

Tribological Investigation of Supramolecular Self-Organization Mechanism
in Introduction into Water of Non-Ionic Surface-Active Substances
and their Combinations with Ionic Ones
in Water-Lubricating Friction Junctions

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Abstract

The article presents the results of the investigation of non-ionic additive surface-active substances (SAS) and their combinations with ionic ones. The results prove positive influence of the combination SAS₄+SAS₅, which is self-organized under the condition of 1%-mass introduction into water, on the value of the friction coefficient and linear wear of water-lubricated bearing couples.

Key words:

Tribology, mesomorphism, wear, friction, liquid crystal, mesogen, adsorption, destruction, sorption, self-organization, supramolecular package.

Introduction

The usage of *lyotropic liquid crystals* in tribology represents the new trend in their utilization. The first reports devoted to the use of *DM* in this sphere appeared in 1988, when the authors of the below mentioned articles [1,2] suggested a new antifriction and antiwear additive, capable of forming column-type structures for lubricant compositions.

A short insight into the history of study of tribological qualities of liquid crystals [5] shows that the intensive development of this area has started not long ago, at the beginning of 80-s of the last century, in spite of the fact that in 1936 V.K. Frederiks has asserted the necessity of such investigations.

After careful examination of the material contained in the quoted monograph [5] it is borne in that when it came out *liotropic LC* hadn't been actually examined in terms of tribology. Much later the authors of these works carried out research into the tribological qualities of phthalocyanine derivatives as additives to various

lubricants and showed the definite role of additives supramolecular organization during the process of friction. Taking into consideration the aforesaid, we examined liotropic mesogens of neol derivatives as additive to water when using it in water-lubricated steams of friction and showed the efficiency of its usage as anti-friction and antiwear additive. In the first case we have chosen liquid-crystal additives, formed by non-ionic surface-active substances and water, as well as by triple combinations NISAS+ ISAS+ water (non-ionic-ionic-water) for our comparative investigations. The additives have been matched in a way that allowed to educe the interrelation between tribological characteristics with molecular mass and fire-fighting features. Basically, we examined neol and its derivatives junctions, as well as ionic SAS – DSSSA (disodium salt of sulfo-succinic acid) (*see table 1*)

1. Tribological Investigations on minitribometer TAU-1 and friction machine SMC-2

During the investigation of tribological features of SAS, soluted on minitribometer TAU-1, the following tasks have been set:

- to investigate the possibility of friction reduction in the area of contact between metals and metals with reinforced polymer by the use of solutes of investigated materials;
- to define the optimal concentration of SAS of mesogen type in water by the parameter of frictional coefficient.

The concentration dependence of frictional characteristics of such additives in water have been investigated on the above mentioned minitribometer by the following procedure [3] for different combinations of friction couples ($M_1 - M_1$, $M_1 - M_2$, $M_1 - M_3$ (for designation *see table 2*)).

Antifriction effect of the additive has been measured by the friction coefficient that has been counted according to the formula: $f_{fr} = 2M_{fr} / P \cdot d$, where M_{fr} is the moment of friction, Nm, P – constant load, N, d – plate diameter, m, friction couples ($M_1 - M_2$, $M_1 - M_3$), friction load reached $P = 80$ N, and the speed of circumduction was $v = 300$ r/min.

The dynamics of tribological processes have been examined on the friction machine SMC-2 by the mentioned technique [2] and including the results of the research [7]. All the experiments are carried out in mode of boundary friction. The friction scheme is the following: the rotating disc (steel 45) – stationary disc (PTFE+8%Cu, Caprolon-B+8%Cu). Antiwear characteristics have been defined by the chord length of wear segment (Δh mm), that is elaborated on motionless sample during the definite time of examination (in our case it is 300 sec), above-referenced normal load, variable speed ($v_1 = 300$ r/МИН, $v_2 = 500$ r/МИН, $v_3 = 1000$ r/МИН), and varying concentration (*fig. 3*). The way of supply of lubricant composition in the friction zone is constant. Under this pressure and during this time of wear there should not ensue any backfins and the value of the groove width of wear will not differ a lot for one and the same experiment.

According to the results of the test (*fig.1, 2, 3*) we have chosen the concentration during which the maximum effect of the input of additive into water has been observed. For the investigated compositions of additives SAS₄+SAS₅ this concentration equalled 0,5 mass. %.

It can be observed that during all the cases the infusion of composition (SAS₄+SAS₅) of liquid crystal nature led to the improvement of water antifriction features (*fig.1-3*) in contradiction to the particular SAS of non-ionic nature.

Table 1

Analyzed SAS [6]

No.	Title	Structural formula
SAS ₁	Neonol 9/6	$ \begin{array}{c} \text{C}_9\text{H}_{19} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{H} \end{array} $
SAS ₂	Neonol 9/10	$ \begin{array}{c} \text{C}_9\text{H}_{19} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H} \end{array} $

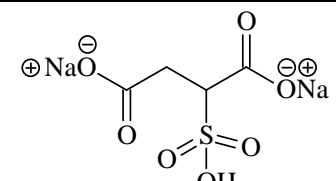
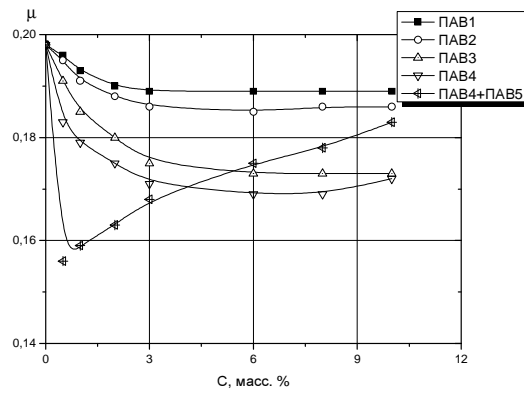
SAS₃	Sintanol BV	$C_n H_{2n+1} O (CH_2 CH_2 O)_m - \underset{\begin{array}{c} \\ CH_3 \end{array}}{CH} - O C_4 H_9$
SAS₄	Fenoksol 9/10 BV	$ \begin{array}{c} CH_3 \\ \\ H - C - O (CH_2 CH_2 O)_{10} - \text{C}_6\text{H}_4 - C_9H_{19} + H_2O \\ \\ O (CH_2 CH_2 O)_{10} - \text{C}_6\text{H}_4 - C_9H_{19} \end{array} $
SAS₅	DNSA	

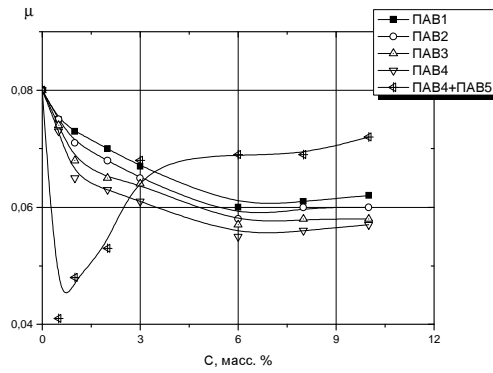
Table 2

Materials of Friction Couples

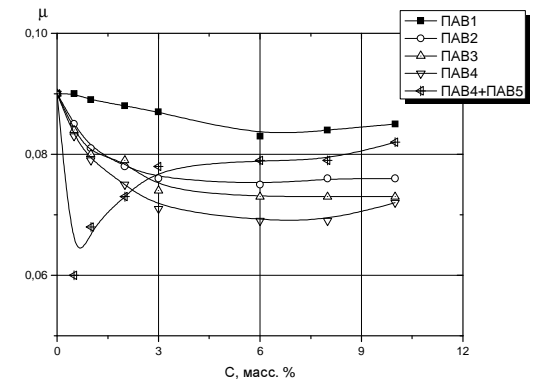
No.	Title	Designation
1	Steel 45	M₁
2	Caprolon-B+8 % Cu	M₂
3	PTFE +8 % Cu	M₃



a



b



c

Fig.1. The dependence of friction coefficient on concentration during model experiments on minitribometer TAU-1 for different friction couples: a – M_1-M_1 , b – M_1-M_2 , c – M_1-M_3 .

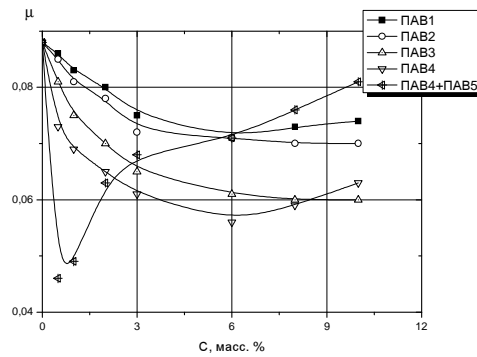
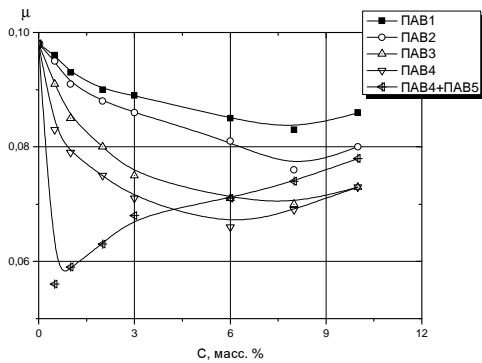
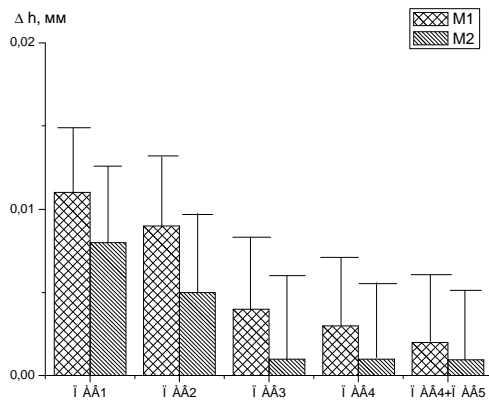
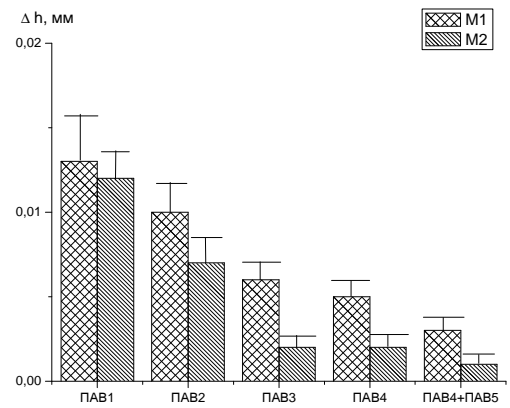


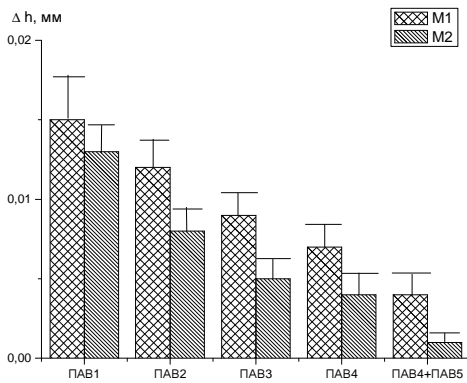
Рис. 2. The dependence of friction coefficient on the additive concentration during the experiments on the friction machinery SMC-2: M_1-M_3 , M_1-M_2



a



б



B

Fig. 3. The dependence of the amount of linear wear of water-lubricating friction couples in 0,5 % of non-ionic SAS and its compositions with ionic ones on the rotatory speed of counterbody (a – $v_1=300$ r/min, b – $v_2=500$ r/min, c – $v_3=1000$ r/min) and constant load in 80 N.

2. Physico-chemical investigations of additives

We paid attention to the sudden fall of friction coefficient during the introduction of composition (SAS₄+SAS₅) mesogen additive along with 0,5 mass. %, which we explain by its self-organization [3, 8] and transformation into mesophase. The temperature of the composition near the friction zone was 50 – 60 °C, and in the friction zone itself it could reach temperature interval of mesophase existence of the given mesogen [8]. We suggested a variety of reasons of such behaviour of the additive: the molecular destruction or polymerization of hydrogen (see fig.4).

But as far as we can see, the main contribution to the reduction of friction coefficient during the introduction of composition (SAS₄+SAS₅) into water is

made by the change of phase state of the additive, i.e. the transformation from liquid phase into the highly-ordered liquid-crystal one (*see fig.4*).Such conclusion is proved by additional experiments of the amalgam with wider interval of metaphase existence, in comparison with particularly taken NSAS, that was in the interval from 63 to 79 °C (*fig. 5*). The temperature control has been realized with the help of thermal imager Funike. This method of temperature registration in the friction zone has been chosen assuming that:

- foremost, it's noncontact, i.e. the conditions of the realization of experimental studies don't influence on instrumental indication, recording the temperature;
- secondly, it allows to get the digital picture of temperature field distribution in friction zone with the possibility of further processing.

Figure 6 represents indicative pictures of temperature field distribution in the friction area for the analyzed lubricant samples.

It's also necessary to make allowance of the fact that during the interaction of SAS₄ and SAS₅ we observe synergistic effect, that's why there isn't such bounce of friction coefficient in particularly introduced NSAS.

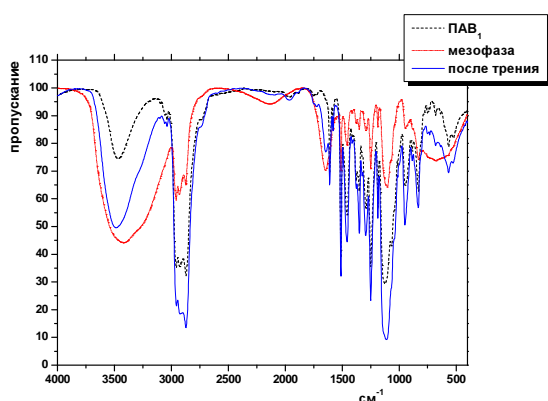


Fig. 4.1. The dependence of transmission coefficient on wave parameter for SAS₁, mesophases before and after friction.

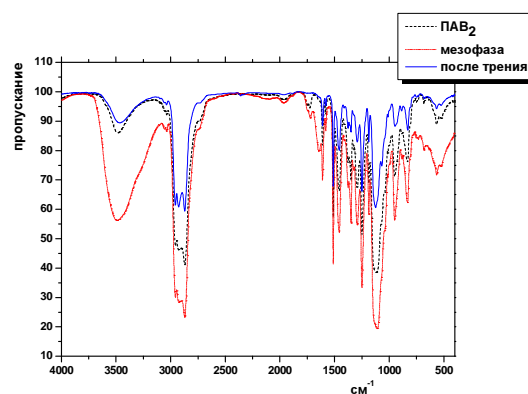


Fig. 4.2. The dependence of transmission coefficient on wave parameter for SAS₂, mesophases after and before friction.

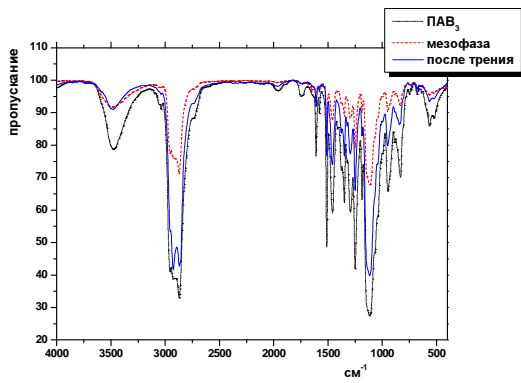


Fig. 4.3. The dependence of transmission coefficient on wave parameter for SAS₃, mesophases before and after friction.

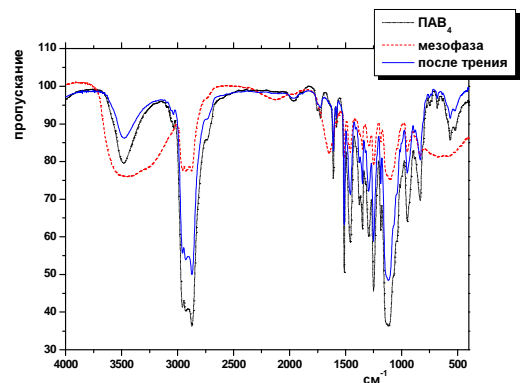


Fig. 4.4. The dependence of transmission coefficient on wave parameter for SAS₄, mesophases before and after friction

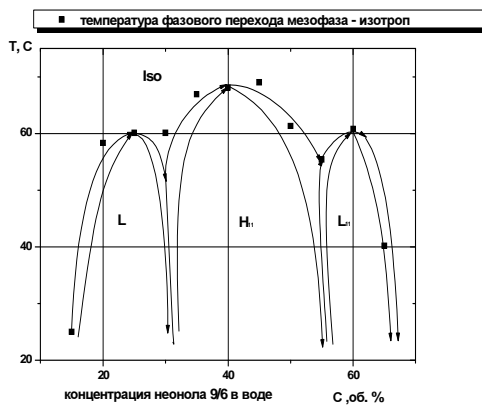


Fig.5.1 Diagram of phase transition of aqueous solutions of SAS₁ – water. Heating procedure.

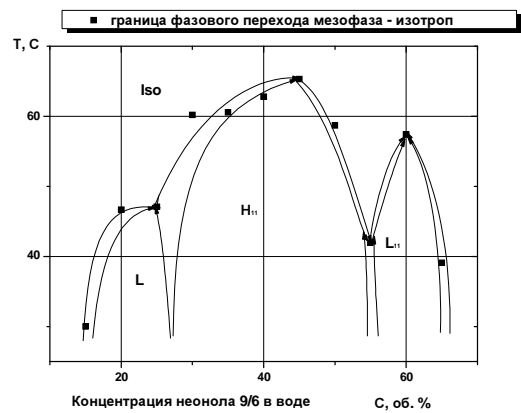


Fig. 5.2. Diagram of phase transition of aqueous solutions of SAS₁ – water. Cooling procedure.



Fig. 5.3. Photomicrograph of solution (SAS₂ 35 r. % in water) under the temperature of 23 °C (x 250). Polyline harp texture.

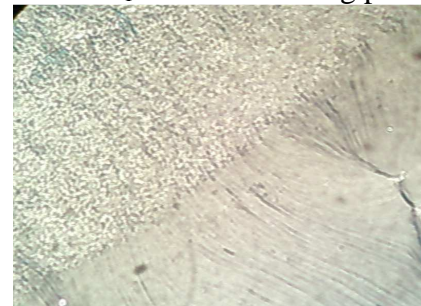


Fig. 5.4. Photomicrograph of solution layer (SAS₁ 55 r. % in water) under the temperature of 23 °C (x 250). Double-phase area.

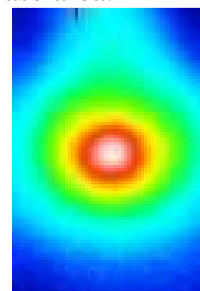
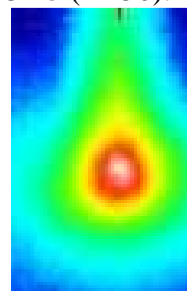
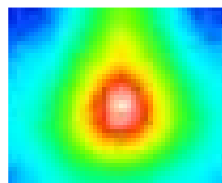
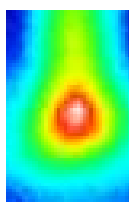


Fig. 6. Temperature field distribution in the friction zone:
a). SAS₁; b). SAS₂; c). SAS₃; d). SAS₄.

The obtained data shows that the molecules of complex SAS₄+SAS₅, sorbing with the flat central part on the contact surface of metal, produce well-ordered supramolecular assemblies [9, 10] that has the reduction of cohesive energy in the line of the action of shear deformation during the transition into mesophase, but it doesn't virtually change the energetic of domain interaction. The influence of additives-mesogens on the wear characteristics of the polymer materials with metal evaporation is ambiguous. Nevertheless, the maximum effect is achieved during the introduction of additive SAS₄+SAS₅ into water. Due to the concentration, the wear rate reduces in 2,5-3 times.

Conclusion

The results of express valuation of water lubricating properties in additive introduction (SAS₄+SAS₅) showed the perspective of their usage in *water lubricant*. Consequently, the fulfilled investigation of tribological characteristics of lubricant compositions, including NSAS from the class of neonol derivatives, point out the effectiveness of its usage as antiwear and antifriction additive. We can also deduce an inference that in some cases it was *LC* phase state of additive of **texogonal type** which led to the improvement of friction conditions in tribocouple.

It's important to note some peculiarities of molecular structure of the analyzed NSAS-additives: a) anisometric features of molecules and the availability of benzene ring that defines *LC* nature of the given class of NSAS. Therewith, all the junctions form the hexagonal packing.

It is set that additives of *hexagonal type*, oriented along the rubbing surface, produce stronger reductive effect either on the friction coefficient or on the amount of linear wear towards, for example, *columnar mesophase*.

Herein, it's necessary to take into account the contribution, made by the molecular structure of the additive, which influences the mechanism of its sorption with metal conjugated surface.

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