

## SURFACE - ACTIVE COPOLYMERS OF VINYL ETHERS

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### ABSTRACT

*This paper describes the results of synthesis and investigation of the physico-chemical properties of water-soluble copolymers of monoethanolamine (MEAVE) and ethylene glycol vinyl ethers (EGVE) with 2-acrylamido-2-methylpropanesulfonate sodium (Na-AMPS) at a low monomer conversion. The copolymer formation is verified by IR - spectroscopy, an elemental analysis and a potentiometric titration.*

*The values of the copolymerization constants show a lower relative activity of vinyl ethers compared with that of 2-acrylamido-2-methylpropanesulfonate.*

*Studying the copolymers hydrodynamic properties, it is identified that they are polyelectrolytes. The adsorption at the aqueous solution-air interface is studied and the values of Rebinder surface activity ( $G_{re}$ ) and the standard free energy of adsorption ( $\Delta_{ads} G_{298}^0$ ) are calculated in order to determine the surface properties of the copolymers of vinyl ethers with 2-acrylamido-2-methylpropanesulfonate sodium. Based on these results it is concluded that the synthesized copolymers are surfactants, while their surface activity increases in the series: poly- Na-AMPS < copolymer EGVE- Na-AMPS < copolymer MEAVE -Na-AMPS.*

*The higher surface activity of the copolymers compared to that of poly(acrylamide-2-methylpropane sulfonate sodium) homopolymer is explained from the viewpoint of improving the hydrophobicity of the macromolecular chain.*

*Keywords:* vinyl ethers, constants of copolymerization, adsorption, surface activity.

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### INTRODUCTION

In recent years, a remarkable development related to the synthesis of copolymers of various salts of 2-acrylamido-2-methylpropane sulfonic acid and the study of their properties as a function of the acidity, the ionic strength of the medium, the conversion, the charge of the cation, etc. is observed [1, 2].

This interest is explained by the fact that the specific features of the behavior of the strong unsaturated electrolytes in the course of the polymerization processes have not been extensively studied, while the laws of radical polymerization and copolymerization of weak unsaturated electrolytes in various media have been

thoroughly analyzed in the monography of Kabanov and Topchiev [3].

On the other hand, the interest towards the synthesis of new high-molecular compounds based on acrylamide derivatives is associated with the continuous increase of their application areas as highly efficient thickening agents, flocculants, soil builders, absorbents, etc. [4].

It should be pointed out that the systematical investigations mentioned above are basically related to the copolymerization of salts of 2-acrylamido-2-methylpropane sulfonic acid with acryl monomers, while there is no data referring to their copolymerization with vinyl ethers.

Despite of the activity law in radical homopolymerization, vinyl ethers are capable to copolymerize with

numerous monomers [5]. It is noteworthy that the available published data on radical copolymerization of vinyl ethers is mainly devoted to reactions with conjugated vinyl monomers, while reactions with ionic monomers have been less studied.

In our case, vinyl ethers containing active functional groups like amino- and hydroxide groups are capable of participation in various reactions under mild conditions. The combination of the polar hydrophilic groups and the nonpolar hydrophobic sections of the chain in the macromolecules can arise surface-active properties of the functional polymers and thus provide their application as effective flocculants, flotation agents, antistatics, dispersant stabilizers, etc. in various fields of industry, agriculture and many other areas.

This paper describes the regularities of the radical copolymerization of vinyl ethers of monoethanolamine and of ethylene glycol with 2-acrylamido-2-methylpropanesulfonate sodium, and some of the physico-chemical properties of synthesized copolymers discussed in view of data reported previously [6].

## EXPERIMENTAL

Monoethanolamine vinyl ether (MEAVE) containing 99.5 % of the main product was dried for 7 - 8 days with potassium carbonate and twice distilled in vacuum.  $T_b = 390\text{K}/92\text{ kPa}$ ,  $n_D^{20} = 1,4382$  (Ltd "Alash", Temirtau, Kazakhstan).

Ethylenglycol vinyl ether (EGVE) was purified by a vacuum distillation.  $T_b = 345\text{K}/30\text{ kPa}$ ,  $n_D^{20} = 1,4356$  (Ltd "Alash", Temirtau, Kazakhstan).

2-acrylamido-2-methylpropanesulfonate sodium (Na-AMPS) monomer was prepared from 2-acrylamido-2-methylpropanesulfonic acid (H-AMPS) (the content of the main product was no less than 99 mass %) purchased from Avocado Research Chemicals Ltd. (Switzerland).

The free-radical copolymerization of MEAVE and EGVE with Na-AMPS was performed in an inert medium at 60°C at various molar ratios of the initial monomers in an aqueous solution (pH 9). The reaction was carried out in the presence of an equimolar mixture of sodium bisulfite and potassium persulfate as a redox initiator. The weight of the initiator was 0.1% with respect to the total comonomers weight.

The volume ratio of the solvent to the monomers was 1: 1. The reaction mixture pH was adjusted to 9

by the addition of 2 mol l<sup>-1</sup> NaOH solution, as the hydrolysis of Na-AMPS salts was prevented under these conditions [7].

The relative rate of copolymerization ( $v_{rel}$ ) was estimated by the dilatometry method at low degrees of monomers conversion [8]. The sealed dilatometer containing the initial mixture subjected to preliminary purging with high-purity argon was placed into a thermostat. The conversion did not exceed 10 %.

The copolymers were precipitated three times from the aqueous solution into acetone and then dried under a vacuum to a constant weight.

The synthesis of the copolymers was confirmed by IR spectroscopy, a potentiometric titration, and viscometry [6]. The composition of the copolymer was determined by IR spectroscopy, a potentiometric titration on EV-74 ionometer with the use of glass and silver chloride electrodes, and by an elemental analysis.

The copolymerization constants  $r_1$  (MEAVE, EGVE) and  $r_2$  (Na-AMPS) of the monomers were determined on the ground of the differential equation describing the composition of copolymers obtained at a low conversion by the methods of Mayo-Lewis and Kelen-Tüdös [9].

The viscosity of polymer solutions in water and NaCl solutions was measured with Ubellode viscometer at 20°C.

The surface tension ( $\sigma$ ) of the polymer sodium 2-acrylamido-2-methyl-propanesulfonate (Na-AMPS) aqueous solution, the copolymer of ethylene glycol vinyl ether-sodium-2-acrylamido-2-methyl-propanesulfonate (EGVE-Na-AMPS), and the copolymer of monoethanolamine vinyl ether - sodium 2-acrylamido-2-methyl-propanesulfonate (MEAVE-Na-AMPS) was estimated at 298 K applying the modified Wilhelmy's method [10]. The  $\sigma$  value of solutions was calculated according to the Eq. (1):

$$\sigma = \frac{(m_p - m_a) g}{2(l + d)} \quad (1)$$

where  $m_p$  and  $m_a$  were the masses of the plate in the solution and the air, respectively,  $g$  was the gravitational acceleration, while  $l$  and  $d$  were the width and the thickness of the submerged part of the plate, correspondingly.

The retraction force of the plate to the solution was measured using a torsion balance VT-500 with an accuracy of  $\pm 10^{-6}$  kg.



Table 1. The effect of the composition of the monomer mixture on the relative reaction rate ( $V_{rel}$ ), on the composition of the copolymers of MEAVE, EGVE ( $M_1$ ), and Na-AMPS ( $M_2$ ).

Composition of initial mixture, mol %		Composition of copolymers, mol %		$V_{rel}$
[ $M_1$ ]	[ $M_2$ ]	[ $m_1$ ]	[ $m_2$ ]	
MEAVE - Na-AMPS				
0	100	-	-	23,0
50,0	50,0	24,7	75,3	7,0
70,0	30,0	31,5	68,5	4,0
90,0	10,0	38,2	61,8	2,0
EGVE - Na-AMPS				
0	100	-	-	23,0
50,0	50,0	30,0	70,0	18,4
70,0	30,0	39,9	60,1	6,0
90,0	10,0	46,2	53,8	3,0

Table 2. Relative activities of monomers in radical copolymerization.

System	$r_1$	$r_2$	$1/r_1$	$1/r_2$	$r_1 \cdot r_2$
MEAVE- Na-AMPS	0,06±0,01	1,20±0,05	16,60	0,83	0,07
EGVE-Na-AMPS	0,07±0,01	2,50±0,15	13,30	0,40	0,19

initial mixture, but it does not exceed 40 mol % - 46 mol %.

The copolymerization constants are calculated on the ground of the values referring to the copolymers composition. As seen from Table 2 and Fig. 1, the copolymerization constants  $r_1 < 1$  and  $r_2 > 1$ . Consequently, the monomers of MEAVE and EGVE are less reactive in a radical copolymerization than Na-AMPS.

There is no inflection point on the composition curves (Fig. 1), i.e. the considered systems do not produce an azeotrope. This is in correspondence with the data of Table 2 ( $r_1 < 1$ ;  $r_2 > 1$ ).

The value of the product of the copolymerization constants is close to zero (Table 2) indicating a tendency to alternate the monomeric units in the macromolecule. However, when comparing the product of copolymerization constants for these two systems, it can be assumed that the propensity to alternation is more pronounced in the MEAVE-Na-AMPS macromolecule, where  $r_1 \cdot r_2$  is closer to zero when compared to that of EGVE-Na-AMC system.

Fig. 2 shows the polymer concentration effect on the reduced viscosities of Na-AMPS–MEAVE copolymer solutions in water and 0.1 mol l<sup>-1</sup> NaCl solution. It is evident that, for aqueous solutions of the copolymer, the viscosity decreases with the increase of the polymer concentration [19], whereas in 0.1 mol l<sup>-1</sup> NaCl solution, the decreased

viscosity tends to increase and this dependence follows a linear pattern (curves 1 - 3). These results testify that the copolymer under study is a typical polyelectrolyte.

An increase of the vinyl ether fraction in a mixture of MEAVE-Na-AMPS monomers leads to a decrease of the intrinsic viscosity of the copolymer (Fig. 2). This is also related to the low relative activity of the latter in radical reactions [14]. The same regularity is observed for EGVE-Na-AMPS system.

It is found that the viscosity values of the solutions of EGVE-Na-AMPS copolymer are much higher than those of the solutions of MEAVE-Na-AMPS copolymer. For example, for identical equimolar ratios of the initial monomers of 50 mol % : 50 mol %, the intrinsic viscosity of the solutions of EGVE-Na-AMPS copolymer is 6.2 dl g<sup>-1</sup>, while that in case of MEAVE - Na-AMPS is 2.10 dl g<sup>-1</sup>. This regularity is in correspondence with the values of the relative rates of copolymerization of the two systems discussed above.

Since the polymer chain of MEAVE-Na-AMPS contains basic amino- and acid sulfo-groups, it is important to look for ampholytic properties in view of the practical application of the copolymer. The dependence of the reduced viscosity on pH of the aqueous solution of the MEAVE-Na-AMPS copolymer obtained with a

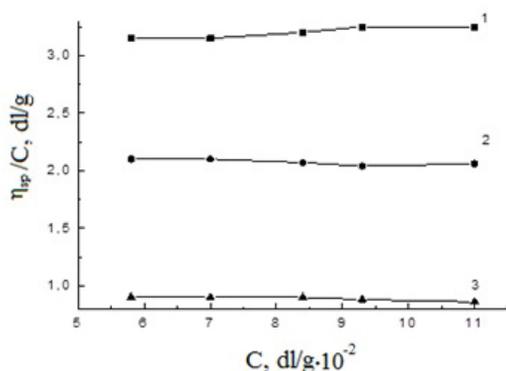


Fig. 2. Dependence of reduced viscosity on concentration of copolymer MEAVE-Na-AMPS in a medium of  $0.1 \text{ mol}\cdot\text{l}^{-1}$  NaCl. 1 - (25 : 75 mol %), 2 - (50 : 50 mol %), 3 - (75:25 mol %).

monomer ratio of 50 mol % : 50 mol % (Fig. 3) shows the presence of an isoelectric point (IEP), which is characteristic for polyampholytes. For MEAVE - Na-AMPS copolymer IEP is reached at  $\text{pH} = 5$ .

**Investigation of the copolymers surface properties. Adsorption of copolymers of EGVE-Na-AMPS and MEAVE-Na-AMPS at the solution-air interface**

The study of the macromolecules behavior at the interface is currently one of the most important tasks, since surface phenomena in polymers and polymeric materials are of great importance for their properties, especially their structural and mechanical properties.

The adsorption at the aqueous solution-air interface at 298 K is studied to determine the surface properties of the obtained EGVE-Na-AMPS and MEVEA-Na-AMPS copolymers.

The tensiograms of the copolymers aqueous solutions (Figs. 4 and 5) show that the equilibrium values

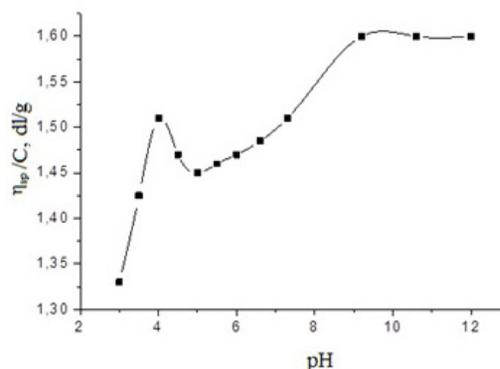


Fig. 3. Dependence of the reduced viscosity of the MEAVE-Na-AMPS copolymer solution on the pH. The monomer (MEAVE) content of the copolymer is 24,7 mol %.

of the surface tension ( $\sigma$ ) are established within several hours (Table 3). This is typical for high-molecular surface-active substances [15].

The isotherm of the surface tension of solutions of MEAVE-Na-AMPS and EGVE-Na-AMPS copolymers (curves 2, 3, Fig. 6) and poly-Na-AMPS homopolymer (curve 1, Fig. 6) is constructed on the ground of the equilibrium values of  $\sigma$ . It is seen that  $\sigma = f(c)$  dependence of MEAVE-Na-AMPS copolymer lies below that of EGVE-Na-AMPS copolymer indicating former greater surface activity. The higher surface activity of MEAVE-Na-AMPS copolymer is explained, as already noted, by the formation of an intramolecular salt bond, which determines the increase of the copolymer hydrophobicity leading to its compactification [16].

The values of Rebinder surface activity (Table 4) of poly-Na-AMPS and of the copolymers of MEAVE-Na-AMPS and EGVE-Na-AMPS are estimated from the isotherms  $\sigma = f(c)$ . Eq. (2) [17] is applied:

Table 3. The relaxation time of adsorption layers of MEAVE-Na-AMPS and EGVE-Na-AMPS copolymers at their various concentrations.

Copolymer	Concentration of copolymer, mass %	Relaxation time $\theta$ , min
MEAVE - Na-AMPS	0,02	145
	0,04	147
	0,09	150
	0,12	152
	0,50	172
EGVE - Na-AMPS	0,02	190
	0,04	423
	0,06	500
	0,08	126
	0,12	87

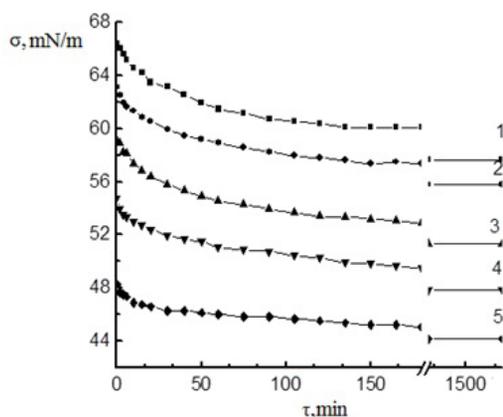


Fig. 4. Tensiograms of aqueous solutions of copolymer MEAVE-Na-AMPS ( $M_2 = 50$  mol %) at various concentrations (mass %): 1 - 0.02; 2 - 0.04; 3 - 0.09; 4 - 0.12; 5 - 0.5.  $T=298$  K.

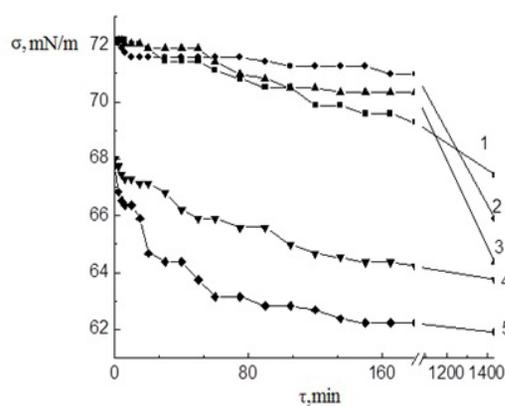


Fig. 5. Tensiograms of aqueous solutions of copolymer EGVE-Na-AMPS ( $M_1 = 50$  mol %) at various concentrations (mass %): 1 - 0.02; 2 - 0.04; 3 - 0.06; 4 - 0.08; 5 - 0.12.  $T=298$  K.

Table 4. Physical-chemical characteristics of surface layers of polymers.

System	$G_{Re} \cdot 10^{-3}$ , ( $mN m^{-1}) / (kmol m^{-3})$	$\Delta_{ads} G_{298}^0$ , kJ/mol
Poly-Na-AMPS	$1,5 \pm 0,3$	$-18,0 \pm 0,1$
Copolymer MEAVE - Na-AMPS	$9,1 \pm 0,3$	$-22,6 \pm 0,1$
Copolymer EGVE - Na-AMPS	$5,2 \pm 0,3$	$-21,2 \pm 0,1$

$$G_{Re} = \lim_{c \rightarrow 0} \left( -\frac{d\sigma}{dc} \right) \quad (2)$$

In addition, the standard free energy of adsorption ( $\Delta_{ads} G_{298}^0$ ) is calculated to elucidate the causes and the mechanism of the surface activity changes and the adsorption of the copolymer. It is so because it is one of the important characteristics of the spontaneous accumulation of the substance at the interface and serves as a measure of the tendency of the surface-active molecules to adsorption.  $\Delta_{ads} G_{298}^0$  is calculated using Eq. (3) [18]:

$$\Delta_{ads} G_{298}^0 = -RT \ln G_{Re} \quad (3)$$

The data of Table 4 shows that the gain of the standard free adsorption energy in the transition from the homopolymer Na-AMPS to the MEAVE-Na-AMPS copolymer amounts to  $4.6$  kJ base-mole $^{-1}$ , while the gain of the standard free adsorption energy upon transition from the homopolymer Na-AMPS to the EGVE-Na-AMPS is  $3$  kJ base-mole $^{-1}$ . Therefore, it can be argued that the adsorption of the MEAVE-Na-AMPS and EGVE-Na-AMPS copolymers at the water-air interface is much easier compared to the adsorption of Na-AMPS homopolymer.

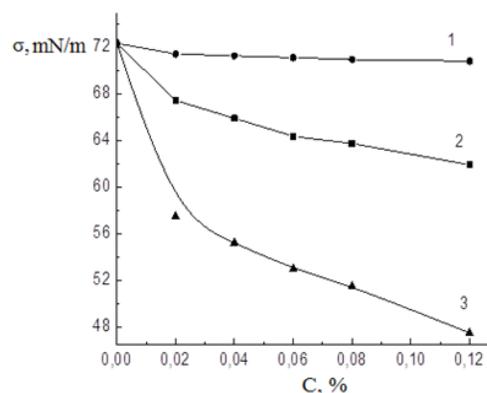


Fig. 6. Isotherms of surface tension of aqueous solutions of poly-Na-AMPS (1), copolymer EGVE-Na-AMPS (2) and copolymer MEAVE-Na-AMPS (3).

## CONCLUSIONS

Water-soluble surface-active copolymers of vinyl ethers of ethylene glycol and monoethanolamine with 2-acrylamido-2-methylpropanesulfonate were synthesized by the method of radical copolymerization at low monomers degrees of conversion. The relative activities of the monomers confirm the lower

activity of the vinyl ethers in this process.

It is found that the copolymers of vinyl ethers with Na-AMPS can reduce the surface tension of water to a considerable extent in comparison with the homopolymer Na-AMPS, i.e. the vinyl ethers units in the polymer chain increase the surface activity of the macromolecules.

It is shown that the copolymers of MEAVE-Na-AMPS are polyampholites and have a higher surface activity than the copolymers of EGVE-Na-AMPS, which is explained in case of MEAVE by the formation of an intramolecular salt bond between the sulfate anion and the amino-group leading to an increase of the hydrophobicity and the compactification of the copolymer.

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