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Intermolecular Interactions of Polymethacrylic Acid with Nonylphenoxypoly(ethoxy)ethanol in Water Solutions

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Abstract—On the basis of concentration pH dependences of binary solutions of anionic polyelectrolyte, polymethacrylic acid, and nonionic surfactant, nonylphenoxypoly(ethoxy)ethanol the role of hydrophobic interaction in the development of associative and aggregative processes was shown. It is established that the criterion of evaluation of the preferred contribution of hydrophobic interaction is the inflection point on the dependence of pH difference of the individual solutions of nonylphenoxypoly(ethoxy)ethanol and binary solutions of polymethacrylic acid and nonylphenoxypoly(ehoxy)ethanol on the logarithm of ratio of their concentrations.

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INTRODUCTION

Modern nanotechnologies suggest wide use of highly disperse systems with the participation of solid and liquid phases. Constant increase in demand of the composite materials causes the search for new effective methods of regulation of the colloid chemical properties of disperse systems on micro and nano level. One of such methods is the use of mixtures of low molecular surfactants and polyelectrolytes. Their effect on the properties of highly disperse systems depends on the intermolecular as well as on interphase interactions. Theoretical aspects of intermolecular interactions in the solutions of surfactants are described in [1], while the investigation of intermolecular interactions between the macromolecules of polyelectrolytes and the molecules of surfactants remains an actual problem of modern chemistry of solutions [2, 3]. Such studies comprise a wide range of problems. They dwell mainly on the investigation of interaction between the molecules of polyelectrolytes with the oppositely charged molecules of surfactants in water solutions [4–13] and the macromolecules of polyethyleneglycol-polypropyleneglycol–polyethyleneglycol block copolymers with the molecules of surfactants [14–17]. Properties of binary solutions of polyelectrolytes and nonionic surfactants are considerably less studied.

In this work we have studied the pH dependence of solutions on the concentration of nonylphenoxypoly(ethoxy)ethanol and polymethacrylic acid. Analysis of these dependencies on the concentration of nonylphenoxypoly(ethoxy)ethanol and the concentration of polymethacrylic acid expressed in the basic moles per liter of solution, that is, corresponding to the concentration of carboxy groups –COOH showed interesting specific features (see Fig. 1).

pH of individual solutions of nonylphenoxypoly (ethoxy)ethanol and polymethacrylic acid decreases at the increase in their concentration (Fig. 1, curve *1*, and the insertion in it respectively) while pH of their binary solutions at the increase in concentration of both components not only does not decrease, but even increases at high concentrations (Fig. 1, curves *2*–*4*). The change in the character of pH dependence of binary solutions as compared to the individual ones begins at the concentrations of nonylphenoxypoly(ethoxy)ethanol significantly lower than critical concentration of micelle formation (CCM). For the understanding of obtained results the possible equilibria which can take place in the individual water solutions of polymethacrylic acid, nonylphenoxypoly(ethoxy)ethanol, and their binary solutions must be considered.

In the individual water solutions of polymethacrylic acid the equilibrium connected with dissociation of carboxy groups is established.

$$-\mathrm{COOH} + \mathrm{H_2O} \xrightleftharpoons{K_1} -\mathrm{COO^-} + \mathrm{H_3^+O}. \quad (1)$$

The constant of this equilibrium is described by the following relationship.

$$K_1 = \frac{a_1 a_{21}}{a_{22}}. \quad (2)$$

Here a_1 is the activity of hydrogen ions, a_{21} and a_{22} are the activities of ionized and non-ionized carboxy groups of polymethacrylic acid respectively.

As is known, non-ionic surfactants like ethoxylates can exhibit in water solutions the properties of anionic surfactants [18]. Therefore despite of the non-ionic character of nonylphenoxypoly(ethoxy)ethanol, the following equilibrium can be established in its water solutions.

$$\mathrm{C_9H_{19}C_6H_4O(CH_2CH_2O)_5H + H_2O}$$
$$\xrightleftharpoons{K_2} \mathrm{C_9H_{19}C_6H_4O(CH_2CH_2O)_4CH_2CH_2O^- + H_3^+O}. \quad (3)$$

The constant of this equilibrium is described by the relationship (4).

$$K_2 = \frac{a_{31} a_1}{a_{32}}. \quad (4)$$

Here a_{31} and a_{32} are the activities of ionized and non-ionized molecules of nonylphenoxypoly(ethoxy)ethanol.

From the equilibrium constants K_1 and K_2 the activity of hydrogen ions in equilibrium solutions of polymethacrylic acid [Eq. (5)] and nonylphenoxypoly(ethoxy)ethanol [Eq. (6)] can be evaluated.

$$a_{12} = \frac{K_1 a_{22}}{a_{21}} = \frac{K_1(a_{20} - a_{21})}{a_{21}} = K_1\left(\frac{a_{20}}{a_{21}} - 1\right), \quad (5)$$

$$a_{13} = \frac{K_2 a_{32}}{a_{31}} = \frac{K_2(a_{30} - a_{31})}{a_{31}} = K_1\left(\frac{a_{30}}{a_{31}} - 1\right). \quad (6)$$

Here a_{20} and a_{30} are the activities of carboxy groups of polymethacrylic acid and molecules of nonylphenoxypoly(ethoxy)ethanol in starting solutions respectively, and a_{12} and a_{13} are the activities of hydrogen ions in equilibrium solutions of polymethacrylic acid and nonylphenoxypoly(ethoxy)ethanol respectively.

If the ionization degrees of carboxy groups of polymethacrylic acid and of nonylphenoxypoly(ethoxy)ethanol molecules are not large, $a_{20}/a_{21} >> 1$ and $a_{30}/a_{31} >> 1$, Eqs. (5) and (6) simplify and permit obtaining the pH dependence of individual solutions of polymethacrylic acid ($\mathrm{pH_2}$) and nonylphenoxypoly(ethoxy)ethanol ($\mathrm{pH_3}$) on the logarithms of their activities for polymethacrylic acid [Eq. (7)] and nonylphenoxypoly(ethoxy)ethanol [Eq. (8)].

$$\mathrm{pH_2} = -\log\left(\frac{K_1}{a_{21}}\right) - \log a_{20}, \quad (7)$$

$$\mathrm{pH_3} = -\log\left(\frac{K_2}{a_{31}}\right) - \log a_{30}. \quad (8)$$

Equations (7) and (8) suggest that pH dependence in individual water solutions of polymethacrylic acid and nonylphenoxypoly(ethoxy)ethanol on the activity logarithm of carboxy groups in polymethacrylic acid and of the molecules of nonylphenoxypoly(ethoxy)ethanol are linear. As the concentrations of surfactant and polyelectrolyte are not large, for checking the obtained Eqs. (7) and (8) instead of the activities of carboxy groups a_{20} and the molecules of nonylphenoxypolyIethoxy)ethanol a_{30} their concentrations c_{20} and c_{30} respectively can be used. Straight line *1* in Fig. 1 experimentally confirms the suggested dependence (8). At the increase in concentration of nonylphenoxypoly(ethoxy)ethanol pH of its solutions decreases and linear dependence can be observed in the pH–log c_{30} coordinates. The curve in the insert of

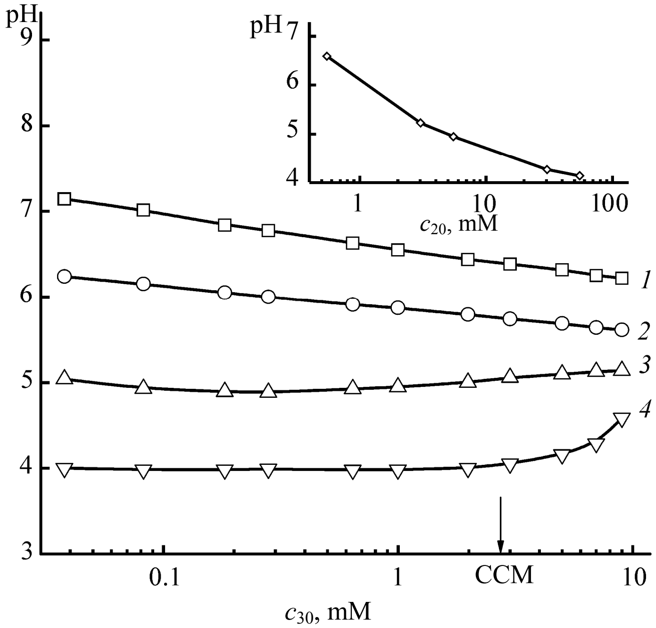

Fig. 1. pH dependence of binary solutions of polymethacrylic acid and nonylphenoxypoly(ethoxy)ethanol on the concentration of surfactant at the concentration of the carboxy groups of polyelectrolute, mM: (*1*) 0.00; (*2*) 0.55; (*3*) 5.50; and (*4*) 55.00.

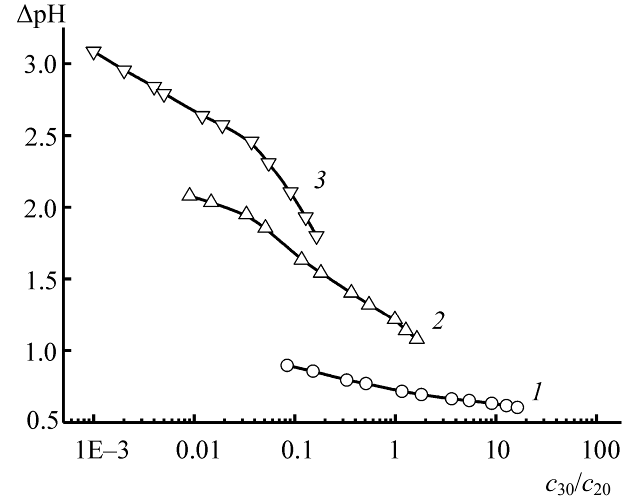

Fig. 2. Dependence of ΔpH of binary solutions of polymethacrylic acid and nonylphenoxypoly(ethoxy)ethanol on the logarithm of the ratio of concentrations of surfactant and of carboxy groups of polyelectrolyte.

Fig. 1 shows that at the increase in concentration of polymethacrylic acid pH of its water solutions decreases, but linear dependence in the pH–log c_{20} cannot be clearly traced. The established insignificant deflection from linearity may be ascribed to the fact that the rate constant K_1 depends on the degree of ionization of polymethacrylic acid macromolecules [2].

At the assumption that in binary solutions of polymethacrylic acid and nonylphenoxypoly(ethoxy)ethanol only two above-mentioned equilibria (1) and (3) take place, the activity of hydrogen ions in them a_{123} considering the simplification of Eqs. (5) and (6) can be expressed as follows.

$$a_{123} = a_{12} + a_{13} = K_1\frac{a_{20}}{a_{21}} + K_2\frac{a_{30}}{a_{31}}. \tag{9}$$

The ratio of activities of hydrogen ions in the binary solutions of nonylphenoxypoly(ethoxy)ethanol and polymethacrylic acid and the activity of hydrogen ions in individual solutions of nonylphenoxypoly(ethoxy)ethanol can be found from Eq. (10).

$$\frac{a_{123}}{a_{13}} = \frac{K_1a_{20}/a_{21} + K_2a_{30}/a_{31}}{K_2a_{30}/a_{31}} = \left(\frac{K_1a_{20}/a_{21}}{K_2a_{30}/a_{31}} + 1\right). \tag{10}$$

Taking the logarithm of the latter equation permits to find the difference between pH of individual solutions of nonylphenoxypoly(ethoxy)ethanol (pH_3) and pH of binary solutions of polymethacrylic acid and nonylphenoxypoly(ethoxy)ethanol (pH_4) [Eq. (11)].

$$\log a_{123} - \log a_{13} = -pH_4 + pH_3$$
$$= \Delta pH = \log\frac{K_1a_{20}a_{31}}{K_2a_{21}a_{30}} + 1. \tag{11}$$

Considering that the activity of hydrogen ions in individual solutions of polymethacrylic acid is significantly higher than their activity in the individual solutions of nonylphenoxypoly(ethoxy)ethanol (which is confirmed by the experiment, see Fig. 1), $(K_1a_{20}a_{31})/(K_2a_{21}a_{30}) >> 1$.

$$\Delta pH \approx \log\left(\frac{K_1a_{20}a_{31}}{K_2a_{21}a_{30}}\right) \approx -\log\left(\frac{K_2a_{21}a_{30}}{K_1a_{20}a_{31}}\right)$$
$$\approx -\log\left(\frac{K_2a_{21}}{K_1a_{31}}\right) - \log\frac{a_{30}}{a_{20}}. \tag{12}$$

The obtained equation suggests that the linear dependence of ΔpH on log (a_{20}/a_{30}) must take place. As the concentrations of components are not large, the ratio of activities of molecules of nonylphenoxypoly(ethoxy)ethanol and of the carboxy groups of polymethacrylic acid may be substituted by the ratio of their concentrations.

As seen from Fig. 2, at lowest concentration of polymethacrylic acid (c_{20} 5.50 mM) a linear dependence in the coordinates ΔpH–log (c_{30}/c_{20}) is observed at the increase in starting concentration of nonylphenoxypoly(ethoxy)ethanol (straight line 1). But at the increase in concentration of polyelectrolyte in binary solutions (curves *2*, *3*) two linear plots can be clearly traced in this dependence. The presence of a inflection on the dependence ΔpH = $f(c_{30}/c_{20})$ shows that in the binary solutions nonylphenoxypoly(ethoxy) ethanol-polymethacrylic acid besides the two above-described processes characterized by the equilibria (1) and (3) other processes causing the change in the activity of hydrogen ions take place.

Such process may probably be the hydrophobic interaction between the molecules of surfactants and macromolecules of polyelectrolyte. It may cause a series of consecutive effects such as rolling up of molecular balls of polymethacrylic acid, the increase in negative volume charge of macromolecules, accumulation of hydrogen ions on the ionized carboxy groups, and due to that a decrease in the concentration of hydrogen ions in the volume of binary solutions [2, 19]. As seen from Fig. 2, the increase in the concentration of the carboxy groups of polymethacrylic acid shifts the inflection of the dependence ΔpH–log (c_{30}/c_{20})

to the side of larger ratio of concentrations of surfactant and polyelectrolyte. At lowest concentration of polymethacrylic acid such inflection was not found. Evidently, at low concentrations of carboxy groups the change in the concentration of hydrogen ions in the binary solutions of polymethacrylic acid and nonylphenoxypoly(ethoxy)ethanol due to the hydrophobic interaction between the molecules of surfactant and macromolecules of polyacid is insignificant and cannot be observed in the experiment. Meanwhile, at the increase in concentration of polymethacrylic acid in binary solutions under study the change in the character of dependence of concentration of hydrogen ions versus the ratio of concentrations of nonylphenoxypoly(ethoxy)ethanol and polymethacrylic acid is clearly traced. The slope of straight lines on the second part of the dependence ΔpH–log (c_{30}/c_{20}) after the inflection increases with the growth of concentration of polymethacrylic acid in binary solutions indicating the increase in the effect of hydrophobic interaction in the solutions with high concentrations of polyelectrolyte and surfactant. Hence, the investigation of concentration dependences of pH of binary solution of polymethacrylic acid and nonylphenoxypoly(ethoxy)ethanol permits to isolate the contribution of hydrophobic interaction in the association processes which significantly appears after the inflection on the dependence ΔpH–log (c_{30}/c_{20}).

As micelle formation in the individual solution of surfactant is connected with the hydrophobic interaction of its diphylic molecules, and CCM is an important characteristic of intensity of this interaction, it is interesting to compare the position of inflections on the dependence ΔpH = $f(c_{30}/c_{20})$ with the ratio (c^*_{30}/c_{20}) where c^*_{30} is the concentration of nonylphenoxypoly(ethoxy)ethanol corresponding to CCM (see the table).

It follows from the presented data that the position of the inflection on the dependence ΔpH = $f(c_{30}/c_{20})$ is located in the concentration range much lower than CCM. It points to the fact that in the binary solutions of polyelectrolyte and surfactant under study the effect of hydrophobic interaction is significantly stronger developed than in the individual solutions of surfactants. The obtained results also well agree with the experimental data of the investigation of the other properties of binary solutions of surfactants and polyelectrolytes, particularly, of the surface tension and viscosity [2, 19]. Dependences of surface tension of binary solutions of polyelectrolyte and surfactant on the concentration of surfactant showed that a significant interaction between the molecules of surfactant with macromolecules of polyelectrolyte determined by the critical concentration of association begins at the concentrations significantly lower than CCM. The significant increase in viscosity of binary solutions of surfactant and polyelectrolyte is also noted at the concentrations smaller than CCM.

c^*_{30}/c_{20} ratio and location of inflection points on the dependences ΔpH = $f(c_{30}/c_{20})$ and $A=f(c_{30}/c_{20})$

c_{20}, mM	c^*_{30}/c_{20}	ΔpH = $f(c_{30}/c_{20})$	$A = f(c_{30}/c_{20})$
0.55	5.04	–	–
5.50	0.50	0.033	0.909
55.00	0.050	0.037	0.127

The studies of optical density of binary polymethacrylic acid–nonylphenoxypoly(ethoxy)ethanol solutions confirm the existence of associative formations which scatter light (Fig. 3). Individual solutions of polymethacrylic acid and nolylphenoxypoly(ethoxy)ethanol in the concentration range under study were optically clear. At the increase in concentration of nonylphenoxypoly(ethoxy)ethanol the turbidity of binary solutions increases, and at high concentrations of carboxy groups of polymethacrylic acid it even passes through the maximum point. The existence of the incubation period confirms the fact that at high concentrations of polymethacrylic acid larger amounts of molecules of surfactant are necessary for the formation of associative complexes. As seen in Fig. 3, the dependences of optical density of binary solutions on the concentration of nonylphenoxypoly-(ethoxy) ethane at high concentrations of poly-methacrylic acid exhibit a maximum point. Its position depends on the ratio of concentrations of surfactant and polyelectrolyte. These maximum points are located in the range of concentrations of surfactant exceeding CCM.

The existence of maximum point on the dependence of optical density of binary solutions on the concentration of nonylphenoxypoly(ethoxy)ethanol indicates the proceeding of at least two simultaneous processes causing opposite effects. First of them favors the aggregation of associates, while the second one prevents it. At low concentrations the hydrophobic interaction favors the rolling up of macromolecules and formation of associates which later aggregate, but at high concentrations of surfactant the hydrophobic

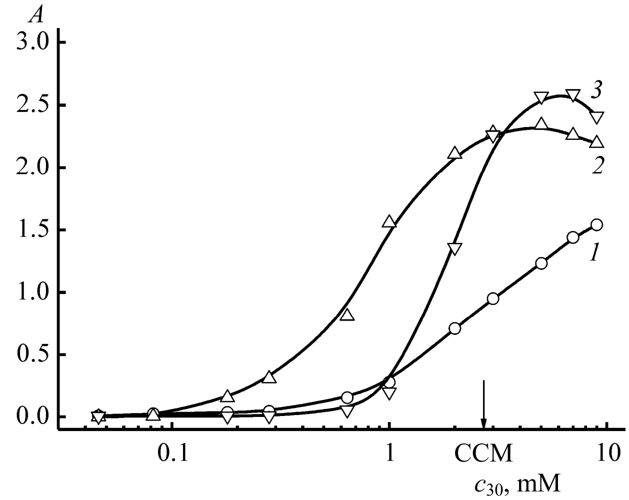

Fig. 3. Dependences of optical density of binary polymethacrylic acid–nonylphenoxypoly(ethoxy)ethanol solutions on the concentration of surfactant at the concentration of carboxy groups of polyelectrolyte, mM: (*1*) 0.55, (*2*) 5.50; and (*3*) 55.0.

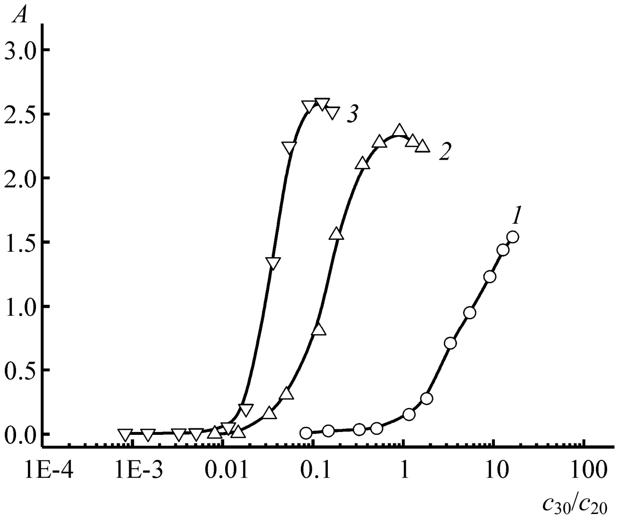

Fig. 4. Dependence of optical density of binary polymethacrylic acid–nonylphenoxypoly(ethoxy)ethanol solutions on the logarithm of ratio of concentrations of surfactant and the carboxy groups of polyelectrolyte.

interaction of molecules of nonylphenoxypoly(ethoxy) ethanol with the rolled macromolecules of polymethacrylic acid causes their liophylization and the increase in the aggregative stability [2,19]. The simultaneous operation of these two factors favors the appearance of maximum point on the dependence of optical density of binary solutions on the concentration of nonylphenoxypoly(ethoxy)ethanol. Its height and location depend on the ratio of concentrations of polyelectrolyte and surfactant. It is interesting to compare the results of investigation of optical density of binary solutions of polymethacrylic acid and nonylphenoxypoly(ethoxy)ethanol with the results of evaluation of the preferred influence of hydrophobic interaction on the association processes.

In Fig. 4 the dependences of optical density of binary solutions on the logarithm of the ratio of concentrations of nonylphenoxypoly(ethoxy)ethanol and polymethacrylic acid are presented. The maximum points on the dependence of the optical density of binary solutions are shifted to the side of higher ratios of concentrations of components of binary solutions as compared to the inflections on the dependences ΔpH–log (c_{30}/c_{20}). The ratio of concentrations of nonylphenoxypoly(ethoxy)ethanol and polymethacrylic acid in binary solutions when maximum point on the dependence $A = f(c_{30}/c_{20})$ is observed also exceeds the ratio of concentration of nonylphenoxypoly(ethoxy) ethanol corresponding to CCM to the concentration of polymethacrylic acid (see the table). The obtained results of investigation of the dependences of pH and optical density of binary solutions of nonylphenoxypoly(ethoxy)ethanil and polymethacrylic acid well agree with one another and confirm significant effect of hydrophobic interaction on the development of the associative and aggregative processes in binary solutions of polyelectrolyte and surfactant.

Hence, it is shown that the development of associative and aggregative processes in binary solutions of anionic polyelectrolyte and non-ionic surfactant is significantly influenced by the hydrophobic interaction. Its contribution may be evaluated from the concentration dependences of pH of binary and individual solutions of components of the system. The criterion of the preferred contribution of the hydrophobic interaction is the inflection on the dependence of difference in pH of individual solution of surfactants and binary solutions of surfactant and polyelectrolyte on the logarithm of the ratio of their concentrations.

EXPERIMENTAL

Following substances were used in these studies:

– polymethacrylic acid, the water-soluble anionic polyelectrolyte with the elementary unit –$C(CH_3)$–CH_2COOH)- and polymerization degree 350.

– nonylphenoxypoly(ethoxy)ethanol C_9H_{19}–C_6H_4O–(CH_2–$CH_2O)_5H$, non-ionic surfactant with critical concentration of micelle formation 2.77 M.

For preparing individual and binary solutions bidistilled water was used with the specific conductivity no more than 0.275 mS m^{-1}. For the achievement of equilibrium the solutions under study were kept at constant temperature 25°C for 3 h. pH measurements were carried out on a pH-150M pH-meter with the glass and silver chloride reference electrodes with the accuracy of ±0.05 [20]. The optical density was evaluated on a KFK-3 photocolorimeter at 540 nm with the accuracy of ±0.001 [21].

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