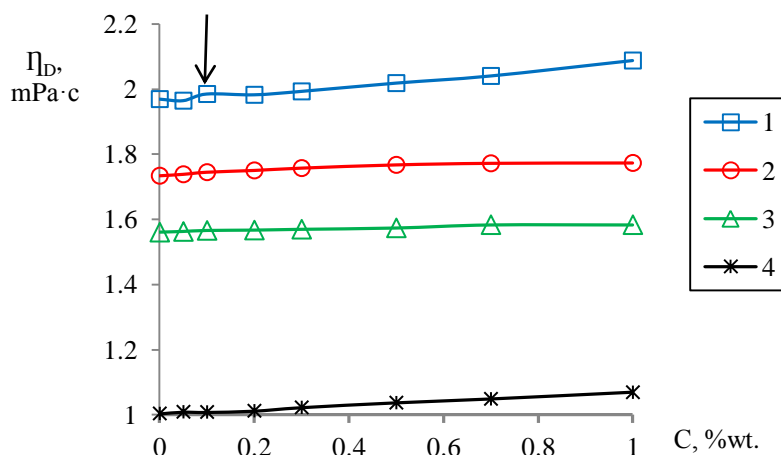


Fig. 9. Dependence of the dynamic viscosity η_D on the concentration of DDSNa in 2% solutions of PAG35 (1), PAG20 (2), PAG8 (3) and DDSNa (4) in water

The presence of a noticeable minimax fragment (Fig. 8, curve 1) in the region of 0.1 %wt. The surfactant can be explained by the formation of IMC PAG35 - DDSNa, since in this range, there is a symbaticity between changes in dispersant properties (Fig. 4-6) and surface activity (Fig. 8). A detailed analysis of the rheological properties of WBS PAG35 - DDSNa (Fig. 9, curve 1) shows that the increase in the dynamic viscosity of WBS PAG35 - DDSNa at a surfactant concentration of 1%wt. reaches 0.118 mPa·s, which is almost 2 times higher than the increase in viscosity with an increase in the concentration of DDSNa in water up to 1%wt. This effect can be explained by the influence of immobilized molecules of anionic surfactant on the conformation of PAG35 macromolecules, which is accompanied by an increase in the radius R_e of the Einstein sphere [13]. A similar effect - elongation of macromolecules with adsorbed surfactant molecules - was found in WBS ethyloxyethyl cellulose - DDSNa [14]. It is characteristic that in WBS PAG20 - DDSNa and PAG8 - DDSNa a significant decrease in the increase in viscosity is observed: $\Delta\eta_D^{WBS}$ (PAG20) = 0.039 mPa·s and $\Delta\eta_D^{WBS}$ (PAG8) = 0.023 mPa·s, which is one and a half and three times less than the increase in $\Delta\eta_D$ (DDSNa) = 0.065 mPa·s. Such differences can be explained by the fact that the interaction of PAG20 and PAG8 macromolecules with DDSNa molecules, i.e. the formation of IMC is accompanied by a change in their conformation, which results in a decrease in the radius R_e of the Einstein sphere, and, hence, in the dynamic viscosity of the WBS. A change in the conformation of macromolecules in PAG20 - DDSNa IMC adsorbed on the freshly formed surface of alloys can strongly affect the density of adsorption layers and CPD, as a result of which the distribution of electron density in surface cations and, as a consequence, the mobility of dislocations change [15].

3.3. ELECTROCONDUCTIVITY PROPERTIES

It is known that additives of anionic surfactants strongly affect both surfactant, rheological, and electrically conductive properties [15-17]. In fig. 10-13 show the results of studying the specific electrical conductivity χ of aqueous solutions of DDSNa (Fig. 10) and WBS PAG - DDSNa (Fig. 11-13) on the concentration of surfactant and Mwt. PAG.

The CMC of DDSNa and WBS PAG - DDSNa were determined from the graphical dependence of the electrical conductivity χ of solutions on the surfactant concentration by the Williams method [18].

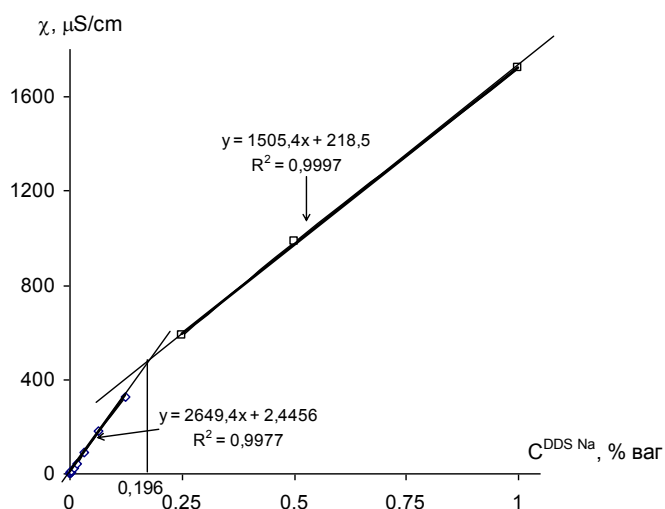


Fig. 10. Dependence of specific electrical conductivity χ on the concentration of aqueous solutions of DDSNa ($T = 20\text{ }^{\circ}\text{C}$)

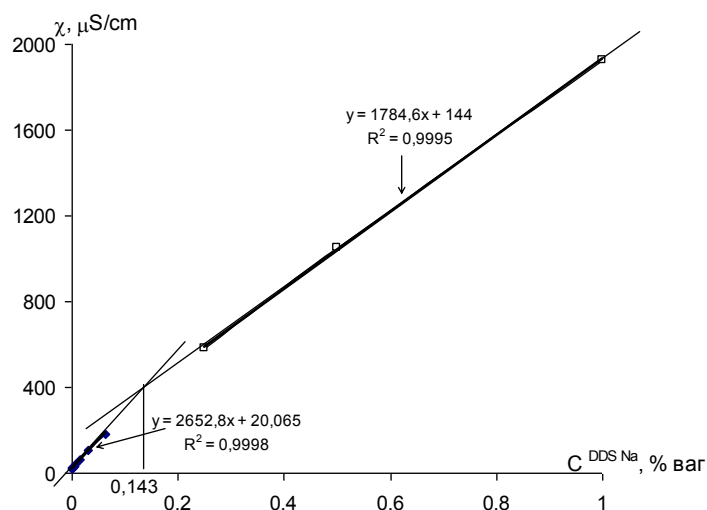


Fig. 11. Dependence of the specific electrical conductivity χ of WBS 2%wt. PAG8 - DDSNa on the DDSNa concentration of DDSNa ($T = 20\text{ }^{\circ}\text{C}$)

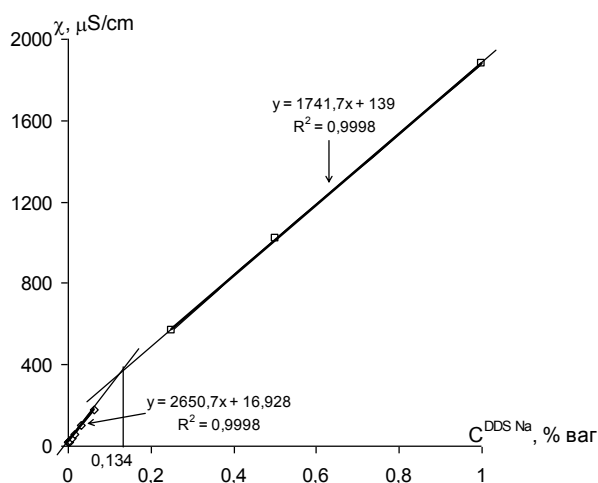


Fig. 12. Dependence of the specific electrical conductivity χ of WBS 2%wt. PAG20 - DDSNa on the concentration of DDSNa ($T = 20\text{ }^{\circ}\text{C}$)

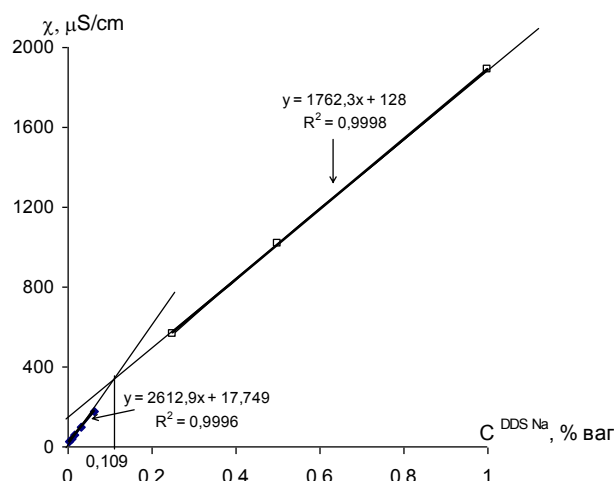


Fig. 13. Dependence of the specific electrical conductivity χ of WBS 2%wt. PAG35 - DDSNa on the concentration of DDSNa ($T = 20\text{ }^{\circ}\text{C}$)

The results are presented in Table 1.

Table 1

Solutions	DDSNa	ПАГ8 – DDSNa	ПАГ20 – DDSNa	ПАГ35 – DDSNa
CMC, %	0,196	0,143	0,134	0,109

As can be seen from the results presented in the table, the CMC values of WBS gradually decrease with an increase in Mwt. PAG, which is consistent with the results of the study of surface tension isotherms (Fig. 8). As is known [10, 12-15], anionic DDSNa has unique properties to donate its Na^+ cation into the composition of mixed micelles in aqueous solutions of nonionic surfactants or to admit ethyl or oxyethyl chains into its micelles, and the interaction energy in such mixed micelles increases with an increase in the number of such chains. The results obtained make it possible to explain the mechanism of immobilization of both individual DDSNa molecules and its micelles in PAG solutions with the formation of IMC, as well as the effect of anionic surfactants on surface-active, rheological, conductometric, and, ultimately, on the dispersing properties of WBS PAG - DDSNa.

IV. CONCLUSION

The concentration dependences of dispersive, surfactant, rheological and conductometric properties of aqueous solutions of PAG, DDSNa and binary solutions of PAG-DDSNa have been studied. The synergism of the dispersing action of the WBS components is found, the value of which is determined by the Mwt. PAG, the DDSNa concentration, and the nature of the alloys. The symbatism of changes in dispersant, surface-active, rheological and conductometric properties is explained by the formation of intermolecular complexes (IMC) PAG35 - DDSNa. The absence or weak synergism of the dispersing action of WBS PAG20 - DDSNa is explained by the change in the conformation of PAG20 macromolecules during the formation of IMC and the competitive adsorption of lauryl sulfate ion on the freshly formed surface of the aluminum alloy.

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