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ABSTRACT

The properties of surfactants of anionic polyelectrolytes are investigated depending on the nature of the medium, conformational states neutralized by organic bases, differing in the length of the hydrocarbon radical. The concept of the role of the state of macromolecules in solution in the indicated processes has been developed. The anionic carboxyl-containing polyelectrolytes synthesized on the basis of methacrylic acid differed not only in the length of the hydrocarbon radical of the organic base - counterion, but also in their branching. The relationship between the state of polyelectrolyte macromolecules in solution and their ability to regulate the properties of natural dispersed systems has been studied.

Key words: surfactants, polyelectrolytes, methacrylic acid, polymethacrylic acid, synthesis, conformation of macromolecules, size of macromolecules, organic counterions, flocculation, structure formation.

INTRODUCTION

The surface-active properties of polyelectrolytes are determined by the molecular parameters of the chains (chemical composition of polar groups, chain charge, molecular weight, structural features of macromolecules, etc.) and their conformational state, which in turn depends on the pH of the medium, the ionic strength of the solution, the composition of the solvent, etc. other factors [1,2]. An important role in this should be played by counter-forces. However, the dependence of the properties of polyelectrolytes (PE) on the nature of counterions has been studied very poorly.

In work [3], the effect of inorganic cations of lithium, sodium and potassium, as well as anions of chlorine, bromine, iodine, on the flocculating properties of PE with respect to mineral dispersions was studied. In particular, it was shown that with an increase in the radius of the counterion, the flocculating effect of PE increases. Previously, the authors of [4] studied the properties of solutions of cationic PE, neutralized with organic carboxylic acids, and the effect of PE on the flocculation and structure formation of mineral dispersions. The concept of the role

of the state of macromolecules in solution has been developed. It has been established that the flocculating effect of the studied polyelectrolytes on mineral dispersions depends on the size of their macromolecules in solution. It is shown that an increase in the length of the counterion radical over the optimal value leads to a decrease in the size of molecular coils due to intra and intermolecular interactions.

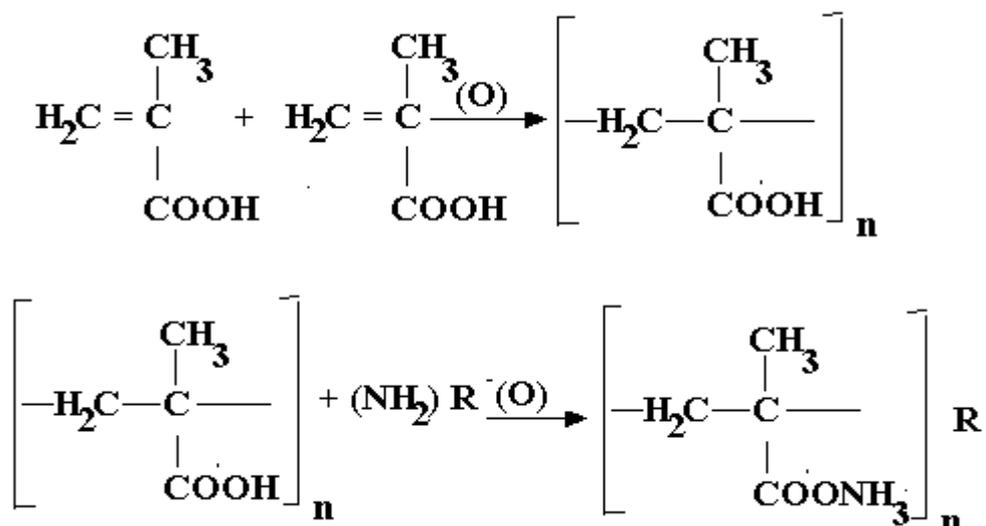
The aim of this work is to study the properties of anionic PE solutions neutralized by organic bases, to investigate the effect of the composition and structure of organic cations, capable of organizing complexes with anionic PE, on the conformational state of macromolecules in solution and their flocculating ability depending on the nature of the dispersed medium. The methods of viscometry, conductometry, potentiometry, calorimetry, IR spectrometry have been used in this study.

EXPERIMENTAL

Carboxyl-containing water-soluble PE based on polymethacrylic acids (PMAA) were obtained in five counterionic forms. PE based on PMAA and amines were synthesized by two independent methods: by neutralization to pH = 7.5 with an amine solution and PMAA obtained by preliminary polymerization of methacrylic acid in an aqueous medium, as well as by polymerization of neutralization products with amines of MAA in PMAA at pH = 7.5 of the reaction mixture.

Organic bases methylamine (MA) - $[\text{NH}_2\text{CH}_3]$ were taken as neutralizing agents for methacrylic (MAA) and polymethacrylic acids (PMAA); ethylamine (EA) - $[\text{NH}_2\text{C}_2\text{H}_5]$; butylamine (BA) - $[\text{NH}_2\text{C}_4\text{H}_9]$; diethyl amine (DEA) - $[\text{NH}(\text{C}_2\text{H}_5)_2]$; triethyl amine (TEA) - $[\text{N}(\text{C}_2\text{H}_5)_3]$. These amines, which later also serve as counterions of anionic PE, differ in the length of the hydrocarbon radical and the degree of substitution of organic amines.

The reaction of MAA polymerization in the presence of amines proceeds according to the following scheme:



The following characteristic frequencies are found in the IR spectrum of PMAA₁-DEA: 1648 cm⁻¹ is an intense frequency related to the stretching vibrations of the carboxyl group of PE. It should be noted that the stretching vibrations of the carbonyl group in the IR spectrum of PMAA itself are found in the 1700 cm⁻¹ band, however, in the PMAA product neutralized with diethylamine, the frequency is underestimated by 50 cm⁻¹ due to the formation of an ammonium salt. The band at 2431 cm⁻¹ corresponds to stretching vibrations of the ionized NH₃⁺ group.

To obtain PMAA by polymerization of MAA in an aqueous medium, 90 g of water was added to the purified monomer in an amount of 10 g, 0.005 g of potassium persulfate was added. The mixture was kept at 50-60°C for 4 hours. The polymerization reaction is complete and vigorous. For the convenience of work, the obtained 10% product was diluted to 5%. The resulting PMAA is soluble in water, methanol, dioxane. Water-soluble ionic PEs were obtained by neutralizing the PMAA solution with a 10% solution of methylamine, ethylamine, diethylamine, butylamine, and triethylamine, bringing the pH value to 7.5. The products obtained by the first method are designated PMAA₁-MA, PMAA₁-EA, PMAA₁-DEA, PMAA₁-BA; the second method is PMAA₂-MA; PMAA₂-EA, PMAA₂-BA.

For pH regulation, the most acceptable concentration is a 10% solution of organic bases, because the use of a more dilute organic amine solution leads to a decrease in the concentration of active substances, and a more concentrated solution above 10% - to the difficulty of the pH regulation process [5].

Chemical analysis, the acid number of the obtained PE was carried out using known methods.

The study of the properties of aqueous solutions of PE, such as viscosity, electrical conductivity, optical density, pH value, size of macromolecules, depending on concentration at usual dilution and isoionic (aqueous KCl solution) dilution, and depending on the pH of the medium, is important for identifying and explaining in the future, the flocculating and structure-forming action of PE on the studied mineral dispersed systems.

Physical and chemical characteristics of synthesized polyelectrolytes

As the physical and chemical characteristics of the synthesized PEs, the viscosity properties were studied (using an Ostwald viscometer, the water outflow time was 72 sec at 25±1°C) and the specific electrical conductivity (a device operating according to the Kohlrausch bridge scheme was used, temperature 25±1°C, constant vessels 0.273 cm⁻¹) their properties depending on concentration, pH of the medium and polymerization conditions. It is shown that the highest viscosity (η) and electrical conductivity (κ) are possessed by PE solutions, which have the largest sizes of macromolecules, the degree of their dissociation, and the values of the ionization constant.

Based on the data obtained using the corresponding equations of the Kuhn-Mark-Houwink type, molecular weights (M) were calculated. The values of the characteristic viscosity $[\eta]$ required for this were determined under the conditions

of iso-ionic dilution of PE solutions with 0.1 M KCl solution, which made it possible to maintain a constant ionic strength of the solution and suppress primary polyelectrolyte effects. The values of the constants K and α in the formula: $[\eta]=K \cdot M^\alpha$ for calculating the molecular weight of PMAA is taken as $K=2.42 \times 10^3$, and $\alpha=0.54$ and $[\eta]=7.9$.

The value of $M_{PMAA}=9.73 \times 10^5$ specific units, while the degree of polymerization was 11.3×10^3 .

The molecular weights of the PMAA samples neutralized with bases turned out to be: for $PMAA_1-MA=1.3 \times 10^6$, $PMAA_1-EA=1.48 \times 10^6$, $PMAA_1-BA=1.80 \times 10^6$.

It was found that the values of specific viscosity (η) and electrical conductivity (κ) increase with increasing solution concentration due to a decrease in intermolecular interactions of polyions by counterions, which leads to a decrease in the degree of PE dissociation, calculated on the basis of ion mobility [6].

The sizes of macromolecules are calculated - the root-mean-square distances between the ends of the chain and the radiuses of the semi-axes of the ellipsoids of rotation, their ratio depending on the number of hydrocarbons of the PE counterion, its concentration in the solution and the pH of the medium. The hydrodynamic volume (V_n), the equivalent hydrodynamic radius (Re) and the ratio of the lengths of the semi-axes of the ellipsoid of revolution (b/a) of macromolecules were calculated using the following equations [6].

$$[\eta] = v * \frac{N_A V_n}{M}, \text{coeff.} - 2.5, N_A - \text{Avogadro's number}$$

$$\eta_{sp/C} = 2,5 * \frac{N_A}{M} * \left(\frac{4}{3} \pi R e^3 \right), R e = \sqrt[3]{\frac{0,3 M \eta}{3,14 N_A C}}$$

C – PE conc., (g/cm^3), n_{sp} - specific viscosity

$$\frac{\eta_{rel}}{C * V_{sp}} = 2,5 \frac{1}{16} (b/a)^2$$

Where V_{sp} is the partial specific volume of the solute (cm^3/g), a and b, respectively, the lengths of the short and long chain of semiaxes, which were

calculated using the ratio $\frac{M}{\rho * N_A} = \frac{\pi}{B} * B * a^2 = \frac{\rho}{B} \left(\frac{B}{a} \right) a^3$ or $a = \sqrt[3]{\frac{6M}{\rho \pi N_A * \frac{B}{a}}}$ $B = \frac{B}{a} * a$

The degree of dissociation of PE was determined based on the data of ion mobility. The characteristics of aqueous solutions of PE of different concentrations at 25°C and the calculated sizes of their macromolecules are given in table. 1.

In this work was also studied the effect of synthesized PE on the clarification of 0.1% hydrosuspension of Keles bentonite (GSB). Optical density was recorded on an FEK-56M photoelectrocolorimeter using 10-mm-thick cuvettes at an incident light wavelength of 540 nm [7].

RESULTS AND DISCUSSION

With the use of narrow fractions of multifunctional and polyfunctional PE, it was previously established [3] that the dependence of the effectiveness of the stabilizing and flocculating action correlates with similar sizes of macromolecules

in solution. It was also revealed that it is the size of the macromolecules, and not the molecular weight of the polyelectrolyte, that determine the effectiveness of their stabilizing and flocculating action.

Table 1

Characteristics of aqueous solutions of polyelectrolytes and the size of their macromolecules, depending on the concentration at 25°C.

PMAA, $M=9.73 \times 10^5$

№	Soln. conc., %	Vol. $V_n \times 10^{18} \text{cm}$	$b \times 10^{-5} \text{cm}$	$a \times 10^{-7} \text{cm}$	b/a	Equiv.radius $R_{eq.} \times 10^6 \text{cm}$
1	0,01	1,73	1,40	1,33	105	1,33
2	0,1	3,92	0,567	0,93	61	9,25
3	1,00	1,62	0,318	0,74	43	0,729

PMAA – MA, $M=1.3 \times 10^6$

1	0,01	110	6,92	2,26	306	2,97
2	0,1	88	3,07	1,08	285	2,84
3	1,0	31,2	1,08	1,08	100	2,02

PMAA – EA, $M=1,48 \times 10^6$

1	0,01	108	32	9,9	332	9,45
2	0,1	86	28	9,5	296	8,7
3	1,0	46	17,5	8,6	203	7,2

PMAA – BA, $M=1.80 \times 10^6$

1	0,01	180	9,52	13,5	70	3,45
2	0,1	108	7,48	29	25,7	2,91
3	1,0	49,2	3,94	22,5	17,5	2,24

Table. 2

PMAA

№	Soln. conc., %	pH	Viscosity (specific)	Electrical conductivity (specific)	Dissociation degree, (α)
1	0,05	4,70	0,39	0,60	0,27
2	0,1	4,55	0,51	1,00	0,23
3	1,00	3,85	2,50	7,40	0.17

PMAA - MA

1	0,05	7,20	6,10	2,80	0.74
2	0,1	7,27	11,0	3,25	0,42
3	1,0	7,50	39,0	10,20	0.13

PMAA - EA

1	0,05	7,21	5,50	2,30	0,78
2	0,1	7,28	9,63	2,65	0,46
3	1,0	7,80	51,3	9.10	0,16

PMAA - BA

1	0,05	7,15	4,80	1,25	0,81
2	0,1	7,20	9,02	1,60	0.52
3	1,0	7,40	41,0	7,30	0,24

PMAA “b/a” = 105, PMAA×MA “b/a”=306, PMAA×DEA “b/a”=332, PMAA×BA “b/a”=70. It was revealed that with an increase in the length of the

PMAA-A hydrocarbon radical, the molecular weight increases, and also, as expected, the viscosity of PE solutions and the size of their macromolecules increase. However, PE PMAA-BA, which has a large molecular weight in comparison with other PE, has the smallest macromolecule size. This is due to the fact that with the elongation of the counterion radical, intramolecular interactions are enhanced, associates of macromolecules are formed, which affect the degree of their coagulation, i.e. to conformational states.

Among the synthesized PE samples, the most effective were the samples: PMAA×EA < PMAA×DEA. The weakening of the effect of action at R of the counterion <C2 is associated with insufficient development of the radical, and at >C2, and at R=C3, C4 of counterions with the development of processes within and intermolecular interactions that contribute to the transition of sufficiently deformed macromolecules to their less deformed states of a static coil with the ensuing the consequences regarding the size of macromolecules and the associated manifestation of the effects of PE.

The study of the stability and flocculation of hydrosuspension of bentonite (HSB), as well as hydrosols (HHB), is of interest due to the fact that clay particles mainly cause turbidity of many natural waters, being in them in a suspended colloid-dispersed state.

Flocculation of HSB and HHB under the influence of PE was concluded by the change in optical density (D), sediment volume ($V_{\text{sed.}}$), relative filtration rate ($U_{\text{rel.}}$) of their 0.1% dispersions depending on the PE dose, settling time, pH of the medium and pH of the added solution of PE [7].

It is noted that at a low concentration of PE, D decreases insufficiently, as a result of which, in that volume of concentration, the amount of added PE is insufficient for aggregation of all or most of the particles of the solid phase. In optimal concentration (2.5-5.0 mg/l.), larger aggregates are formed, which quickly settle, as a result of which the greatest clarification of the dispersion medium is observed and the optical density has a minimum value.

However, the optimal concentrations of various PEs required to achieve the greatest degree of suspension clarification differ from each other depending on the number of counterions of the functional groups of PEs of the PMAA×A type. The effectiveness of the flocculating action was assessed by the value of the critical concentration, which was taken as the minimum amount of it in the solution at which the flocculating action began to manifest itself. The greatest decrease in the optical density of the drains is observed after 15 minutes.

CONCLUSION

1. The flocculating and structure-forming effect of PE is accompanied by their chemisorption interaction with particles, and with an excess of PE concentration, complex complexes may form due to the hydrophobic interaction of adsorbed macromolecules and macromolecules in solution, which increases the hydrophilicity of particles and the stability of the sol.

2. It is noted that the flocculating and structure-forming effect of PE is associated with their complete irreversible adsorption on mineral particles; in this case, adsorption is of an exchange nature, which determines the effect of polyelectrolytes on the electric double layer of adsorbed ions.

3. The relationship has been established between the agronomic structure created by polyelectrolytes in soil dispersions and the improvement of their water-physical properties. Recommendations have been developed for the use of synthesized polymer electrolytes for the purification of turbid waters of the Doslyq Canal, the Amu Darya River, as well as for structuring and improving the agrophysical properties of saline soils in the Aral Sea region.

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