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Flocculation kinetics of an ochre suspension in salt(NaCl)-containing aqueous media in the presence of anionic and cationic acrylamide copolymers

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Abstract The sedimentation kinetics of an ochre suspension in salt (NaCl)-containing aqueous media was studied in the presence of ionogenic (anionic, A, and cationic, C) acrylamide copolymers with high molecular weight ($M > 2 \times 10^6$) using a VT–0.5 torsion balance. The ionic strength of the dispersion medium varied in the wide range from 0.001 N to 0.4 N. The flocculation proceeded predominantly by a 'bridge' mechanism, and the fraction of macromolecules inactive in the acts of floccule formation was significantly higher for C copolymer as compared with A copolymer. A drastic fall in the flocculating activities of A and C copolymers when passing from salt-free to salt-containing media is caused mainly by two following events:

1. The change in the conformational state of macromolecules, primarily, in their effective dimensions
2. The participation of a certain part of electrolyte in the formation and modification of an electrical double layer around disperse phase particles

After introducing binary compositions of A and C flocculants into salt-containing media their resultant flocculating effect depends on the introduction mode of polymeric components. A strong difference in the magnitudes of the flocculating effect for A and C copolymers is observed in water. In the region of high ionic strengths (0.1–0.4 N) this difference becomes far less distinct. The flocculating activities of A and C copolymers were compared when introduced as the first (λ_A and λ_C) and the second (λ'_A and λ'_C) additives. It was shown that $\lambda_A/\lambda'_A > 1$ and $\lambda_C/\lambda'_C > 1$. Such relationship between λ_A and λ'_A, λ_C and λ'_C indicates that selective interactions between A and C copolymers play an essential role in the flocculation processes. The last statement was indirectly confirmed in the present work by the data of electrochemical and viscosimetric studies. When using C copolymer as the second additive in the region of low ionic strengths its main function undergoes reversal, and the copolymer begins to operate not as a flocculant, but as a stabilizer of disperse phase particles ($\lambda_C < 0$).

Key words Flocculation · Ionic strength · Ionogenic copolymers · Sedimentation kinetics · Viscosimetry

Introduction

One of the most important problems in contemporary physical and colloid chemistry is searching simple and effective ways of wide-range controlling the sedimentation (kinetic) stability of real disperse systems (DSs) [1, 2]. The most promising line in deciding this problem is introducing into the system small portions of various water-soluble synthetic or natural polymers (copolymers) able to affect strongly the sedimentation (as well as aggregative) stability of dispersions [3, 4]. Among the broad spectrum of synthetic water-soluble polymers on the market today, polyacrylamide flocculants (PAMFs) – that is, statistical, block and graft copolymers of acrylamide (AM) – enjoy the widest use due to their availability, high flocculating and environmental properties, and moderate price [4].

AM copolymers are widely used in paper-making as efficient flocculants (the good point is that residual small content of a PAMF in pulp improves physicomechanical properties of paper), in oil production, in ore extraction and processing, in regeneration of valuable mineral resources as well as in wastewater and sewage treatment, trapping and isolating heavy metal ions and toxic compounds [4–8]. AM copolymers application is very effective (in the economic and social senses) in various branches of industry as an alternative to aluminum and iron salts, lime, etc., in wastewater treatment, flocculation, coagulation, precipitation, and dehydration technologies [6–8].

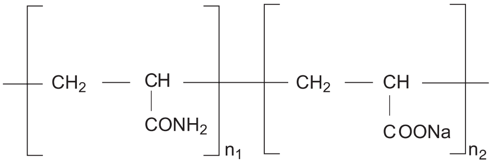
It had been found using a number of real and model DSs that the highest flocculation performance is reached, as a rule, with ionogenic (anionic and cationic) PAMFs [4]. Primarily that is due to the fact that the structure of these polymeric additives include positively and negatively charged fragments able to attach effectively to the local sites on the surface of charged particles of a dispersed phase (DP). Besides, presence of ionogenic groups leads to the rise of an effective macromolecule size, thus increasing the flocculation indices [8–17].

When comparing the efficiency of PAMF application to real DSs we deal mostly with multicomponent systems containing inclusions of various natures (surfactants, salts, acids, bases, organic substances, etc.) which may in general affect strongly the sedimentation stability of DSs. Among the whole range of the substances, salt additives are more often used as potentially active ingredients of a dispersion medium markedly influencing the sedimentation stability of real DSs in various industrial processes, primarily water pretreatment, sewage treatment, and oil production [5, 18]. This is the reason why systematic investigations into the effect of specific potentially active additives on the sedimentation in the model systems, particularly the effect of salt additives on flocculation indices of PAMFs, are of great interest today. It should be noted that only using model systems allows one to assess rather correctly the effect of a given parameter or a component (here a salt additive) on the sedimentation stability of the system. An attempt at such analysis was made previously [19], where the influence of anionic PAMFs was considered for a model DS (ochre suspension). It may be noted that the ochre sedimentation in a salt-containing aqueous medium in the presence of an anionic PAMF was performed in the mode of hindered settling. To develop the results of [19] it was interesting to study the kinetic regularities of sedimentation in the presence of both anionic and cationic PAMF, as well as their compositions in salt-containing (NaCl) aqueous media. It is important and urgent both in fundamental and applied sense to assess the influence of the mode of component introduction into a system, since several authors [4, 20, 21] report that the sedimentation stability depends on the sequence of active additives introduction.

The problems mentioned are analyzed in this report for an ochre suspension as a model system in the mode of free setting in the presence of ionogenic PAMFs with intermediate ionogenic units concentration under ionic strengths varied in a wide range.

Experimental

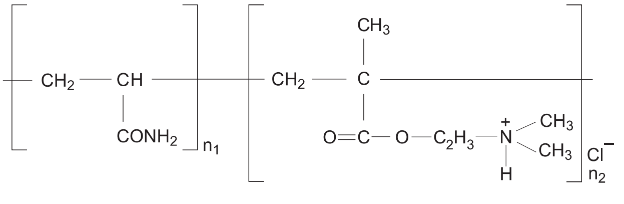
Ionogenic (anionic (A) and cationic (C)) AM copolymers were used as PAMFs. The A sample had the following structural formula:



$$\left[-CH_2-\underset{CONH_2}{\underset{|}{CH}}-\right]_{n_1}\left[-CH_2-\underset{COONa}{\underset{|}{CH}}-\right]_{n_2}$$

and represented statistical copolymer of AM with sodium acrylate having the viscosity average molecular weight $\overline{M_\eta} = 5.4 \cdot 10^6$ and ionogenic units content $\beta = 17.4\%$. It was obtained by alkaline hydrolysis of high molecular weight polyacrylamide in soft conditions (t = 60 °C, hydrolytic agent: NaOH) [11].

The C sample represented statistical copolymer of AM with dimethylaminoethylmethacrylate hydrochloride having $\overline{M_\eta} = 2.3 \cdot 10^6$ and $\beta = 16.3\%$. It had the following structural formula:



$$\left[-CH_2-\underset{CONH_2}{\underset{|}{CH}}-\right]_{n_1}\left[-CH_2-\overset{CH_3}{\overset{|}{\underset{O=C-O-C_2H_3-\underset{H}{\overset{+}{N}}(CH_3)_2}{\underset{|}{C}}}}-\right]_{n_2}Cl^-$$

and was obtained by radical copolymerization of appropriate monomers in aqueous medium.

Distilled water was used in the experiments on ochre flocculation kinetics, and bidistillate was used in physicochemical analysis.

In this series of experiments the kinetics of ochre suspension flocculation in the presence of ionogenic PAMF samples and electrolyte (NaCl) was studied in the mode of free (unhindered) settling. The sediment accumulation on the pan of a VT–0.5 torsion balance in a cylinder with a working volume of 400 cm^3 was traced. The concentration c_d of DP particles in all the experiments was constant and equal to 0.8%. Prior to the experiment ochre was kept in the dispersion medium for 24 h. The stirring of suspension in a cylinder was performed by 10-fold slow vertical moving the disc stirrer with 12 orifices.

From the analysis of the dependence of ochre suspension sedimentation rate on pH values of the dispersion medium (with no flocculant added) it was found that the isoelectric state of an ochre suspension (corresponding to the maximum sedimentation rate) is achieved at pH ~ 4.9. To be more specific, it should be mentioned that all the flocculation processes involved (with electrolyte and A/

C copolymer addition) were studied in the pH $\sim 8.2 \pm 0.1$ range, i.e., the flocculation proceeded sufficiently far beyond the isoelectric state of the disperse phase particles.

To evaluate the kinetic regularities of ochre sedimentation in the mode of free (unhindered) settling [4, 14], the dimensionless parameter $\frac{m(t)}{m_{\max}}$ was used (where $m(t)$ and $m_{\max}$ are the current and the maximum reached masses correspondingly of the sediment on the balance pan in a given experiment, and t is the exposure time). The application of this parameter instead of the commonly used $m(t)$ [4, 23] allows one to perform more objective comparative evaluation of the kinetic regularities of sedimentation with the varied nature and content of the additives introduced into a complicated multicomponent system. It should be noted as a positive point that such an approach in any case leads to the satisfied normalization condition $\left(\frac{m(t)}{m_{\max}} = 1\right)$.

"Zolotistaya" ochre (TU 301–10–019–90) was used in the study with a mean DP particle size $\overline{R} = 9.25 \cdot 10^{-6}$ m. It should be particularly mentioned that ochre is used in Russia (along with the another model DS, kaolin) as a standard for the evaluation of the flocculation activity of PAMFs. The integral curve in Fig. 1 shows the particle size distribution analysis data. It indicates that the disperse system under study has only slight polydispersity. This is supported, particularly, by a relatively small difference between the sizes of extreme fractions: $R_{\min} = 4.2 \times 10^{-6}$ m and $R_{\max} = 21.4 \times 10^{-6}$ m.

The viscosimetric analysis of aqueous PAMF solutions was carried out using an Ostwald viscosimeter with capillary diameter of 0.54×10^{-3} m; the correction for the kinetic energy of liquid flow was less then 2% and so was neglected when calculating the viscosity numbers. The electrophoretic mobility of ochre particles was measured by means of a PARMOQUANT automatic measuring microscope (Carl Zeiss Jena). The measurements were carried out at 20 °C and a current of 1.5 mA and 10 mA for side liquid with the NaCl concentration equal to 0.004 N, 0.04 N, and 0.4 N correspondingly.

An MBS–10 biological microscope with a micrometer graticule was used for assessing the size of ochre aggregates. The number of particles of a certain fraction within the visual field was counted. After doping the calculated doses of flocculants to the ochre suspension it was stirred for 5 min (at a stirrer rotation rate of 100 ppm) and then a sample (6–10 drops) was taken for microscopy.

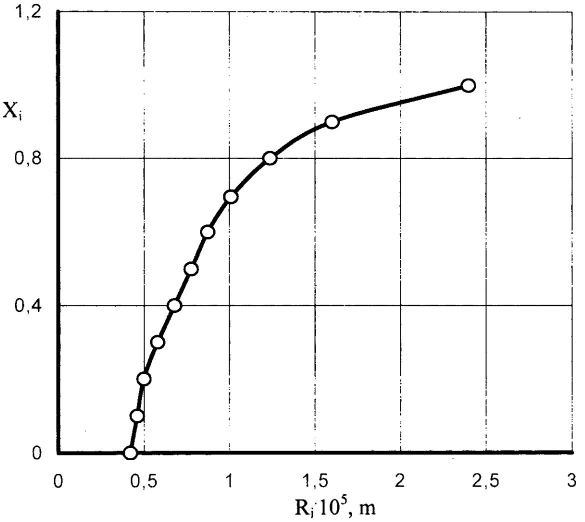


Fig. 1 The integral curve of particle size distribution for ochre. X_i is the integral mass percentage of the ith fraction

The electric conductivity of the solutions of A and C copolymers and NaCl was measured using an IMPULS conductometer. A conductometric cell with platinum electrodes was used.

Results and discussion

Even at the preliminary stage of the analysis of the main macroscopic sedimentation regularities in complicated multicomponent DSs such as the systems under study (ochre suspension with binary additives of ionogenic flocculants and NaCl) the information is necessary, at least on the character of interactions between components, for a number of simpler 'basic' objects. In our case the following objects may serve as such basic systems:

1. Water + ochre + A (or C)
2. Water + ochre + NaCl
3. Water + A (or C) + NaCl
4. Water + A + C

The preliminary discussion will be started from the evaluation of PAMF addition influence on the kinetics of ochre settling process in pure water ([NaCl] = 0). As seen from Fig. 2a, b, introducing small additives of anionic (A) and cationic (C) flocculants ($\sim 10^{-6}$% to 10^{-5}%, practically, microdoses) results in marked acceleration of DP particles sedimentation and this effect is enhanced with [PAMF] increase. Even qualitative comparison of the kinetic curves in Fig. 2a, b leads to the conclusion that the anionic copolymer A has essentially higher flocculation performance as compared to the cationic copolymer C, particularly taking into account the difference in their dosages ([C] > [A]). More strict judgement may be deducted from the comparison of flocculation effects D and flocculation activities λ of the analyzed A and C copolymers.

The dimensionless parameter D is calculated from the kinetic analyses data using the relationship [24]

$$D = \frac{\overline{V}}{\overline{V_0}} - 1 \ ; \qquad (1)$$

where $\overline{V}$ and $\overline{V_0}$ are average sedimentation rates of DP particles doped with a flocculant and without a flocculant, respectively. It should be noted that in all the consequent computations $\overline{V}$ and $\overline{V_0}$ values were taken for the strictly fixed values of $\frac{m(t)}{m_{\max}} = 0.7$.

The inequalities $\overline{V} > \overline{V_0}$ and $D > 0$ indicate the accelerating action of polymeric additives on the sedimentation process, and the higher the parameter D value, the more expressed is this effect. The conditions $\overline{V} < \overline{V_0}$ and $D < 0$ indicate that the polymer introduced plays the role of an agent stabilizing DP particles.

To make the quantitative comparison of the efficiency of various flocculants it is helpful to use the parameter of flocculation activity λ [4, 25, 26]:

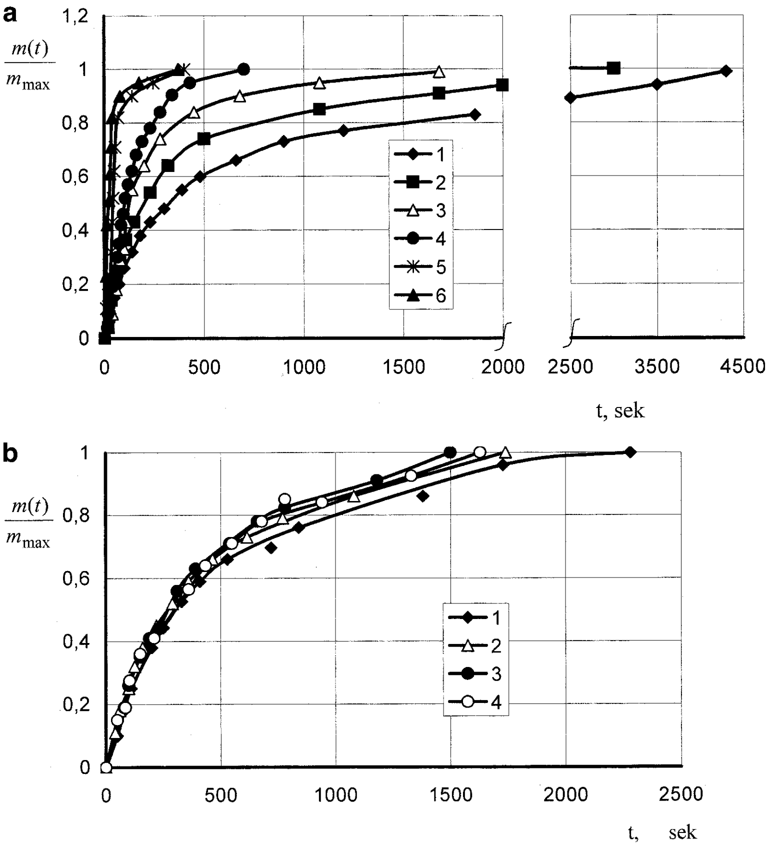
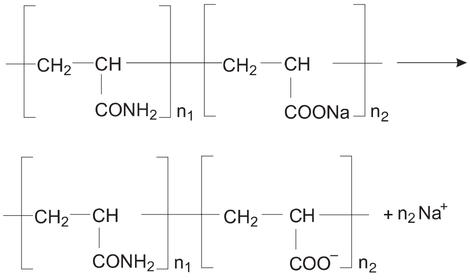


Fig. 2a, b The kinetic curves of ochre suspension sedimentation in the presence of: **a** A copolymer; **b** C copolymer. [A] × 10^6, %: 0 (1), 2 (2), 3 (3), 4 (4), 6 (5), 10 (6); [C] × 10^6, %: 0 (1), 5 (2), 15 (3), 35 (4)

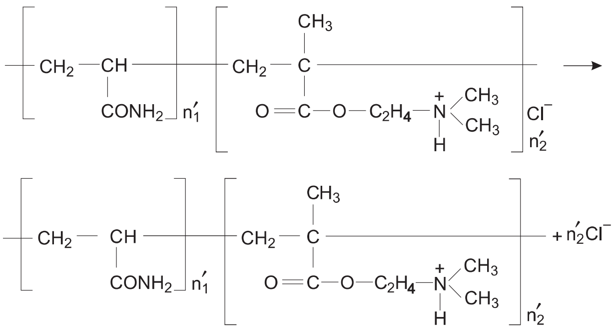
$$\lambda = \left(\frac{\overline{V}}{\overline{V_0}} - 1\right)\frac{1}{c} = \frac{D}{c} \tag{2}$$

where c is flocculant concentration.

It is easy to demonstrate by the simple treatment of kinetic data from Fig. 2, that $D_A > D_C$ (it is helpful to perform the comparison under the condition [A] = [C]) and $\lambda_A > \lambda_C$. Taking into account the charge signs of A and C macroions and DP particles such a relationship between the flocculation activities of A and C copolymers is rather unexpected, even remembering that $\overline{M_\eta}(A) > \overline{M_\eta}(C)$. The later circumstance cannot cause the experimentally observed relationship $\lambda_A > \lambda_C$ since there is only little correlation between λ and $\overline{M_\eta}$ values for $\overline{M} > \overline{M_{cr}}\left(\overline{M_{cr}} \sim 1 \cdot 10^6\right)$ [4, 27]. It should be mentioned that $\overline{M_\eta}(C)$ and $\overline{M_\eta}(A)$ exceed significantly the critical value of $\overline{M}\left(\overline{M_\eta}(A) > \overline{M_\eta}(C) > \overline{M_{cr}}\right)$. The condition $D_A > D_C$ unambiguously suggests the bridge (not neutralization) [3] mechanism of flocculation, since ochre particles carry a negative charge, i.e., a charge of the sign identical to that of an A macroion and opposite to that of a C macroion. The signs of A and C macroions may be judged from the ionization scheme of ionogenic groups of macromolecules for these copolymers:



$$\left[-CH_2-\underset{\substack{|\\CONH_2}}{CH}-\right]_{n_1}\left[-CH_2-\underset{\substack{|\\COONa}}{CH}-\right]_{n_2} \longrightarrow \left[-CH_2-\underset{\substack{|\\CONH_2}}{CH}-\right]_{n_1}\left[-CH_2-\underset{\substack{|\\COO^-}}{CH}-\right]_{n_2} + n_2Na^+$$



$$\left[-CH_2-\underset{\substack{|\\CONH_2}}{CH}-\right]_{n_1'}\left[-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\O=C-O-C_2H_4-\overset{+}{N}H(CH_3)_2}}{C}}-\right]_{n_2'}Cl^- \longrightarrow \left[-CH_2-\underset{\substack{|\\CONH_2}}{CH}-\right]_{n_1'}\left[-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\O=C-O-C_2H_4-\overset{+}{N}H(CH_3)_2}}{C}}-\right]_{n_2'} + n_2'Cl^-$$

To explain marked differences in D and λ values for A and C copolymers, it is necessary in principle to take into account the parameters difficult to assess such as microstructure and thermodynamic flexibility of macromolecules [28], specific features of the interface (the concentration and the distribution character of localized and non-localized adsorption centers, the surface energy pattern, the balance of hydrophilic/hydrophobic property at certain surface sites, the nature, location and concentration of defective structural elements, etc.), as well as the extent of an electrical double layer (EDL), the sign and magnitude of the electrokinetic potential ζ. As to the differences in the flocculation indices, not only lower λ_C values (in comparison with λ_A) should be mentioned, but also the fact that for [C] $> 10^{-5}$% the D fall takes place (see Fig. 2b). This indicates that with such dosages $\lambda_C < 0$, and the C copolymer begins to act as a stabilizer of DP particles.

The amphoteric nature of the C copolymer mentioned above is mainly due to the mosaic character of the surface charge sign of ochre particles. Together with negative charges arising predominantly from silanolic groups, the surface has positively charged sites due to the presence of Fe^{+3} ions. It should be taken into account that an important role in the PAMF adsorption on ochre is played not only by localized (predominantly produced by positively/negatively charged ions and functional groups), but also by non-localized adsorption centers on the surface of DP particles [29, 30]. It is supported by a very high adsorption degree of non-ionogenic polyacrylamide (N) on ochre: more than 98% N macromolecules are practically irreversibly adsorbed on the surface of DP particles [31] (the same is valid for ionogenic PAMFs, A and C). It may be suggested that the complicated dynamics of adsorption (in principle the desorption must also be taken into account, especially at the initial stages of the process) of separate ionogenic and non-ionogenic (AM) fragments of A and C on charged and non-charged sites of the interface determines the essential difference between adsorption of A and C macromolecules. A clear-cut distinction needs to be drawn between PAMF macromolecules involved in forming bridge bonds with two or more DP particles (their number denoted by N_1) and those adsorbed on a sole particle of DP and inert as regards flocculation (their number denoted by N_2) [4, 14].

It is obvious from the increasing ratio $y_1 = \frac{N_1}{N_1+N_2}$ and decreasing $y_2 = \frac{N_2}{N_1+N_2}$, all other factors being the same, that the efficiency of polymer in macroscopic flocculation process improves. Since $\lambda_A \gg \lambda_C$, $y_1(A) > y_1(C)$ and $y_2(A) < y_2(C)$. What this means is that the fraction of macromolecules anchored to a sole DP particles, and so inefficient in the acts of bridge bond formation for cationic copolymer, is significantly higher than that for anionic copolymer. Based upon the data of Fig. 2, the following copolymer concentrations were chosen as optimal in all subsequent experiments on ochre flocculation in the presence of binary PAMF additives: $[A] = [C] = 5 \times 10^{-6}$% (some experiments were carried out with lower flocculant concentrations $[A] = [C] = 4 \times 10^{-6}$%).

Now we turn to the assessment of ionic strength (I) influence on ochre sedimentation. Within the unhindered settling regime ($c_d = 8\%$) a modest decrease in the ochre sedimentation rate with increasing [NaCl] was observed which is due to the rise in the density of the dispersive medium when passing from salt-free to salt-containing suspensions [19]. A completely different character of NaCl effect on ochre sedimentation rate is observed in the regime of free (non-hindered) settling (Fig. 3). For salt-containing aqueous systems with I ≥ 0.04 N the sedimentation rate is more than 3 times higher compared with that for a salt-free medium (Fig. 3). A sharp difference in NaCl influence on ochre sedimentation rate between free and hindered settling regimes is partly due to the fact that a significant part of electrolyte is actually removed from a dispersion medium and participates in forming the electrical double layer around the DP particles. This important statement was proved by comparing the specific conductivity values of salt-containing aqueous solutions before and after contact with ochre. To do this, a proper NaCl amount was added to the suspension of carefully washed up 'zolotistaya' ochre ($c_d = 0.8\%$) to obtain the following I values: 0.001 N; 0.004 N; 0.01 N. After keeping salt-containing aqueous solutions in contact with ochre for 10 days, certain volumes of supernatant liquids were sampled and their $(\aleph - \aleph_0)$ values were measured (here $\aleph$ and $\aleph_0$ are the conductivity of the solution and that of the dispersion medium). For the above ionic strength levels these values were equal to 0.51×10^{-4} Sm cm^{-1}, 2.15×10^{-4} Sm cm^{-1}, and 5.03×10^{-4} Sm cm^{-1}, respectively. Using the calibration plot given in Fig. 4 $[NaCl]_x$ in each sample was determined (0.35×10^{-3} N, 1.66×10^{-3} N, 4.37×10^{-3} N correspondingly). Then the NaCl binding degree γ was calculated according to

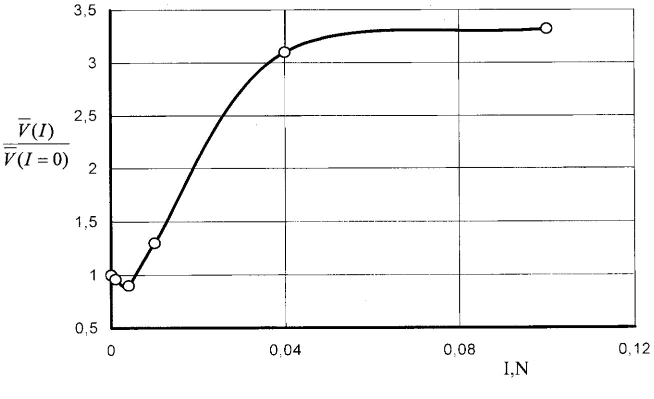


Fig. 3 The sedimentation rate of ochre suspension as a function of the ionic strength *I*

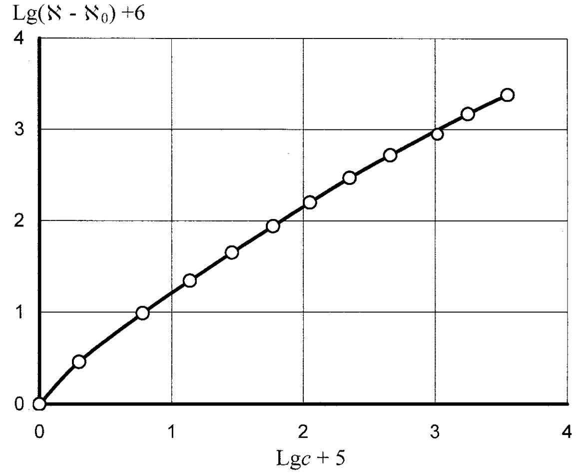


Fig. 4 The reference plot of the specific electrical conductivity ($\aleph - \aleph_0$) of the solutions vs electrolyte (NaCl) concentration

the formula: $\gamma = \frac{I - [NaCl]_x}{I}$. For the systems under study with ionic strength of 0.001 N, 0.004 N, and 0.01 N, γ values were equal to 0.650, 0.585, and 0.563 respectively. Thus, γ tends to rise with falling I.

The analysis performed demonstrates that a considerable part of NaCl transfers from aqueous solution to the electrical double layer of ochre. The rise of NaCl content in the electrical double layer results in its compression accompanied by the drop in ζ-potential of ochre. The data of the experiment using a PARMOQUANT instrument support this conclusion: with two magnitude order increase in I (from 0.004 N through 0.04 N to 0.4 N), ζ-potential values decrease from −38 mV to −27 mV and to −16 mV. Undoubtedly, in the presence of the ionogenic copolymers A and C, not only NaCl but also PAMF macromolecules participate in forming the EDL structure [29–31].

The aggregative and sedimentation stability vary in parallel with the changes in ζ as a function of [NaCl]. This is caused primarily by the drop in electrostatic repulsion between two ochre particles having like (negative) charges but approaching each other closely enough to bring about EDL overlapping.

The data of optical spectroscopy also indicate the drop in aggregative stability when one passes from salt-free ($I = 0$) to salt-containing solutions ($I = 0.01$ N). Such a transfer causes more than 40% increase in the size of DP particles, and the size polydispersity of ochre aggregates also rises [32].

Besides the direct effects mentioned above, NaCl addition affects the physicochemical indices of localized and non-localized adsorption centers, the effective solvation degree, as well as the intensity of the electrostatic, and, to a smaller-extent, Van der Waals interactions at the surface of DP particles etc. [4, 22].

Now let us turn to the consideration of the NaCl influence on the conformation of an ionogenic PAMF in solution. According to the foregoing ionization schemes, the macromolecules of A and C copolymers in aqueous media at pH ~5–9 are in the form of macroions. The polyelectrolyte properties of A and C copolymers are witnessed by the data of electrochemical measurements (Fig. 5, where equivalent conductivity $\Lambda = \frac{\aleph - \aleph_0}{PAMF}$ and viscosimetric curves. The plots of the reduced viscosity $\left(\frac{\eta_{sp}}{c}\right)$ vs concentration adhere to the Fuoss equation with three constants [28]. To make approximate estimate of macromolecules (more exactly, macroions) the Flory equation [33] may be used:

$$[\eta] \cdot M = \phi\left(\overline{R^2}\right)^{1.5}, \tag{3}$$

where $[\eta]$ is limiting viscosity number, and ϕ is the Flory constant.

To a first approximation, taking viscosity number $\left(\frac{\eta_{sp}}{c}\right)$ instead of $[\eta]$ for very low concentrations $c \sim 1 \times 10^{-5}$ g/cm^3, it may be demonstrated that $\left(\overline{R^2}\right)_C^{0.5} > 1 \cdot 10^3\,\mathring{A}$ and $\left(\overline{R^2}\right)_A^{0.5} > 1 \cdot 10^3\,\mathring{A}$. It must be emphasized that for the concentrations under study ($c \sim 1 \times 10^{-5}$ g/cm^3) the macromolecular coils do not overlap as may be judged by the satisfied necessary condition: $[\eta] \times c < 1$ [34, 35]. Having regard to the high thermodynamic and kinetic flexibility of acrylamide fragments [36, 37], the A and C macroions in water may be conceived as highly swollen and rather extended coils [35, 38]. A somewhat different conformation of A and C macroions is observed when they are adsorbed on DP particles: a coil turns into an asymmetric form resembling a strongly prolated ellipsoid [30].

After adding inorganic salt to the solution of A and C copolymers the charge screening along a macroion chain

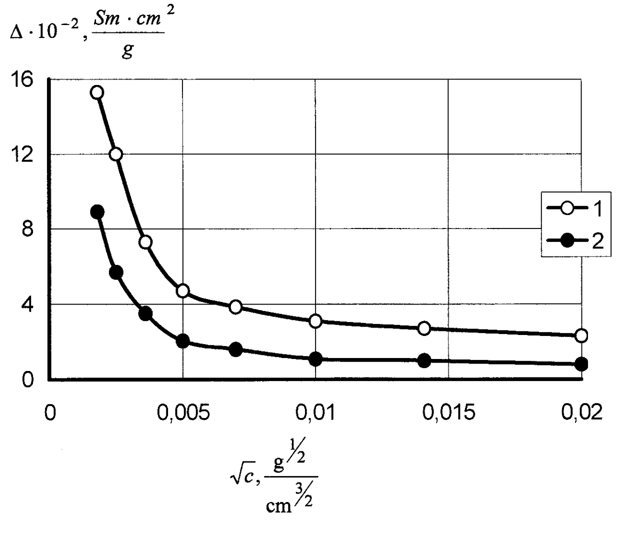


Fig. 5 Concentration dependence of the equivalent electrical conductivity of salt-free aqueous solutions of C (1) and A (2) copolymers

takes place, resulting in decreased electrostatic repulsion potential followed by a fall in $\left(\overline{R^2}\right)^{0.5}$ and $\left(\frac{\eta_{sp}}{c}\right)$. The pronounced compression (decrease in $\left(\overline{R^2}\right)^{0.5}$) of A and C macroions is evidenced by viscosimetry data in Fig. 6. Recall that according to Flory's relationship Eq. (3) $\left(\overline{R^2}\right)^{0.5}$ and $\left(\frac{\eta_{sp}}{c}\right)$ correlate and, to a first approximation, it may be assumed that $\left(\frac{\eta_{sp}}{c}\right)^{1/3} \sim \left(\overline{R^2}\right)^{0.5}$. It will be shown further that NaCl introduction also effects strongly the flocculation indices of PAMFs (both A and C).

Let us next consider the problem of interaction between copolymers A and C in salt-containing aqueous solutions. The presence of the interactions between macromolecules of different nature is conveniently judged from viscosimetric analysis data provided that the total copolymer concentration is constant (here, [A] + [C] = constant) [28, 34].

Denoting the mass content of A and C components by $w_A = \frac{[A]}{[A]+[C]}$ and $w_C = \frac{[C]}{[A]+[C]}$, and the calculated viscosity numbers by $\left(\frac{\eta_{sp}}{c}\right)_{calc}$, the following expression can be written assuming that the additivity rule applies to viscosity number [35]:

$$\left(\frac{\eta_{sp}}{c}\right)_{calc} = w_A\left(\frac{\eta_{sp}}{c}\right)_A + (1 - w_A)\left(\frac{\eta_{sp}}{c}\right)_C \tag{4}$$

(clearly, for the binary mixture, $w_C = 1 - w_A$).

To estimate the selective interactions between A and C copolymers it is convenient to use the parameter F proposed in [4]:

$$F = \left(\frac{\eta_{sp}}{c}\right)_{exp} \cdot \left(\frac{\eta_{sp}}{c}\right)_{calc}^{-1} - 1 \tag{5}$$

The condition $\left(\frac{\eta_{sp}}{c}\right)_{exp} = \left(\frac{\eta_{sp}}{c}\right)_{calc}$ and $F = 0$ correspond to the absence of appreciable interactions between A and C polymers.

If $\left(\frac{\eta_{sp}}{c}\right)_{exp} > \left(\frac{\eta_{sp}}{c}\right)_{calc}$ and $F > 0$, the components A and C interact with each other. In this case the heterocontacts AC result in increasing effective dimensions of macromolecular coils, i.e., $\left(\overline{R^2}\right)_C^{0.5}$ and $\left(\overline{R^2}\right)_A^{0.5}$ rise.

The condition $\left(\frac{\eta_{sp}}{c}\right)_{exp} < \left(\frac{\eta_{sp}}{c}\right)_{calc}$ and $F < 0$ correspond to the compression of macromolecular coils in the presence of macromolecules of another kind. In this case $\left(\overline{R^2}\right)_C^{0.5}$ and $\left(\overline{R^2}\right)_A^{0.5}$ values fall. The selective interactions of this sort took place for all binary (A + C) mixture compositions in our study, since for all mixtures under consideration the necessary condition was satisfied: $\left(\frac{\eta_{sp}}{c}\right)_{exp} \cdot \left(\frac{\eta_{sp}}{c}\right)_{calc}^{-1} < 1$ and $F < 0$ (Fig. 7).

To estimate the selective interactions between the ionogenic PAMFs besides the viscosimetric parameter F the electrochemical parameter F' was used:

$$F' = \frac{(\aleph - \aleph_0)_{exp}}{(\aleph - \aleph_0)_{calc}} - 1 \tag{6}$$

Assuming that the additive scheme is applicable to the conductivity, the calculated $(\aleph - \aleph_0)_{calc}$ value is determined by the formula

$$\aleph - \aleph_0 = w_A(\aleph - \aleph_0)_A + (1 - w_A)(\aleph - \aleph_0)_C \tag{7}$$

Figure 7 shows the dependence of F' and F on the composition of a binary mixture of A and C copolymers. It should be mentioned that the condition [PAMF] = constant is fulfilled for each point of the curves in Fig. 7. Note that the functions analyzed have the opposite

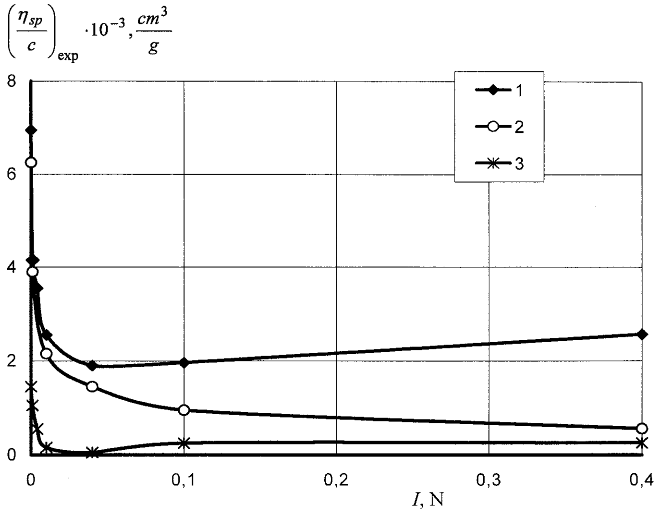


Fig. 6 The viscosity numbers for A (1) and C (2) copolymers and their 1:1 mixture (3) vs the ionic strength I. [A] = [C] = [{A + C}] = 0.03%

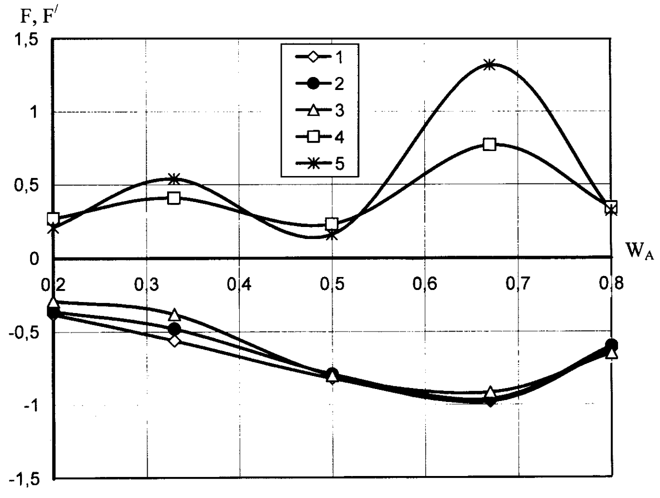


Fig. 7 Parameters F (1–3) and F′ (4, 5) vs composition of the mixture of A and C copolymers ([A] + [C]) × 10^4 g/cm^3: 1 (1), 0.5 (2, 4), 0.25 (3, 5)

signs: $F < 0$ and $F' > 0$. The interpretation of the condition $F < 0$ has been given above, and the condition $F' > 0$ is a consequence of the fact that the interaction between A and C macroions is accompanied by NaCl formation followed by the increase in $\aleph$. The distinct extremum of the analyzed functions observed near $w_A = 0.667$ (maximum for F and minimum for F') is direct evidence of the selective interactions between ionogenic groups of A and C copolymers. Taking into account the difference in $\overline{M_\eta}$ and $\overline{\beta}$ for A and C, the selective interactions of the type of 'one molecule A + one molecule C' may be considered.

The rise of stable interactions between A and C macroions is primarily a result of the opposite sign of their charges. This leads to the formation of interpolymer complexes between them [36, 37]. The process of complexation between A and C copolymers is favored by the commonness of non-polar fragments in the chemical structure of copolymer macromolecules (AA units) as well.

Viscosimetric data in Fig. 6 (curve 3) for (A + C) copolymer mixture with $w_A = 0.5$ also suggest strong negative deviation from the additive scheme (Eq. 4) in a salt-containing aqueous medium under various I. For this system an extraordinary behavior of $\left(\frac{\eta_{sp}}{c}\right)$ vs I for the region $I \geq 0.1$ N should be pointed to, namely, $\left(\frac{\eta_{sp}}{c}\right)$ rises with I. This phenomenon appears to be a result of the disintegration of the AC interpolymer complex, which must be accompanied, according to the theoretical consideration, by increasing $\left(\overline{R^2}\right)^{0.5}$ and $\left(\frac{\eta_{sp}}{c}\right)$ [29]. It would be expected that selective contacts arising between A and C copolymer macromolecules influence such macroscopic processes as adsorption and flocculation.

Let us consider more complicated objects, such as water + ochre + NaCl + A + C. Obviously, in these systems, as compared to the 'basic' ones considered above, a great number of new complicating factors occur. In particular, with certain dosages of A and C copolymers, the recharging of DP particles may take place. The data in Fig. 8 illustrate this fact. The transition from the system with negatively charged ochre particles ($\zeta < 0$) to the system with $\zeta > 0$ (curves 1–3) was carried out by adding C copolymer. More complicated recharging behavior of DP particles was observed for curves 1*–3*: preliminary introduction of 0.01% C into the system causes positive charge of DP particles ($\zeta > 0$), but after introducing a certain amount of the anionic copolymer A ochre particles again acquire negative charge. The comparison of the curves with each other leads to the conclusion that the recharging process is essentially affected by the ionic strength value.

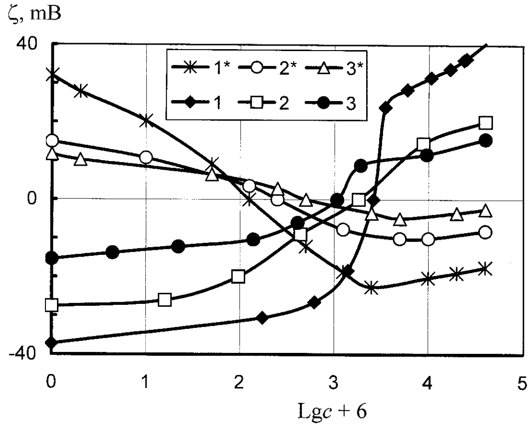


Fig. 8 ζ-Potential of ochre vs PAMF concentration in the media of varied ionic strength I, N: 0.004 (1, 1*); 0.04 (2, 2*); 0.4 (3, 3*). 1–3 – after introducing measured amount of C copolymer ($c = [C]$); 1*–3* – preliminary introduction of 0.01% C copolymer followed by adding measured amount of A copolymer ($c = [A]$)

Some of the kinetic curves illustrating the ochre sedimentation in the presence of binary PAMF-NaCl additives are given in Fig. 9. Previously the flocculating effect for ochre was demonstrated to depend on the sequence of introducing PAMF and NaCl into the system. For all the subsequent series of experiments, A and C copolymers were added to the salt-containing media, i.e., after NaCl introduction. The following three procedures of introducing the binary PAMF additives were examined:

1. (A + C), C after A
2. (C + A), A after C
3. {A + C}, A and C were added simultaneously

It should be mentioned that the total polymer contents from all three modes of A and C copolymer introduction were identical. Even the data given in Fig. 9 shows that the flocculating effect depends strongly on the mode of introducing the polymer components. A minimum value of D for the third mode can be predicted taking into consideration the strong selective interactions between A and C macroions causing the decrease in effective dimensions of macromolecular coils. The reason why flocculation indices differ for the first and the second modes of polymer introduction is less apparent. The experimental data obtained indicate that the structure of secondary floccules (those formed after introducing the second polymeric additive) is dependent upon the structure of primary floccules (those formed after introducing the first PAMF additive) in a complicated and ambiguous way [39]. This concept is of basic importance both in the scientific and application senses and conforms with modern theories of adsorption and flocculation [22, 30] based on the postulate that the adsorption of polymeric flocculants on DP particles is practically irreversible.

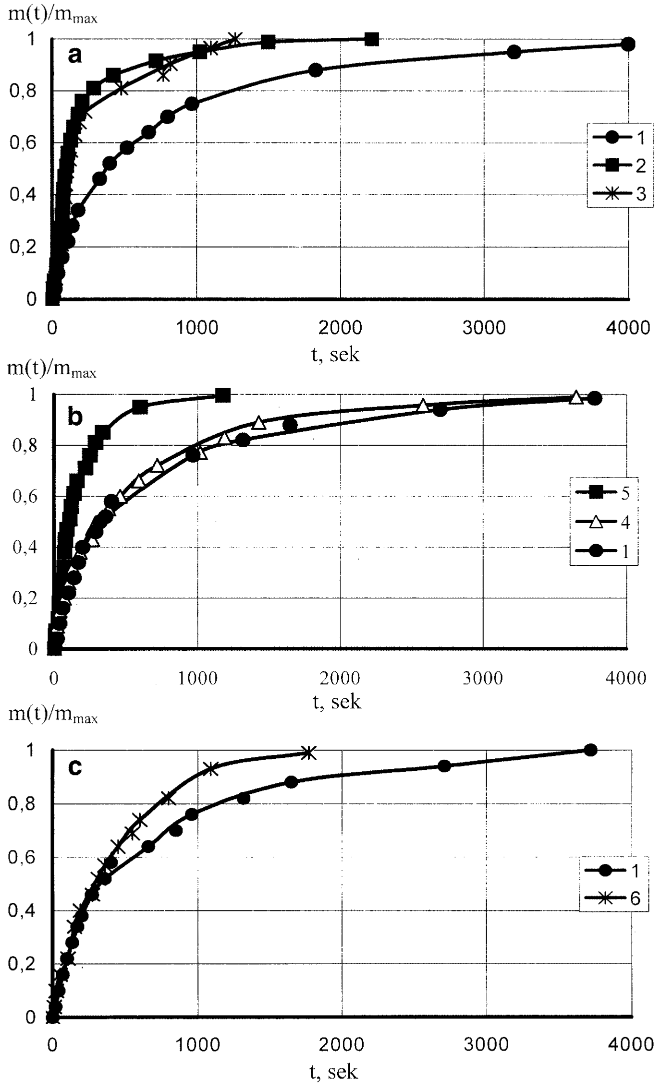


Fig. 9a–c The kinetic curves of ochre suspension sedimentation in a salt-free aqueous medium ($I = 0.004$ N) in the presence of A and C flocculants. $[A] = [C] = 5 \times 10^{-6}\%$. The mode of component introduction: **a** first; **b** second; **c** third. 1 – no flocculant added; 2–6 – with additives: 2 – A; 3 – A + C; 4 – C; 5 – C + A; 6 – {A + C}

The calculated value of flocculating effect D_{calc} used in treating the kinetic curves of ochre sedimentation in the presence of A and C copolymers (Fig. 9) was determined from the assumption that the principle of additive contributions of components to the resulting flocculating effect is applicable to the systems analyzed ((A + C) and (C + A)) [4]:

$$D_{calc} = \lambda_A \lambda_C [A][C] + \lambda_A [A] + \lambda_C [C] \qquad (8)$$

The summary data on ochre flocculation in the presence of binary additives of A and C copolymers in salt-containing media with various ionic strength are given in Table 1 and Fig. 10. It is evident from the given data that the experimental D value is less than the calculated one and the condition $D < D_{calc}$ is met for different I. This provides an added evidence for the key role played by selective interactions between the anionic and cationic copolymers which favor the decrease in the effective macroion size $(\overline{R^2})^{0.5}$ and retard secondary floccules enlargement both for the first (A + C) and second (C + A) flocculation modes.

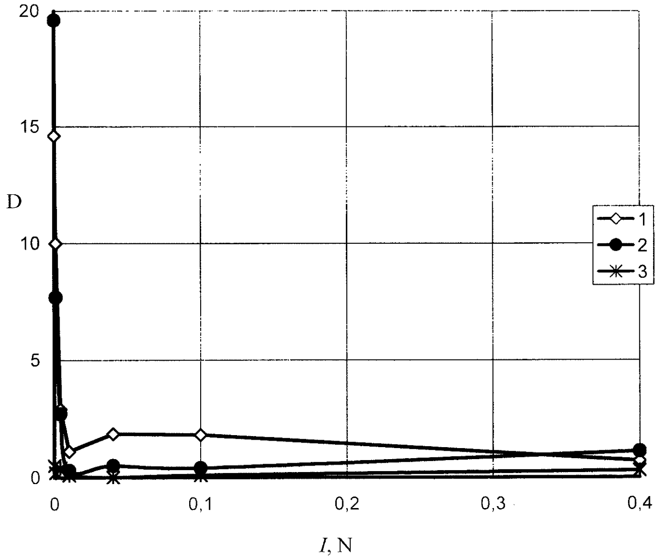


Fig. 10 The flocculating performance by ochre vs ionic strength with added binary compositions of A and C copolymers, $[A] = [C] = 5 \times 10^{-6}\%$. The mode of component introduction: 1 – first (A + C); 2 – second (C + A); 3 – third ({A + C})

When treating the kinetic data of Fig. 9 we calculated not only λ_A and λ_C but also the flocculating activities of appropriate components when they served as the second additive. The altered component function is designated by a primed symbol; so λ'_A and λ'_C mean the flocculating activities of A and C components with the first and the second modes of their introduction, correspondingly. The analysis of the data given in Table 1 shows that not only $\lambda_A > \lambda_C$ but $\lambda'_A > \lambda'_C$ as well. What this means is that as one passes from the primary floccules (in the presence of A or C) to the secondary ones (in the presence of (A + C) or (C + A)) the anionic copolymer is more active in the process of floccule enlargement. It should also be noted that the flocculating activities of A and C copolymers tend to fall in the acts of secondary floccule formation: $\frac{\lambda'_A}{\lambda_A} < 1$, $\frac{\lambda'_C}{\lambda_C} < 1$. These results – as well as such an 'anomalous' fact as negative λ'_C values for a number of systems with low electrolyte content ($I \le 0.004$ N, see Table 1) – indirectly testify to the important role of selective interactions between A and C macromolecules. They also suggest the above-mentioned specific features of C macroions interaction with a charged surface of DP particles.

Table 1 Summary data on ochre flocculation in salt-containing aqueous media in the presence of binary additives of A and C ionogenic copolymers

I, N	$[A] \cdot 10^6 = [C] \cdot 10^6$, %	PAMF introduction mode	D	D_{calc}	$\lambda_A \cdot 10^{-3}$, m^3/kg	$\lambda_C \cdot 10^{-3}$, m^3/kg	$\lambda'_A \cdot 10^{-3}$, m^3/kg	$\lambda'_C \cdot 10^{-3}$, m^3/kg	$\frac{\lambda'_A}{\lambda_A}$	$\frac{\lambda'_C}{\lambda_C}$
0	5	1. A + C	14.6	22.8	324.0	–	–	−1.82	0.864	−0.238
		2. C + A	19.8		–	7.66	280	–		
		3. {A + C}	0.059		–	–	–	–		
0.00033	5	1. A + C	10.0	14.7	236.0	–	–	−2.86	0.515	−0.627
		2. C + A	7.69		–	4.56	121.5	–		
		3. {A + C}	0.242		–	–	–	–		
0.004	5	1. A + C	2.85	4.02	65.6	–	–	−2.00	0.671	−0.581
		2. C + A	2.75		–	3.44	44	–		
		3. {A + C}	0.415		–	–	–	–		
0.01	5	1. A + C	1.14	1.14	16.7	–	–	3.24	0.106	0.994
		2. C + A	0.267		–	3.26	17.7	–		
		3. {A + C}	0.097		–		–	–		
0.04	5	1. A + C	0.86	1.09	10.0	–	–	4.83	0.492	1.02
		2. C + A	0.516		–	4.74	4.52	–		
		3. {A + C}	0.06		–	–	–	–		
0.1	5	1. A + C	0.86	1.08	12.8	–	–	2.72	0.547	1.94
		2. C + A	0.45		–	1.40	7.0	–		
		3. {A + C}	0.08		–	–	–	–		
0.4	5	1. A + C	0.72	1.27	12.6	–	–	1.09	0.881	0.139
		2. C + A	1.16		–	7.80	11.1	–		
		3. {A + C}	0.38		–	–	–	–		
0.04	4	1. A + C	0.765	0.857	12.5	–	–	4.41	0.470	0.741
		2. C + A	0.529		–	5.95	5.88	–		
		3. {A + C}	0.036		–	–	–	–		
0.1	4	1. A + C	0.625	0.871	9.2	–	–	4.69	0.725	0.509
		2. C + A	0.733		–	9.2	6.67	–		
0.4	4	1. A + C	0.75	0.923	16.2	–	–	1.56	0.406	0.373
		2. C + A	0.474		–	4.18	6.58	–		
		3. {A + C}	0.556		–	–	–	–		

The data in Table 1 witness that with increasing I the difference between λ_A and λ_C significantly diminishes. This circumstance supports the decreasing role of the electrostatic effects with rising I [35]. The correlation between D vs I (Fig. 10) and $\left(\frac{\eta_{sp}}{c}\right)$ vs I (Fig. 6) curves should also be noted. This is additional evidence for the close interconnection between the flocculating performance of (co)polymers and the conformational state of their macromolecules (macroions). Certainly, in the flocculation process the dimensions of macromolecular coil are the most important parameters for estimating conformational state of macromolecules. The comparative analysis of kinetic data on ochre suspension flocculation in salt-containing aqueous media in the presence of the ionogenic copolymers A and C with low content of ionogenic units ($\beta < 20\%$) makes it possible to conclude that the additives introduced (A, C, NaCl) in the experimental conditions operate in an antagonistic manner. The last statement should not be treated as absolute, since for a number of other disperse systems in the presence of water-soluble polymeric flocculants, the improved flocculating indices were observed after adding inorganic electrolytes to the system [40, 41]. The enhanced flocculating indices of a system when anionic and cationic polymers are introduced into a DP in succession were reported in the monograph [42]. Even greater difference is observed in the interactions pattern between components for the system (ochre + PAMF + NaCl); more specifically, the change in copolymer composition ($\beta > 60\%$) and the increase in $\frac{[A]}{c_d}$ and $\frac{[C]}{c_d}$ ratios by an order of magnitude led to the distinct synergetic action of anionic and cationic AM copolymers in the presence of NaCl when ochre was flocculated in the mode of free settling [35]. These data are further evidence that PAMFs have a considerable potential for application as highly efficient flocculants and hence a careful search of the best way of their application in the complicated, multicomponent systems is in order [4]. When making comparative estimation of PAMF efficiency for different sets of experiments in such systems one should take into account the synthesis conditions of the flocculants, their individuality, since macroscopic processes of adsorption and flocculation depend on a number of ‘fine’ (co)polymers parameters difficult to control, such as microstructure and branching degree of macromolecules, chemical heterogeneity, molecular weight polydispersity, concentration and nature of end and defect units, etc. [4, 28, 44, 45].

Conclusions

The sedimentation kinetics of ochre suspension in the mode of free (unhindered) settling has been studied in the presence of acrylamide copolymers of anionic (A) and cationic (C) nature. The ionic strength of a dispersion medium varied in a wide range: from 0.001 N to 0.4 N.

1. Ochre flocculation in the presence of acrylamide ionogenic copolymers proceeds by a 'bridge' mechanism, with flocculating activity of cationic copolymer (λ_C) significantly lower than that of anionic one (λ_A). The difference between λ_A and λ_C becomes less pronounced with increasing ionic strength.
2. When employing binary additives of A and C flocculants the resulting flocculating effect depends on the conformational state of macromolecules and on the mode of polymer component introduction into an ochre suspension. With low ionic strength, introducing C copolymer as the second additive (after A) results in lowered flocculating performance of the system, i.e., a C flocculant begins to work as a stabilizer of the system. The complicated flocculation character in the case of binary A and C additives is essentially a manifestation of selective interactions between polymer components.
3. With certain dosages of A and C ionogenic copolymers the recharging of the disperse phase particles was observed.

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