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**INVESTIGATION OF SURFACE-ACTIVE PROPERTIES OF NITROGEN-CONTAINING DERIVATIVES OF 2-PROPENYLPHENOL COOLIGOMERS WITH MALEIC ANHYDRIDE**

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By the reactions of double cooligomers of 2-propenylphenol and maleic anhydride (M~4500) with various amines their water-soluble nitrogen-containing derivatives have been synthesized. The surface-active properties of latter ones at the border of aqueous solution-air have been investigated and some parameters of micelle formation have been determined

**Key words:** *2-propenylphenol, amines, cooligomers, surface tension*

As it was known the chemistry of surface-active substances (SAS) is referred to the intensively developing field of modern science. Especially it concerns water- and oil-soluble polymer and copolymer compounds containing various functional groups in its structures [1-4]. Many of them are used in the oil-extraction, purification of water surfaces from oil pollutions, in biotechnologies, in the production of additives to lubricating oil, medical products and other valuable products. Due to availability of potentially necessary fragments in the structures of SAS even at their low concentrations it is possible to decrease considerably surface (interphase) tension at the border of solution with air, liquid or solid body. The amphoteric SAS containing various types of acidic and basic groups and also intramolecular salts in the structures take an important place among them [5].

We with the aim of preparation of new water-soluble SAS, which can found an application at purification and oil collection and oil products with water surface have carried out the investigations on synthesis of double cooligomers of 2-propenylphenol and maleic anhydride and their chemical conversions on anhydride ring and phenol hydroxyl – reactions with aliphatic and cyclic amines.

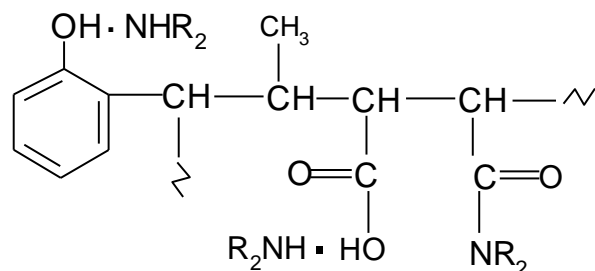
In this paper the results of the investigations on revealing of surface-active-active properties of the synthesized nitrogen-containing derivatives at the border of solution-air and determination of some parameters of micelle formation allowing to estimate their behaviour in the studied systems depending on structure and concentration are presented.

## EXPERIMENTAL

2-propenylphenol used in work has been prepared on known methodology by isomerization of 2-allylphenol in the presence of methanol solution of KOH [6]. 2-propenylphenol cooligomers with maleic anhydride have been synthesized at temperature 80°C by free-radical cooligomerization at molar ratio 1:1. The process was carried out in glass ampoules in the presence of initiator – dinitrile of azoisobutyric acid for 3 h. A yield of cooligomers is 97-98%. They were white substances with softening temperature 133-135°C. Comonomer – maleic anhydride was recrystallized from solution of acetone by heptane and used in fresh view.

The modification of cooligomers by amines (diethylamine, diethanolamine, piperidine, morpholine) was carried out in the moderate conditions (at temperature 35-40°C) at molar ratio from 1:1 to 1:3 mol and duration for 1.5-2 h. The yields of the modified cooligomers were from 82 to 94%. They were the substances of light-yellow color well soluble in water.

It has been revealed that a ratio taken for modification of amine to cooligomer shows an essential influence on structure of the prepared nitrogen-containing derivatives. At ratio 1:1 mol a reaction proceeds on OH-group (with formation of phenol salt). At ratio cooligomer : aliphatic amine=1:3 mol, i.e. in excess of amine the latter one undergoes the reaction both on OH-group of phenol and on anhydride group of maleic link with formation of nitrogen-containing derivatives of the following structure (on an example of cooligomer reaction with diethylamine (comp.I) and diethanolamine (comp.II)):



where R-C<sub>2</sub>H<sub>5</sub>(I), -CH<sub>2</sub>-CH<sub>2</sub>OH(II).

The formation of these compounds is confirmed by data of IR-spectroscopy. In the field of 1650-1450 cm<sup>-1</sup> the absorption bands corresponding to amide group, ammonium ion, the bands corresponding to C=O group -1772 cm<sup>-1</sup> have been detected. The absorption bands referring to OH-group have been not revealed.

For estimation of adsorption properties of substance three parameters are basic: its concentration in phase volume (C), adsorption or surface concentration (G), and also surface tension (σ), measured at definite temperature (T).

For estimation of surface-active properties of the synthesized nitrogen-containing derivatives the samples prepared at ratio cooligomer : amine – 1:3 mol were used.

The values of surface tension from aqueous solutions at the border with air by stalagmometric method [7] were determined on formula:

$$\sigma = V_k \rho g / 2\pi r$$

where  $r$ -radius of capillary,  $V_k$ -volume of liquid drops,  $\rho$ -liquid density.

Based on the results some colloid-chemical parameters of aqueous solutions of the synthesized nitrogen-containing derivatives of cooligomers have been calculated (I-IV).

For this purpose it was drawn a plot of isotherm of surface tension in coordinates  $\sigma$ - $C$  and  $\sigma$ - $\ln C$ . On an isotherm in semilogarithmic coordinates two points responsible for achievements of limit adsorption  $\Gamma_{\max}$  (transition from curvilinear to straight site of isotherm and CCM (critical conversion of micelle formation) are noted. Both curves are tangent. Tangent of a slope of tan-

gent line conducted to an isotherm is equal to  $\frac{d\sigma}{d \ln C}$ .

A maximum value of adsorption of  $G_{\max}$  can be calculated on formula [8]:

$$G_{\max} = - \frac{1}{RT} \frac{d\sigma}{d \ln C}$$

where  $R$ -universal gas constant (8.314 J/molK),  $T$ -absolute temperature.

For determination of surface pressure ( $\pi$ ) of solutions of nitrogen-containing cooligomers at the border of aqueous solution-air was used a formula:

$$\pi = \sigma_0 - \sigma_{\text{CCM}}$$

where  $\sigma_0$ -value of surface tension at the border of liquid-air without SAS,  $\sigma_{\text{CCM}}$  - value of surface tension corresponding to CCM.

The value of free Gibbs energy of micelle formation ( $\Delta G_{\text{mic}}$ ) was calculated on formula [8]:

$$\Delta G_{\text{mic}} = -RT \ln X_{\text{CCM}}$$

where  $X_{\text{CCM}}$ -concentration of critical concentration of micelle formation of SAS.

Free Gibbs energy of adsorption process at the border of liquid-air calculated on formula:

$$\Delta G_{\text{ads}} = \Delta G_{\text{mic}} - 6.023\pi A_{\text{min}}$$

It has been also calculated a minimum surface area of cross-section of polar groups ( $A_{\text{min}}$ ) of the synthesized cooligomers on formula [8]:

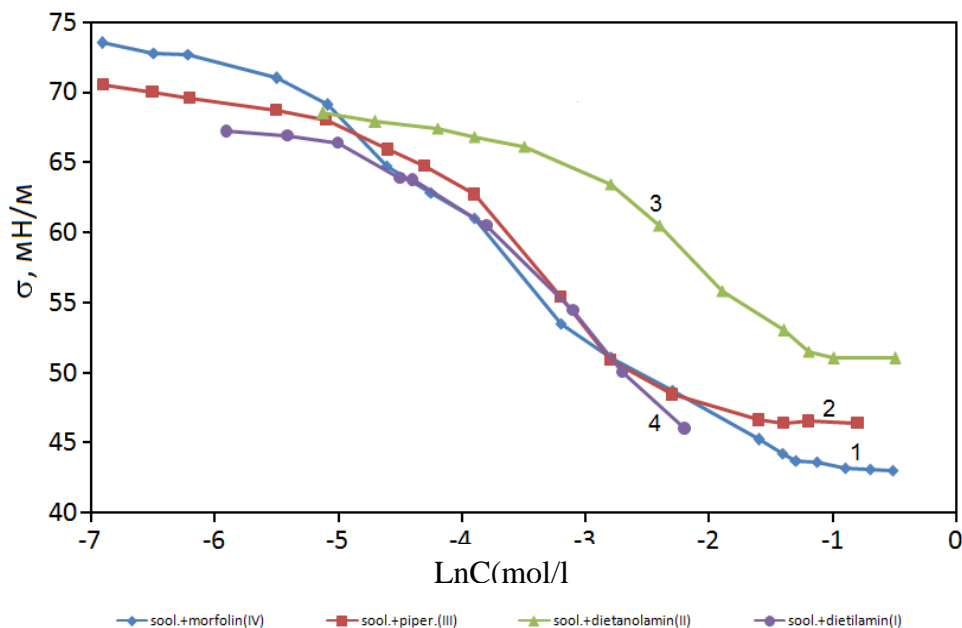
The investigated SAS are diphyll molecules consisting of polar (hydrophilic) and non-polar (hydrophobic) parts able actively to interact with surfaces of various polarity, to be adsorbed at the border of water-air and water-oil and to decrease surface tension of solutions.

A determination of surface tension of SAS is important as on the basis of obtained data one can calculate many characteristics as adsorption, work of adsorption, surface activity, etc.

A surface tension is the free energy of surface layer being a function of molecular forces, geometry of molecule and also a quantity of atoms.

## RESULTS AND DISCUSSION

The isotherms of surface tension (in coordinates  $\sigma$ - $\ln C$ ) of investigated nitrogen-containing compounds (I-IV) in their various concentrations in the distilled water at the border of aqueous solution-air at temperature 25°C are presented in Fig.1.



**Fig.1.** Dependence of surface tension of aqueous solution of comp.(I-IV) at the border with air on content

An analysis of character of isotherm of surface tension (on an example of compound 1 prepared by interaction of cooligomer with diethylamine) shows that it consists of three sites. On a curvilinear site (in accordance with Gibbs equation) it takes place an adsorption; further on achievements of limit adsorption a dependence  $\sigma$ - $\ln C$  has a linear character. Finally, the third straight site (straight, parallel to the axis  $\ln C$ ) evidences about formation of micelles, in which a surface tension is not practically further decreased owing to achievements of CCM. An isotherm of surface tension of compound II is close to an isotherm of compound I.

As follows from character of cr.2, and in a case of nitrogen-containing cooligomer prepared by its reaction with diethanolamine a regularity on decrease of surface tension to achievements of CCM, one can say, is kept. Isotherms of surface tension of compounds containing cyclic amines fragments in the structures are rather differed between themselves.

The found values of CCM for cooligomers of 2-propenylphenol with maleic anhydride modified by diethylamine (I), diethanolamine (II), piperidine (III), morpholine (IV) are the following: 0.326; 0.133; 0.103; 0.256 mol/l. It has been established that in these values of CCM it is

observed a decrease of surface tension to 50.2;46.0; 46.4; 43.0 mN/m, while its value at the border of distilled water-air is 72 mN/m.

Based on isotherms of surface tension of the investigated nitrogen-containing cooligomers there have been calculated some parameters characterizing the adsorption processes and micelle formation in the systems of aqueous solutions-air which are presented in Table 1.

As follows from data presented in Table the investigated compounds differing from each other by nature of bonded amine, on its surface-active properties, one can say, are close. Their investigation in aqueous systems containing oil pollutions on surface showed that they can be successfully used for oil collection.

**Table 1.** Parameters of adsorption processes and micelle formation of compounds

Compound	CCM·10 <sup>1</sup> , mol dm <sup>-3</sup>	Q <sub>max</sub> ·10 <sup>2</sup> , mol sm <sup>-2</sup>	A <sub>min</sub> ·10 <sup>2</sup> , nm	π <sub>CCM</sub> mH m <sup>-1</sup>	π <sub>CCM</sub> mH m <sup>-1</sup>	p C <sub>20</sub>	G <sub>mic</sub> ,kJ mol <sup>-1</sup>	G <sub>ads</sub> kJ mol <sup>-1</sup>
I	1.33	1.63	101.7	46.0	26.0	1.19	-5.0	-6.6
II	3.26	1.29	128.7	50.2	21.8	0.64	-2.8	-4.5
III	1.03	4.31	38.5	46.4	25.6	1.27	-5.7	-6.8
IV	2.56	2.71	61.2	43.0	29.0	1.32	-3.4	-5.2

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