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Surface - Active and Complexforming Copolymers of Sodium 2-acrylamido-2-methylpropanesulfonate with Ethyleneglycol Vinyl Ether

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Abstract

A new water-soluble polyelectrolyte - the copolymer of sodium 2-acrylamido-2-methylpropanesulfonate and ethylene glycol vinyl ether has been synthesized by free-radical copolymerization in aqueous medium. Synthesis of the linear structure water-soluble copolymer of sodium 2-acrylamido-2-methylpropanesulfonate (Na-AMPS) and ethylene glycol vinyl ether (EGVE) has been confirmed by IR spectroscopy method, potentiometric titration and viscometer. The concentration behavior of the reduced viscosity of copolymer solutions that is typical for polyelectrolytes has been revealed.

The reactivity ratios for the copolymerization of the monomers estimated by the Mayo–Lewis method have indicated lower reactivity of ethylenglycol vinyl ether in comparison with sodium 2-acrylamido-2-methylpropanesulfonate.

Also it was shown the decrease of reaction's relative rate with an increase of molar fraction of EGVE in the initial mixture of monomers.

Adsorption at the air-water solution interface was studied by measure of surface tension (σ) in order to determine the surface properties of new copolymers of ethyleneglycol vinyl ethers – sodium 2-acrylamido-2-methylpropanesulfonate.

It was shown that copolymers of sodium 2-acrylamido-2-methylpropanesulfonate and ethylenglycol vinyl ether have higher surface activity compared to sodium 2-acrylamido-2-methylpropanesulfonate homopolymer.

The isotherm of copolymer's surface tension based on equilibrium value of σ was constructed together with the isotherm of surface tension water solution poly- Na-AMPS. Based on isotherms the surface activity on Rebinder (G_{Re}) for poly- Na-AMPS and copolymer Na-AMPS-EGVE was determined.

The values of polymer's standard free energy of adsorption ($\Delta_{ads}G^{0}_{298}$) were calculated in order to identify the causes and mechanism of change in surface activity and adsorption. Results show that the gain in standard free energy adsorption in the transition from homopolymer to copolymer Na-AMPS-EGVE is about 4 kJ/base-mole.

Interpolymer reaction of the Na-AMS–EGVE copolymer with poly- *N,N*-dimethyl-*N,N*-diallylammonium chloride (PMAAC) has been studied. Higher surface activity of mixtures of copolymer and PMAAC than of individual polyelectrolytes was discovered. This effect testified to the formation of interpolymer complex of the Na-AMS–EGVE copolymer with polycations due to electrostatic interactions.

Introduction

Interest aroused in the synthesis of new high-molecular compounds based on acrylamide derivatives is associated with a continuous widening of their application areas as highly efficient thickening agents, flocculants, soil builders, absorbents, regulators of rheological characteristics of drilling fluids, and film-forming materials for prolonged pharmaceutical preparations, stabilizing and antistatic agents for photomaterials [1-4]. Among acrylamide derivatives, 2-acrylamido-2-methylpropanesulfonic acid and its salts attract particular attention since they allow one to synthesize diverse water-soluble polymers [5, 6].

We have selected ethylenglycol vinyl ether (EGVE) as the second comonomer for copolymerization with the sodium salt of 2-acrylamido-

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2-methyl-propane sulfonic acid (Na-AMPS). EGVE is of particular interest since it contains ether oxygen nearby double bond and functional OH- groups capable to participate in various reactions under mild conditions in order to obtain new valuable high-molecular compounds.

The vinyl ether of ethylene glycol (EGVE) with acrylamide (AA), acrylonitrile, butyl methacrylate (BMA), vinyl acetate, methyl methacrylate and hydroxyethyl methacrylate (HEMA) copolymers synthesized by radical copolymerization [7-9]. Synthesized copolymers have novel hydrophilic linear and crosslinked structure. It was shown copolymer hydrogels EGVE -BMA have relative low thermo sensitivity, which can be regulated by introduction of ionic unit of AA into polymer network. It was shown that polymer network of EGVE -HEMA and EGVE -BMA have typical physicochemical properties of thermo-sensitive hydrogels which can be regulated by varying hydrophilic-hydrophobic balance of macromolecule in the wide range.

It should be noted that no published data is available on the copolymerization of sodium salt of 2-acrylamido-2-methyl-propane sulfonic acid (Na-AMPS) with ethylenglycol vinyl ether (EGVE).

Experimental

The Na-AMPS monomer was prepared from 2-acrylamido-2-methylpropanesulfonic acid (H-AMPS) (the content of the main product was no less than 99 wt.%) purchased from Avocado Research Chemicals Ltd. (Switzerland). This substance was used as received.

EGVE was purified by vacuum distillation (T_b=72 ºC/30 kPa, n_D^{20} = 1.4356) ("Alash", Temirtau, Kazakhstan).

The commercial sample of poly(N,N-dimethyl-N,N-diallylammonium chloride) (PMAAC) (Sterlitamak, Russia) with $M = 7{\cdot}104$ was reprecipitated from aqueous solution into acetone and vacuum dried at room temperature.

The free-radical copolymerization of Na-AMPS and EGVE was performed in an inert medium in sealed dilatometers at 60 °C at various molar ratios of the initial monomers in 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 weight of comonomers.

The relative rate of copolymerization (v_{rel}) was estimated by dilatometry method at the low degrees of monomers conversion [10]. Dilatometer after purging with high-purity argon and sealing was placed into thermostat.

The relative reaction rate was calculated by tangency angle incidence dependency of the relative change in volume of the reaction mixture (ΔV/V) from the reaction time (τ); where $\Delta V = \pi r^2 \Delta h$, V – initial monomer's mixture volume in dilatometer, r – radius of the capillary, cm, Δh – change in the level of the meniscus of the capillary during the reaction, cm. Shrinkage of the polymer was measured on a graduated scale. The conversion did not exceed 10%.

The resulting copolymer was precipitated two times into acetone and vacuum dried at 40 °C to a constant weight.

The composition of the copolymer was determined by IR-spectroscopy and potentiometric titration on an EV-74 ionometer with the use of glass and silver chloride electrodes.

The viscosity of polymer solutions in water and NaCl (0.1 mol/l) solutions was measured with an Ubbelode viscometer at 25 °C.

The IR-spectra of copolymers were taken on an Avatar 370 CsI FTIR spectrometer in the spectral region of 400-4000 cm^{-1}.

To measure the spectra of the Na-AMPS–EGVE polycomplex with PMAAC, the samples were prepared as Vaseline emulsions on KRS-5 plates.

The optical density D of the solution of polymer mixtures was determined on an SF-16 spectrophotometer at an incident light wavelength of 600 nm. The as-prepared aqueous solutions of polymers were used within two days.

The polycomplexes of the polymers were prepared through the gradual addition of a solution of one polymer to a solution of the second polymer under intense stirring. The solution thus prepared was allowed to stand for 24 h for the equilibrium state to be attained at room temperature. Thereupon, the viscosity and pH of the test solution were measured. In calculations of concentrations of PMAAC solutions, the molecular mass of the repeating unit of the polymer (base-mole/l) was used; in the case of the Na-AMPS–EGVE copolymer, the average molecular mass M_{av} of the repeating monomer units was taken

$$M_{av} = M_{\text{Na-AMS}} \cdot v_{(\text{Na-AMS})} + M_{\text{EGVE}} \cdot v_{(\text{EGVE})}$$

where M and v are the molecular mass and molar fraction of the monomer unit of the copolymer, respectively.

In mixtures with polyelectrolytes, the relative concentration of the copolymer was expressed as the ratio between the molar concentration of the active monomer unit (Na-AMPS) involved in interpolyelectrolyte interaction and the molar concentration of the other polymer.

Results and Discussion

Synthesis of the new copolymer Na-AMPS–EGVE has been confirmed by IR spectroscopy method (Fig. 1).

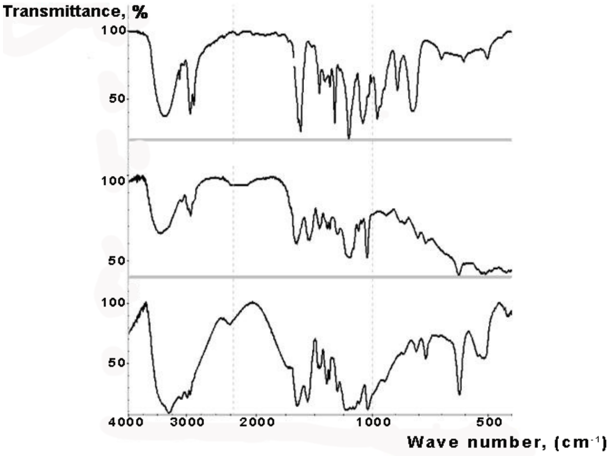
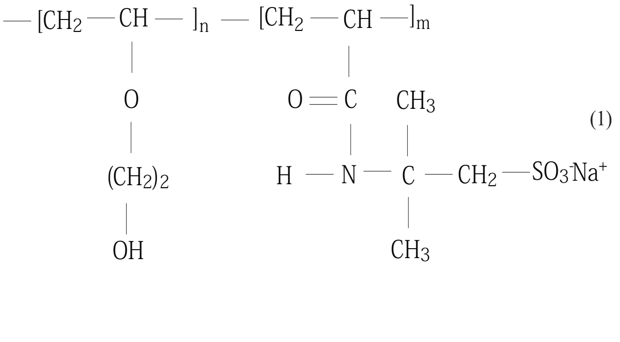


Fig. 1. IR spectra of EGVE (1), copolymer Na-AMPS–EGVE containing 70 mol.% Na-AMPS (2) and poly- Na-AMPS (3).

The IR spectra of the EGVE demonstrate absorption band at 1620 cm^{-1} characteristic of the -C=C- double bond, while the spectra of copolymer don't have such band at this field. The spectra poly- Na-AMPS has absorption band at 1647 cm^{-1} characteristic of the stretching vibrations of –C=O groups, while in the spectra of copolymer characteristic absorption band of the carbonyl groups displaced (1713 cm^{-1}). In addition, the spectra of copolymer demonstrate broad absorption bands at 3327-3444 cm^{-1} characteristic of the stretching vibrations hydroxide and amide- groups. Comparison of the IR spectra of the copolymer vinyl ether monoethanolamine (MEAVE) and Na-AMPS with IR spectra EGVE -Na-AMPS copolymer also confirms the formation of copolymer [11].

IR spectroscopy, potentiometric titration and viscometer confirmed that the free-radical polymerization yielded the new linear structure water-soluble copolymer Na-AMPS–EGVE of the general formula:



$$-[CH_2-CH(O(CH_2)_2OH)-]_n-[CH_2-CH(C(=O)-NH-C(CH_3)_2-CH_2-SO_3^-Na^+)-]_m \qquad (1)$$

The composition of the copolymers, as estimated by potentiometric titration (Table 1), testifies that, at any initial comonomer ratios, the copolymer enriched with Na-AMPS (M_2) units is formed. Thus, results show more relative reactivity Na-AMPS in comparison with EGVE in free -radical copolymerization.

Table 1
Copolymerization EGVE (M_1) and Na-AMPS (M_2) at various ratios of initial mixture

Composition of the initial mixture, mol %		The nitrogen content, N %	Composition of the copolymer, mol %		[η], dl/g	ν_{rel}
M_1	M_2		M_1	M_2		
0	100	-	-	-	15.6	2.30
50	50	5.25	30.0	70.0	6.2	1.84
70	30	4.87	39.9	60.01	5.1	0.60
90	10	4.51	46.2	53.8	2.1	0.30

Figure 2 shows the effect of polymer concentration on the reduced viscosities of Na-AMS- EGVE copolymer solutions in water and 0.1 mol/l NaCl solution. This evident that, for aqueous solutions of the copolymer, viscosity decreases with an increase in the polymer concentration (curve 1), whereas in 0.1 mol/l NaCl solution, the reduced viscosity tends to increase and this dependence follows the linear pattern (curves 2-4). These results testify that the copolymer Na-AMPS–EGVE under study is a typical polyelectrolyte. With increasing the units of EGVE in the monomer mixture indicate a decrease in the values of the intrinsic viscosity of the copolymers (Table 1), which is associated with a low relative activity of the copolymer in radical reactions [12, 13].

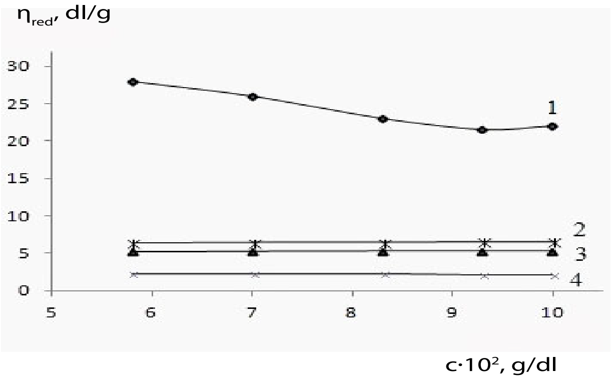


Fig. 2. The reduced viscosity of the Na-AMPS-EGVE copolymer solution (1) in water and (2-4) 0.1 mol/l NaCl the concentration of the polymer. The content of EGVE in the copolymer is (1, 2) 30, (3) 39.9, and (4) 46.2 mol.%.

The reactivity ratios for the copolymerization of the monomers, as estimated by the Mayo-Lewis method [14], were $r_1 = 0.075$ and $r_2 = 2.5$ (Table 2). These values show that the reactivity of EGVE is lower than that of Na-AMPC. Such as a low reactivity of EGVE radicals in copolymerization with other vinyl monomers is explained by the fact that oxygen of vinyl ether has no unoccupied stable orbitals. Therefore, the resonance stabilization between a vinyl radical and an oxygen atom is impossible [15].

Table 2

Relative activity EGVE (M_1) and Na-AMPS (M_2) in radical copolymerization

r_1	r_2	$1/r_1$	$1/r_2$	$r_1 \bullet r_2$
0.07	2.50	14.3	0.40	0.17

We investigated the radical copolymerization of MEAVE with sodium 2-acrylamido-2-methylpropanesulfonic acid (Na-AMPS) previously, and relative activity of MEAVE has been found to be equal $r_1 = 0.06$ which was close to the relative activity EGVE [11].

Hence, in the during of copolymerization, the growing radical end-capped with the EGVE unit predominantly interacts with the Na-AMPS monomer, while Na-AMPS radical interacts with any growing radical easily.

The values of reaction's relative rate (v_{rel}) is decreased with an increase of EGVE molar fraction in the initial mixture (Table 1). It shown that increasing the units of EGVE in initial monomer mixture leads to decrease the reaction rate. This depends on the low activity of vinylether in radical copolymerization [11].

Adsorption of Na-AMPS-EGVE copolymers at the air-water solution interface was studied by measure of surface tension (σ). The kinetics of the surface tension reduction of aqueous solutions of the Na-AMPS-EGVE copolymer at various concentrations and $T = 298$ K show that equilibrium value of σ is reached for during several hours as typical for high molecular surface active compounds. Based on the dependence of σ on the time the values of adsorption layer relaxation time were calculated according to equation [16], (Table 3):

$$\lg(\sigma_\tau - \sigma_\infty) = \lg(\sigma_0 - \sigma_\infty) - \tau/2{,}3\,\vartheta \qquad (2)$$

where σ_τ – surface tension value of solution to time τ, mN/m; σ_0 – initial value of surface tension at $\tau = 0$, mN/m; τ – equilibrium value of surface tension (after 24 h), mN/m; ϑ – relaxation time of adsorption layer, min.

Table 3 shows that values of adsorption layer relaxation time passes through maximum with increase of copolymer solution concentration. This fact may be explained in the following way. In the aqueous solution macromolecules are adsorbed disorderly in starting stage, i.e. they are held firm as chance segments. Then reorientation of macromolecular segments on polarity is taken place at the interface, which elapses for long time. Subsequent increase of copolymer solution concentration raises quantity of simultaneously adsorbing macromolecules which leads to decrease of vacant place on surface. As a result the reorientation of macromolecular segments on polarity at the air-solution interface is difficult and so decrease relaxation time of adsorption layer occurs [15].

Table 3

The relaxation times of adsorbed layers of copolymer Na-AMPS–EGVE

The concentration of copolymer mass. %	The relaxation time ϑ, min
0.02	190
0.04	423
0.06	500
0.08	126
0.12	87

The isotherm of copolymer surface tension based on equilibrium value of σ was constructed (Fig. 3, curve 2), together with the isotherm of surface tension water solution poly- Na-AMPS (curve 1).

Based on isotherms the surface activity on Rebinder (G_{Re}) for poly-Na-AMPS and copolymer Na-AMPS-EGVE was determined according to equation [17]:

$$G_{\text{Re}} = \lim\left(-\frac{d\sigma}{dc}\right)_{c\to 0.} \qquad (3)$$

Figure 3 and Table 4 demonstrate that surface activity of copolymer exceeds those of homopolymer approximately 3 times.

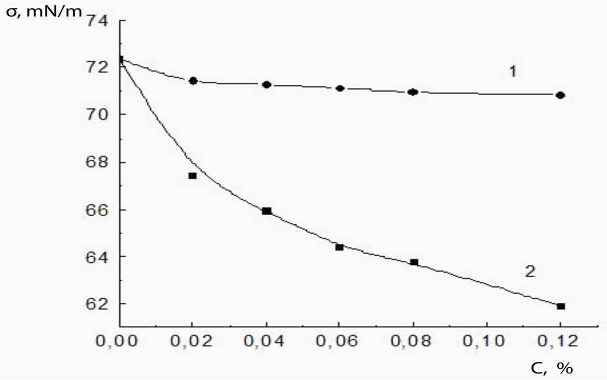


Fig. 3. The surface tension isotherms of aqueous solutions of poly- Na-AMPS (1) and copolymer Na-AMPS–EGVE containing 70 mol.% Na-AMPS (2) at $T = 298$ K.

Table 4

Physical-chemical parameters of the adsorbed layers polyelectrolytes and their complexes $T = 298$ K

Component	$G_{Re} \times 10^{-3}$, mJ·m^{-2}/kmole·m^{-3}	$\Delta_{ads}G^o_{298}$, kJ/base-mole
Poly-Na-AMPS	1.5	-18.0
Na-AMPS–EGVE	5.2	-21.2
PMAAC	8.0	-22.0
PMAAC – (Na-AMPS–EGVE)	10.8	-23.01

The values of error in determining of G_{Re} and $\Delta_{ads}G^o_{298}$ has not exceed 0.3 mJ·m^{-2}/kmole·m^{-3} and 0.1 кJ/base-mole respectively. The values of polymer's standard free energy of adsorption ($\Delta_{ads}G^o_{298}$) were calculated in order to identify the causes and mechanism of change in surface activity and adsorption. In addition, $\Delta_{ads}G^o_{298}$ is the important characteristic of a spontaneous accumulation of substance at the interface and is a measure of the surface active macromolecule's desire to adsorb.

The standard free energy of adsorption was calculated according to the equation [18]:

$$\Delta_{ads}G^o_{298} = -RT \ln G_{Re}, \tag{4}$$

where T – the absolute temperature, R – the universal gas constant.

As seen from the values shown in Table 4, the gain in standard free energy adsorption in the transition from homopolymer to copolymer Na-AMPS-EGVE is about 4 kJ/base-mole.

Thus, the results of this study lead us to conclude that in aqueous solutions the Na-AMPS–EGVE copolymer has higher surface activity and adsorption at the interface solution-air proceeds easier than poly-Na-AMPS.

As is known, interpolymer reactions giving rise to polymer–polymer complexes (polycomplexes) are frequently used for modification of polymer properties and widening the scope of their practical applications [19, 20]. Moreover, gaining insight into the mechanism governing variation in polymer properties in the course of inter-polymer reactions opens wide possibilities for controlling their physical-chemical and surface characteristics. In this study, we have examined the complexing of the Na-AMPS–EGVE copolymer with poly- N,N-dimethyl-N,N-diallylammonium chloride polyelectrolyte.

Figure 4 demonstrates that the surface tension isotherms of mixtures are below than those of the individual polyelectrolytes, which means higher surface activity of mixtures of copolymer and PMAAC. Consequently, it can be confirmed that the adsorption of macromolecules from a mixture of copolymer and PMAAC at the water-air interface is energetically more favorable process than the adsorption from solutions of individual polyelectrolytes. This effect testified to the formation of interpolymer complex between polyelectrolytes by electrostatic interactions:

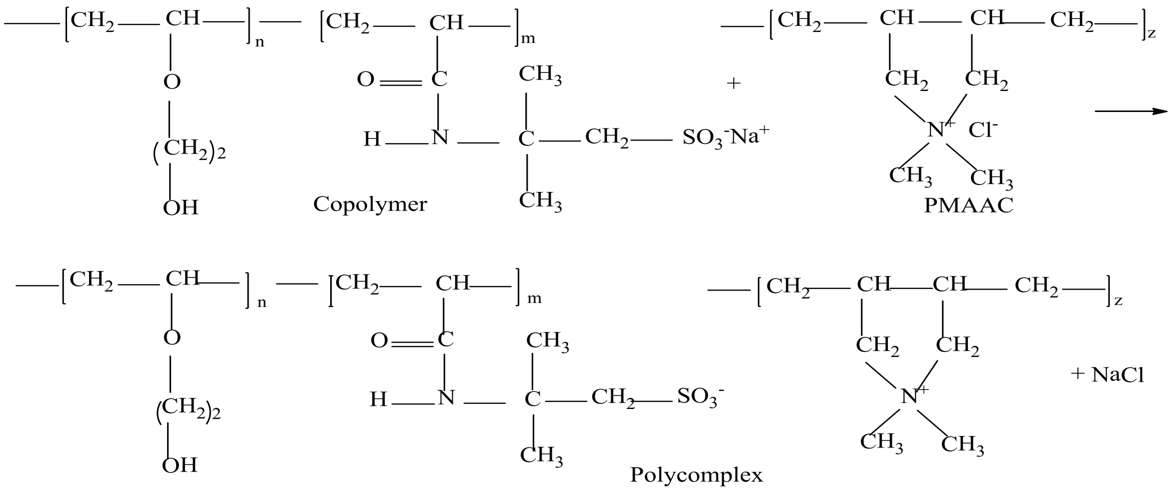


Figure 5 depicts variations in the pH, reduced viscosity and optical density of the aqueous solution Na-AMPS–EGVE copolymer with the addition of the solution PMAAC. As is seen, the pH of the PMAAC solution insignificantly reduces with an increase in the relative concentration of the added copolymer, but the viscosity reduces sharply with a simultaneous increase in optical density of solution. In this case, insignificantly increase the pH of the aqueous solution due to formation of interpolymer complexes not only with electrostatically mechanism and acid–base mechanism.

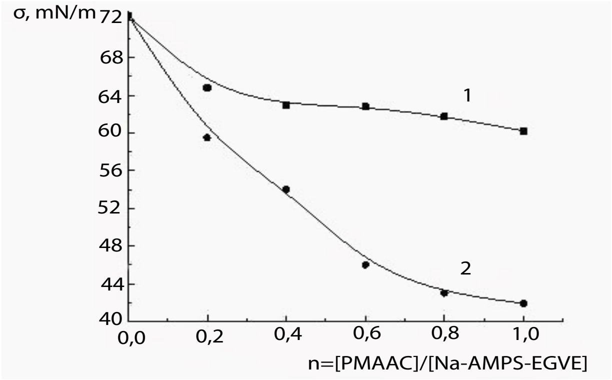


Fig. 4. The surface tension isotherms of aqueous solutions PMAAC (1) and mixtures PMAAC – copolymer Na-AMPS–EGVE (2). [Na-AMPS- EGVE] = $5 \cdot 10^{-3}$ base-mole/l; *T* = 298 K.

Owing to the blocking of negatively charged sulfonate groups by the quaternary ammonium groups of PMAAC, hydrophobic interactions between hydrocarbon radicals of macromolecules are enhanced which leads to the formation the polycomplex by the compact structure. As a result, the reduced viscosity of the copolymer solution is decreased.

The hydrophobization of polycomplex macromolecules is accompanied by the worsening of their solubility, as evidenced by an increase in the optical density of the copolymer solution with a rise in the relative concentration of PMAAC in the mixture. Figure 5 (curve 3) shows that the curve of optical density versus relative concentration of the added PMAAC passes through the maximum. Such change in optical density is possible due to the formation of more soluble nonstoichiometric polycomplex with the addition of the PMAAC at first, further increase in the concentration of polyelectrolyte leads to the formation of an insoluble precipitate, which consists of macromolecules stoichiometric polyelectrolyte complexes.

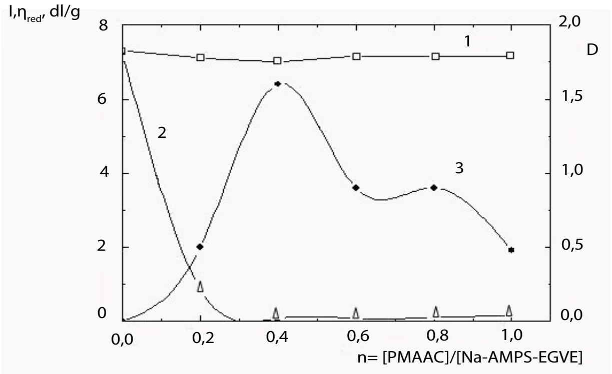


Fig. 5. The effect of the relative concentration of the added PMAAC on (1) pH, reduced viscosity (2) and the optical density(3) of the aqueous solution of the Na-AMPS–EGVE copolymer containing 70 mol.% Na-AMPS. [Na-AMPS–EGVE] = $5 \cdot 10^{-3}$ base-mole/l.

Thus, it was shown that the blocking polar functional groups of polyelectrolytes in formation of interpolymer complex leads to an increase in hydrophobicity, and consequently, to an increase in surface activity of polycomplexes. The results of this study lead us to conclude that through use of interpolymer reactions of copolymer Na-AMPS–EGVE we can control its surface-active properties.

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