Adsorption of Polycomplexes at Solution/Air Interface

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Abstract

The effect of complex formation of polyacids (polyacrylic (PAAc) and polymethacrylic (PMAAc)) with polyacrylamide (PAA) on their surface properties at solution/air interface has been studied by surface tension, electric conductivity and potentiometric measurements at 293±0.2 K. The relaxation time and surface activity of polycomplexes were calculated from kinetic data on the surface tension. It was found that during complex formation the relaxation time of a surface layer has a maximum and the surface activity of macromolecules is increased. Also the standard free energy of adsorption for PAA and polyacid-PAA polycomplexes were calculated. They are equal $\Delta_{ads}G^o_{293} = -19.1\pm0.1$ kJ/base-mol. for PAA, $\Delta_{ads}G^o_{293} = -21.2\pm0.1$ kJ/base-mol. for PMAAc-PAA polycomplex and $\Delta_{ads}G^o_{293} = -23.0\pm0.1$ kJ/base-mol. for PAAc-PAA polycomplex (calculation per base-mole of PAA monomer link).

It is shown that the surface activity and ability to decrease of the water surface tension is less for PMAAc-PAA than for PAAc-PAA. Such anomalous behaviour of PMAAc-PAA polycomplex probably is caused by an excessive strengthening of inner- and intermolecular hydrophobic interactions in macromolecules of PMAAc-PAA polycomplexes due to the presence of α-methyl groups in PMAAc macromolecules. Because of the rebuilding of macromolecule segments of complex by polarity at the interface is becoming a difficult one.

Introduction

Intermacromolecular reactions resulting in the formation of a new class of polymer materials have the significant theoretical and practical interest because it is possible to use these reactions for regulation of colloid-chemical properties of polymers and to extend the field of their application.

In our earlier works [1-4] the influence of complex formation of polyacids with both polyethylene glycol (PEG) and polydimethylaminoethylmethacrylate on the adsorption of macromolecules at solution-air interface has been investigated. It has been established that the complex formation between complementary macromolecules results in a change of the surface layer formation kinetic as well as of the macromolecule adsorption properties.

The authors [5] studied the colloid-chemical properties of polyacid-polyacrylamide complexes by measurements of the surface tension, viscosity and pH of solution. The surface tension of polymer solutions was determined by the ring method. However, it is known that the ring method is a dynamic one; conse-

quently the surface tension values obtained by this method are not equilibrium ones. Therefore it is difficult to obtain the true data about the change of polymer surface properties during complex formation.

The aim of this work is a study of the effect of complex formation of polyacids with polyacrylamide (PAA) on the adsorption kinetics and the surface properties of macromolecules at solution/air interface.

According to [6] the complex formation of polyacids (PMAAc and PAAc) with PAA occurs due to an appearance of hydrogen bonds between carboxyl groups of polyacids and amide groups of PAA. The compositions of [PMAAc]:[PAA]=1:1 and [PAAc]:[PAA]=1:1 mol/mol were determined from the minimums and bending points of viscometric and potentiometric titration curves in aqueous solution [5,6]. In this case the hydrophobic interactions play a significant role in the stabilization of these complexes.

Experimental

Materials

PMAAc was synthesized by radical polymeriza-

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tion of methacrylic acid and then was fractionated according to [7]. The fraction with $M_h=3\times10^5$ determined in methanol at 298±0.2 K by viscometric method according to the following equation [8] $[\eta]=24.2\times10^{-4}M^{0.51}$, was used.

PAAc was synthesized by the radical polymerization of acrylic acid and then was fractionated according to [9]. The fraction with $M_h=1.5\times10^5$, determined in dioxan at 303±0.2 K by viscometric method according to the equation $[\eta] = 7.6\times10^{-4}M^{0.5}$, was used.

PAA produced in "Caprolactam" Corp. (Dzerzhinsk, Russia) was used. The fraction was purified from impurities by dialysis. The molecular weight of PAA determined in water at 298±0.2 K according to the equation $[\eta] = 6.8\times10^{-4} M^{0.66}$, was equal 2.0×10^6.

Methods

The surface tension (σ) of polymer solutions was determined by Wilhelmy-plate method [10] using a platinum plate with the rough surface and size of 0.015×0.015 m. The contact angle of plate with water as well as with polymer aqueous solution was close to 0°. It affords to increase the accuracy of σ determination [11]. The measurements of σ for each aqueous solution were carried out for the first 3 hours and then solution with plate was left for a night. The equilibrium values of the surface tension were measured after 24 hours.

The preliminary studies showed that the surface tension equilibrium values (σ_∞) of polymer solutions and their mixtures were stable during 5-6 hours. The average value σ_∞ was calculated from the measurements performed several times. The accuracy of the surface tension measurements was ± 0.3 mN/m.

Electric conductivity of solutions was measured by *Testo 240* conductivity measuring instrument with accuracy ± 1×10^{-5} $\Omega^{-1}\cdot m^{-1}$. pH of solutions was controlled by *Testo 230* pH and temperature measuring instrument with accuracy ± 0.01. All of the experiments were carried out at 293±0.2 K.

Preparation of polycomplex

The polymer complexes were obtained by gradual addition of PAA aqueous solution into aqueous solution of polyacid at intensive mixing. The solutions of polymers were prepared one day before the experiment and were used during two days. For calcu-

lation of the polymer concentration the weight of the monomer unit was taken as a molecular weight (base-mol/L). At the same time the polyacid concentration in the mixture was constant and equal to 5×10^{-3} base-mol/L. The polymer solutions were prepared in bidistillated water with electric conductivity is 3.4×10^{-4} Ω^{-1} m^{-1} at $T = 295\pm0.2$ K.

Results and Discussion

The kinetics of the surface tension change of polyacid solutions and their mixtures with PAA at varying base-mole ratios n=[PAA]/[polyacid] of components are presented in Figs. 1 and 2. It is seen that the equilibrium values of surface tension (σ_∞) of polyacid solutions and their mixtures with PAA are stabilized during several hours.
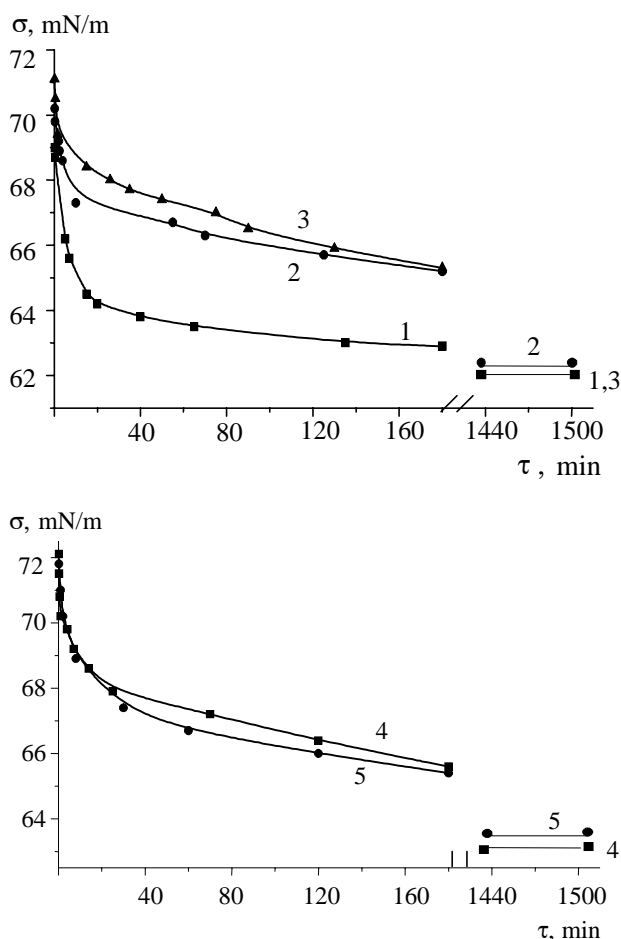

Fig. 1. Kinetics of surface tension change for PAAc-PAA mixture solutions at different base-mol components ratio n = [PAA]/[PAAc]: 1- 0.2; 2- 0.4; 3- 0.6; 4- 0.8 and 5-1.0. [PAAc] = 5×10^{-3} (base-mol)/L; T = 293±0.2 K.

It is known that the formation of polymer surface

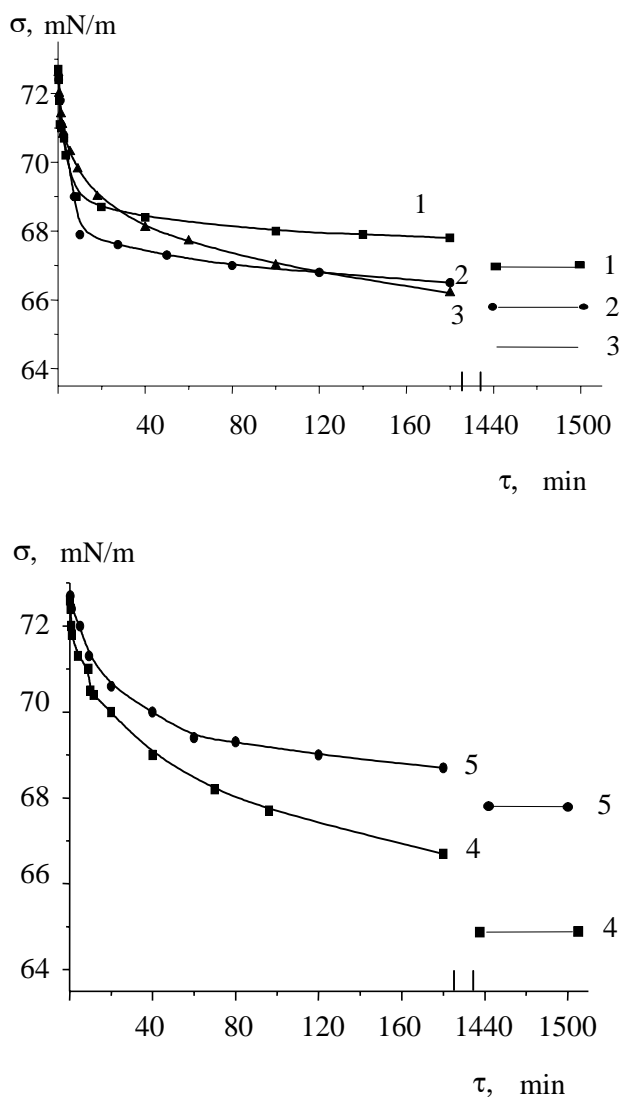Fig. 2. Kinetics of surface tension change for PMAAc-PAA mixture solutions at different base-mole components ratio n = [PAA]/[PMAAc]: 1– 0.2; 2 – 0.4; 3 − 0.6; 4 − 0.8 and 5 − 1.0. [PMAAc] = 5×10^{-3} (base-mol)/L; T = 293±0.2 K.

layer is a long-time process [12,13]. It consists of two stages:

1) diffusion of macromolecules to the interface, and
2) rebuilding of some macromolecule segments by polarity at the interface under the action of a surface force field.

In the case when the macromolecule adsorption is limited by diffusion the process is described by the equation suggested by Ward and Tordai [14]:

$$\Gamma \approx 2c_0(D\tau/3.14)^{1/2} \qquad (1)$$

where Γ is the adsorption, c_0 is the initial polymer concentration in solution, D is the diffusion coefficient, and τ is the time.

This equation can be written via the surface pressure [15]:

$$\pi = \sigma_0 - \sigma = 2c_0RT(D\tau/3.14)^{1/2} \qquad (2)$$

where σ_0 and σ are the surface tensions of water and solution respectively, π is the surface pressure, R is the universal gas constant.

The preliminary analysis of the surface tension kinetic data by a construction of dependence of π on $\tau^{1/2}$ for polyacids and their mixtures at n = 1.0 showed that the linear dependence between π and $\tau^{1/2}$ for polyacid solutions and polycomplexes took place at the initial period of adsorption. The time interval, during that the process of surface layer formation is controlled by diffusion, is not higher than few minutes. Therefore the long-duration process of σ decrease in solutions of polyacids and their complexes is caused basically by conformation rebuilding of macromolecules at the interface.

In the case, when the adsorption is controlled by the conformation rebuilding as a rule the equation suggested by is used for description of the adsorption kinetics [12]:

$$\log(\sigma_\tau - \sigma_\infty) = \log(\sigma_0 - \sigma_\infty) - \tau/2.3\vartheta \qquad (3)$$

where σ_0 and σ_τ are the surface tension of solution at the initial time ($\tau = 0$) and at the moment τ, respectively, σ_∞ is the equilibrium surface tension, and ϑ is the relaxation time of adsorption layer.

Figures 3 and 4 demonstrate the dependence of $\log (\sigma_\tau - \sigma_\infty)$ on τ. The satisfactory linear dependencies indicate an applicability of the above mentioned equation for this system. The relaxation times of the adsorption layers were calculated from the plots and are presented in Figure 5. It is seen that the relaxation time of adsorption layers of polyacids and polymers mixtures pass through the maximum at n = 0.4.

The $\sigma_\infty = f(c)$ isotherms constructed from the surface tension equilibrium values of mixture solution (after 24 hours) are presented in Figure 6. Also the isotherms of electric conductivity and the curves of the potentiometric titration are presented in Figures 7 and 8.

The surface activity of PAA and polymer-polymer complexes was calculated from the surface tension isotherms according to Rebinder (G_{Re}) method using the equation [15]:

$$G_{Re} = - (d\sigma/dC)_{C \to 0} \qquad (4)$$

and presented in Table 1.

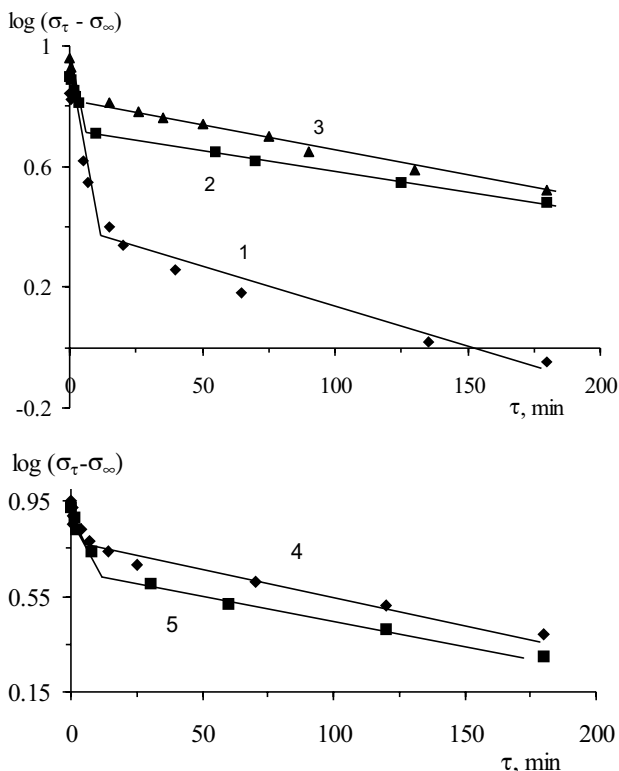In order to ascertain the reasons and the mechanism of surface activity and adsorption of macro-

Fig. 3. Dependence of log($\sigma_\tau - \sigma_\infty$) on time for mixtures of PAAc with PAA at different base-mole components ratio n = [PAA]/[PAAc]: 1 − 0.2; 2 − 0.4; 3 − 0.6; 4 − 0.8 and 5 − 1.0. [PAAc] = 5×10^{-3} (base-mol)/L; T = 293±0.2 K.

Fig. 4. Dependence of log($\sigma_\tau - \sigma_\infty$) on time for mixtures of PMAAc with PAA at different base-mole components ratio n = [PAA]/[PMAAc]: 1 − 0.2; 2 − 0.4; 3 − 0.6; 4 − 0.8 and 5 − 1.0. [PMAAc] = 5×10^{-3} (base-mol)/L; T = 293±0.2 K.

Fig. 5. Dependence of the relaxation time of adsorption layers of PAAc with PAA (1) and PMAAc with PAA (2) aqueous solutions mixture on base-mole components ratio. [Polyacid] = 5×10^{-3} (base-mol)/L; T = 293±0.2 K.

molecules change the standard free energy of adsorption ($\Delta_{ads}G^o$) can be calculated because it is one of the most important characteristics of the spontaneous process of substance accumulation at the interface and is a tendency measure of the surface-active molecules to adsorption.
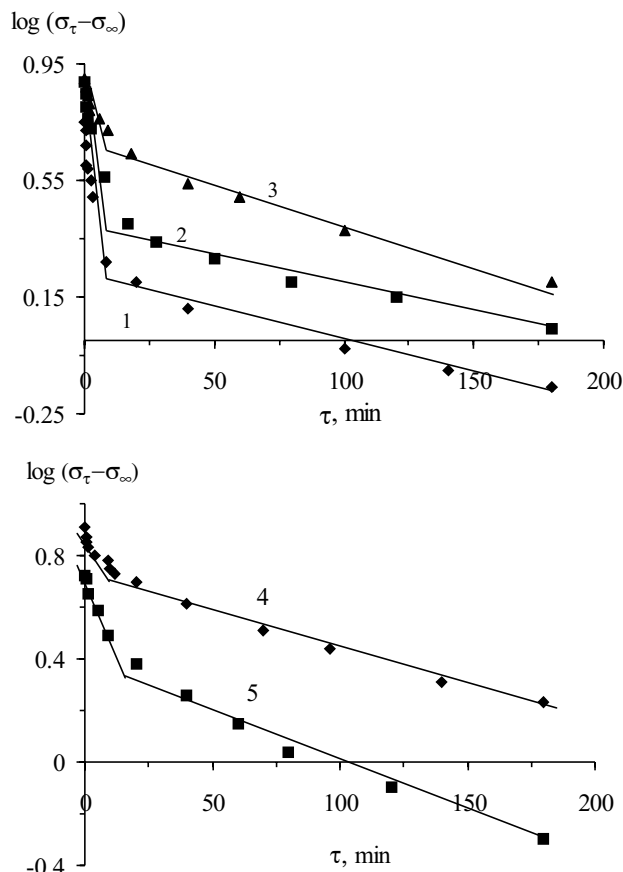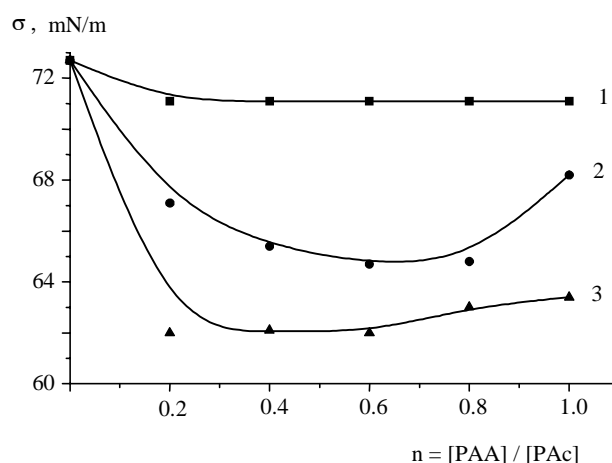

Fig. 6. Dependence of surface tension of PMAAc with PAA (2) and PAAc with PAA (3) aqueous solutions mixture on base-mole components ratio. Curve 1 is an isotherm of surface tension of PAA aqueous solutions. [Polyacid] = 5×10^{-3} (base-mol)/L; T = 293±0.2K.
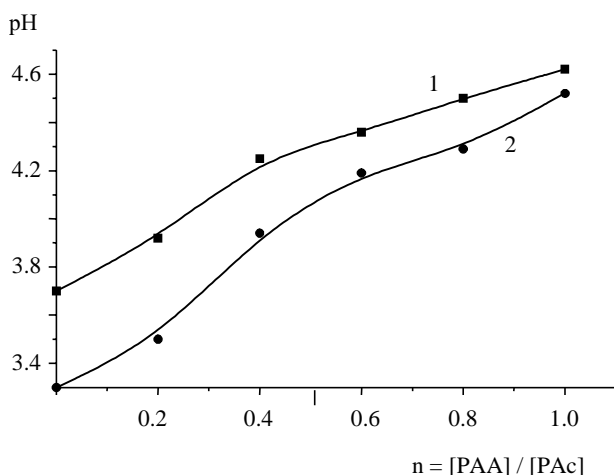
There are some methods of calculations of the

Fig. 7. Dependence of pH of PMAAc with PAA (1) and PAAc with PAA (2) aqueous solutions mixture on base-mole components ratio. [Polyacid] = 5×10^{-3} (base-mol)/L; T = 293±0.2 K.
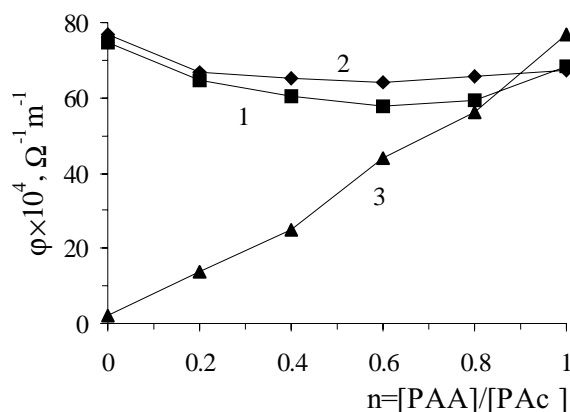

Fig. 8. Dependence of electric conductivity of PMAAc with PAA (1) and PAAc with PAA (2) aqueous solutions mixture on base-mole components ratio. [Polyacid] = 5×10^{-3} (base-mol)/L; T = 293±0.2 K. Curve 3 is an isotherm of electric conductivity of PAA aqueous solutions.

Table 1

Adsorption parameters of PAA and its complexes with polyacids at T = 293±0.2 K.

Components	$G_{Re} \cdot 10^{-3}$, (mN·m^{-1})/(base-kmol·m^{-3})	$\Delta_{ads}G^{\circ}_{293}$, kJ/(base-mol)
PAA	2.5 ± 0.1	-19.1 ± 0.1
PAAc-PAA	12.7 ± 0.3	-23.0 ± 0.1
PMAAc-PAA	5.9 ± 0.2	-21.2 ± 0.1

of the defined standard state of the volume and surface phases, because the absolute value of the standard free energy of adsorption depends on that.

If the standard state in the Surface-active Substance (SAS) -interface system is fixed as $\alpha = 1$ kmol/m^3 and $\pi = 1$ mN/m (α is the activity and $\pi = -\Delta\sigma$ is the surface pressure of adsorption layer) then it is possible to write the value of standard free energy of adsorption by the following equation [16]:

$$\Delta_{ads}G^{\circ} = -RT\ln(K_p) = -RT\ln(\pi/\alpha) \quad (5)$$

where K_p is the adsorption equilibrium constant, π and α are equilibrium value of surface pressure and activity, respectively, R is the universal gas constant, T is absolute temperature.

In the field of an ideal behaviour of adsorptive layer (Henry's field) there is a linear dependence between surface pressure and surface activity of SAS ($\pi = G_{Re} \alpha$). In this case it is possible to consider that the activity is equal to the concentration of SAS in solution. In accordance with this assumption the surface activity by Rebinder may be presented by the following formula [16]:

$$G_{Re} = -(d\sigma/dC)_{C \to 0} = (d\pi/dC)_{C \to 0} \cong \pi^*/C^* \quad (6)$$

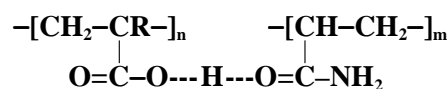and the standard free energy of adsorption:

$$\Delta_{ads}G^{\circ}_{293} = -RT\ln(G_{Re}) \quad (7)$$

In this study the standard free energy of adsorption of PAA and its complexes with PAAc and PMAAc was calculated by the equation (7). The $\Delta_{ads}G^{\circ}_{293}$ values are presented in Table 1.

The table data show that the complex formation between macromolecules results to an increase of surface activity and decrease of standard free energy of adsorption for PAA. For example, the decrease of the standard free energy of adsorption for PMAAc-PAA polycomplex is approximately equal to 2 kJ/(base-mol) and 4 kJ/(base-mol) for PAAc-PAA polycomplex.

The change of macromolecule adsorption parameters in polymers mixtures can be explained by formation of hydrogen bonds between polyacid and polyacrylamide according the following scheme [5,6]:

−[CH$_2$−CR−]$_n$ −[CH−CH$_2$−]$_m$
O=C−O---H---O=C−NH$_2$

and

−[CH$_2$−CR−]$_n$ −[CH−CH$_2$−]$_m$
O=C−O---H---NH$_2$−C=O

standard free energy of adsorption [16-18] which according to [16] give the same results. One of them is an estimation of $\Delta_{ads}G^{\circ}$ from the values of the surface activity [16]. A necessary condition is a choice

where $R \equiv H$ or CH_3.

An increase of pH (Fig. 7) and a decrease of the electric conductivity (Fig. 8) of polyacid solutions with the growth of PAA concentration in the mixture indicate it. The observed phenomena are due to the screening of polar groups of polyacids. At the same time it causes the increasing of macromolecules hydrophobicity and strengthening of inner- and intermolecular hydrophobic interactions in polycomplexes (compaction of macromolecules) [5,6].

So, the hydrophobization of macromolecules during the complex formation causes the increasing of their surface activity and adsorption ability at the interface and the decreasing of the standard free energy of macromolecules adsorption.

It should be noted that the surface activity and ability to decrease σ of water is less for PMAAc-PAA than for PAAc-PAA. Although it could be expected the opposite, because the hydrophobicity of PMAAc is higher than for PAAc. The similar deviation was observed by us earlier at the study of surface properties of polyacid-polyethylene glycol and polyacid - polyvinyl-N-pyrrolidone systems [3,19]. Such anomalous behaviour of PMAAc-PAA polycomplex probably is caused by an excessive strengthening of inner- and intermolecular hydrophobic interactions in macromolecules of PMAAc-PAA polycomplexes due to the presence of α-methyl groups in PMAAc macromolecules. At the same time the possibility of an aggregate formation from PMAAc-PAA polycomplex particles directly at the interface can not be excepted because of the rebuilding of some macromolecule segments of complex by polarity at the interface is becoming a difficult one. It causes the decreasing of the ability of polycomplex macromolecules to reduce the water surface tension.

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