



Flocculating properties of 2-acrylamido-2-methyl-1-propane sulfonic acid-co-allylamine polyampholytic copolymers

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Abstract

In this study, 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) and allylamine (AA) were copolymerized in an aqueous solution via free radical polymerization using ammonium persulfate as the initiator. The chemical structure and compositions of the copolymers were confirmed by elemental analysis, Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR). Monomer reactivity ratios were determined by Fineman-Ross ($r_{\text{AMPS}} = 0.91 \pm 0.01$ and $r_{\text{AA}} = 0.40 \pm 0.02$), Kelen-Tudos ($r_{\text{AMPS}} = 1.10 \pm 0.02$ and $r_{\text{AA}} = 0.45 \pm 0.01$) and inverted Fineman-Ross ($r_{\text{AMPS}} = 0.85 \pm 0.01$ and $r_{\text{AA}} = 0.31 \pm 0.03$) methods. AMPS was found to be more reactive than AA and copolymers had a random composition. The flocculation performance of the copolymer was evaluated in $\text{Fe}(\text{OH})_3$ hydrosol. When the concentration of the copolymer in the hydrosol was more than 15 mg/L, the concentration of Fe^{3+} ions decreased up to 15 times due to flocculation of hydrosol particles. Effect of the concentration of AMPS-AA copolymer on the electropotential (zeta) and particle size of the hydrosol $\text{Fe}(\text{OH})_3$ were also studied systematically. It was determined that the zeta potential of the particles decreased from +58 to +20 mV and the average particle size of the hydrosol increased approximately 30 times when copolymer concentration in the hydrosol reached to 20 mg/L.

Keywords 2-Acrylamido-2-methyl-1-propane sulfonic acid · Allylamine · Radical copolymerization · Reactivity ratios · Flocculation · Electrokinetic potential

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Introduction

Polymeric ampholytes (polyampholytes) find broad practical application in many economically important areas. For example, polyampholytes are widely used as retention aids in the paper industry [1, 2]. Polyampholyte-based ion exchangers have a high sorption capacity, permitting facile separation of ions from mixtures in hydrometallurgy [3]. Due to the high content of functional groups along the chain, polyampholytes are effective flocculants [4, 5] and complexing agents [6–8]. Polyampholytes can also be used as polymerization catalysts [9], drug prolongators [10–12] and as model systems for studying electrostatic interactions in proteins and biopolymers [13].

An oft-employed monomer in polyampholytes is 2-acrylamido-2-methyl-1-propane-sulfonic acid (AMPS) which is readily copolymerized with other monomers via free radical methods. AMPS copolymerization has been carried out in various media. For example, radical copolymerization reactions involving AMPS have been done in water [14, 15], organic media and water/organic solvent mixtures [16–18] and are usually initiated by ammonium persulfate (PSA), potassium persulfate (KPS) [19, 20], the dinitrile of azobisisopropyl formic acid (DAFA) [21] and redox via KPS/disodium sulfite (SDS) complex [22–24] at a temperature of 40–70 °C.

AMPS-based (co)polymers are applied as drilling fluids [25–27], antibacterial agents [28], hydrogels for removing organic matter and cationic dyes [29–31], interpolymer complexing agents [31], magnetic hydrogels for removing metal ions [32], drug delivery vehicles [33] and as regulators of the rheological properties of fresh cement pastes [34]. Allylamine (AA) is difficult to polymerize with usual free radical initiators [35], but polyallylamine has been synthesized by using γ -rays [36]. Currently, some (co)polymers and hydrogels based on allylamine and its derivatives are known and they have been obtained by free radical copolymerization in the presence of an initiator [37–39] and under the influence of γ -rays [36, 40].

This work is devoted to the synthesis of a new polyampholyte—a copolymer of AMPS and AA (AMPS-AA copolymer), which has flocculating and biocidal properties against corrosive microorganisms (against microbiological corrosion of metal products and structures). The choice of the specified monomers is due to the negatively charged sulfonate groups of AMPS that will provide an electrostatic interaction of the copolymer (flocculant) with positively charged dispersed particles of suspensions and sols, permitting the amino groups of AA to coordinate with metal ions. Besides, these monomers are inhibitors of microbiological corrosion, and water-soluble copolymers (ampholytes) of monoallyl amine with monomers containing sulfonic groups (such as AMPS) can minimize water loss from pulp during well cementing [41, 42].

Experimental

Materials

AMPS (purity 99.0 wt%, density 0.962 g/mL), AA (purity 98.5 wt%) and iron (III) chloride (reagent grade, $\geq 98\%$) were purchased from Sigma-Aldrich and used

without additional purification. Ammonium persulfate $((\text{NH}_4)_2\text{S}_2\text{O}_8)$, purity 99.7 wt%) was kindly provided by LaborPharma Ltd. (Almaty, Kazakhstan). Acetone (purity 99.9 wt%) and 1,4-dioxane (purity 99.9 wt%) were purchased from Labhim-prom Ltd. (Almaty, Kazakhstan). Argon gas (purity 99.995 wt%) was purchased from Ikhsan Ltd. (Almaty, Kazakhstan). Distilled water with a conductivity 2.4 $\mu\text{S}/\text{cm}$ at 20 °C was used in all experiments.

Methods

FTIR and NMR measurements

The FTIR spectra of AMPS-AA copolymers were obtained on an Avatar 370 CsJ FTIR spectrometer, in the spectral range 4000–400 cm^{-1} from tablets prepared by compressing 2 mg of a sample with 200 mg of KBr. The ^1H and ^{13}C NMR spectra were recorded on a JNN-ECA Jeol 400 spectrometer (Japan) (frequency 400 and 100 MHz, respectively) in D_2O solvent at 20 °C. Chemical shifts were measured relative to signals of residual protons of the deuterated solvent.

Flocculation tests

The flocculating properties of AMPS-AA copolymers were studied in a hydrosol $\text{Fe}(\text{OH})_3$. The hydrosol was prepared according to the known method as follows [43]: 10 mL of 2 wt% aqueous solution of FeCl_3 was added to 250 mL of boiling distilled water with vigorous stirring. After cooling to room temperature, a 0.1 wt% aqueous solution of AMPS-AA copolymer was added dropwise into 10 mL hydrosol with vigorous stirring, and then, the total volume of the mixture was adjusted to 20 mL by adding distilled water. Then, the resulting mixture was left to stand for 24 h. The flocculation of particles under the action of a copolymer was determined by measuring the optical density (D) of the hydrosol. Optical density of the hydrosols was measured at 740 nm with a KFK-3–01 spectrometer (Russia). Distilled water was used as a reference.

Particle size and zeta (electrokinetic) potential analysis

Average particle size and zeta potential (ζ) of the hydrosol of $\text{Fe}(\text{OH})_3$ were determined with a Zetasizer Nano ZS Malvern at room temperature. The measurement error of the particle size was not more than $\pm 1\%$. The accuracy of the ζ -potential's measurement was ± 1 mV.

Copolymerization

The AMPS-AA copolymer was synthesized in a three-necked flask by radical copolymerization of AMPS with AA in an aqueous solution at 70 °C under argon atmosphere and constant stirring of the mixture in the presence of an initiator $((\text{NH}_4)_2\text{S}_2\text{O}_8)$ (0.05 wt. % by total weight of the monomers) for 2–3 h at various

mole ratios of monomers (Fig. 1). The total mole concentration of monomers in the mixture was equal to 5 mol/L. After the synthesis, copolymers were precipitated from the reaction environment into the mixture of 1,4-dioxane and acetone (50:50 vol. %) and washed with this mixture three times for an hour in order to remove the residual monomers. Then, copolymers were dried in vacuum at 40 °C to constant weight. The structure and mole composition of AMPS-AA copolymers were determined by FTIR and NMR spectroscopy, elemental analysis for H, C and N. The yields of the copolymers were determined gravimetrically.

Determination of the monomer reactivity ratios

The monomer reactivity ratios are a key parameter for describing the copolymer composition and microstructure ultimately. From the monomer feed ratio and resultant copolymer composition, the monomer reactivity ratios were determined by Fineman-Ross equation, Kelen-Tüdös and inverted Fineman-Ross methods [44–46].

Determination of the concentration of iron (III) ions in a hydrosol in the presence of a copolymer

The concentration of iron (III) ions in the $\text{Fe}(\text{OH})_3$ hydrosol was determined using an Agilent 240Z Atomic Absorption Spectrometer (USA) at room temperature. The measurement error of the Fe^{3+} was not more than 2%.

Results and discussion

The results of infrared spectroscopic studies

The FTIR spectrum of the AMPS-AA copolymer (Fig. 2) contains a broad band at 3476 cm^{-1} , characteristic of the NH-group of the secondary amide in AMPS, as well as the primary amino group NH_2 of the AA monomer. At 3050 cm^{-1} , the adsorption band of the $-\text{CH}_3$ groups appears, while the adsorption band associated with the methylene linkages is indicated at 2950 cm^{-1} .

In the region of 1643 cm^{-1} , an absorption band characteristic of the carbonyl group $\text{C}=\text{O}$ is detected. At a frequency of 1155 cm^{-1} , the absorption band is also detected, due to the stretching vibrations of the $-\text{O}-\text{SO}_2-$ group.

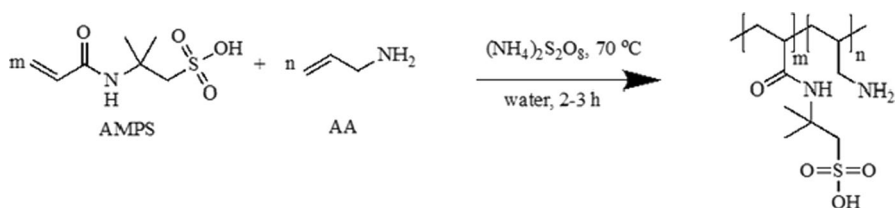


Fig. 1 The free radical copolymerization of AMPS and AA monomers

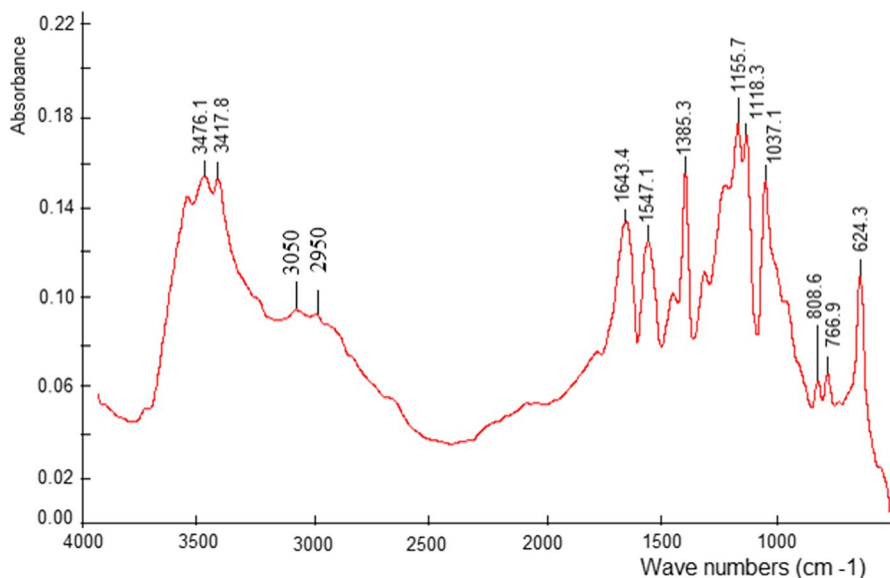


Fig. 2 FTIR spectrum of AMPS-AA copolymer

Analysis of the NMR spectra of poly-AMPS and AMPS-AA copolymer

According to the literature, the assignment of ^1H NMR proton signals of the homopolymer poly(AMPS) in deuterated water should be as shown in Fig. 3. We used these data to determine the compositions of the AMPS-AA copolymers. Characteristic for the poly(AMPS) is the signal at 3.56 ppm, corresponding to the methylene protons adjacent to the sulfonate group of the monomer unit.

In the spectrum of the AMPS-AA copolymer (Fig. 4), which was synthesized from a mixture of monomers having an initial composition of 60:40 mol%, new signals appear that are characteristic of the structure of allylamine units in addition to the ones associated with the poly(AMPS) homopolymer. Interestingly, the doublet signal appeared at 3.42–3.43 ppm, which denotes the methylene group with the protons labeled “12” of the copolymer structure and the methylene group of the non-polymerized allylamine or terminal groups (16) with unsaturated hydrogen atoms. The above assumptions were used for calculating the composition of the copolymer. If the composition of the copolymer is calculated from the integral proton intensities, the mole content of the AMPS was calculated by the protons labeled at position 8 (2H at $\delta=3.56$ ppm) of the methylene group, while the protons labeled at positions 12 and 16 protons (2H at $\delta=3.42$ –3.43 ppm) are from the methylene groups of the poly(AA) units and allylamine monomer. Therefore, from the integrated peaks, the mole composition of copolymer with respect to AMPS can be determined as $F_{\text{AMPS}} = 34.8/(34.8 + 20.2) = 63.2$ mol%.

However, we should correct for the composition of the copolymer, taking into account the unpolymerized allylamine which could not be removed. Our calculations thus far assumed that all of the AA methylenic protons were in the copolymer.

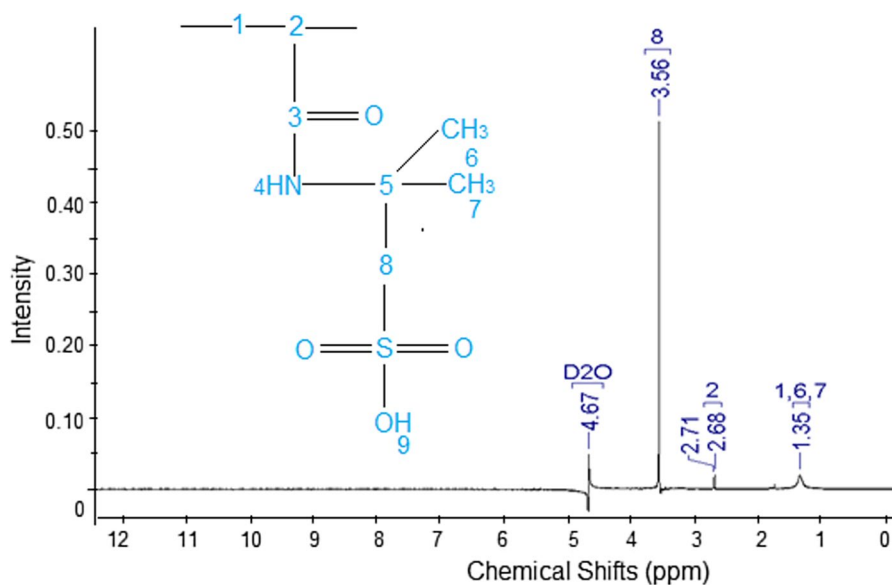


Fig. 3 ^1H NMR spectrum of poly(AMPS) homopolymer in D_2O . The various protons are labeled and correlated to the position in the chemical structure

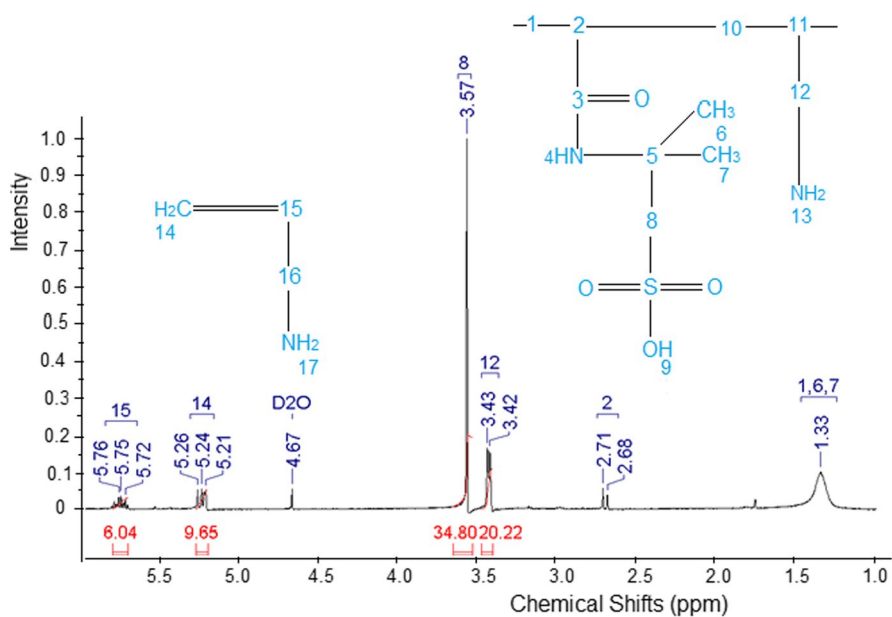
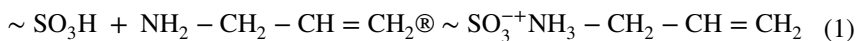


Fig. 4 ^1H NMR spectrum of the AMPS-AA copolymer, obtained from 60:40 mol% monomers in D_2O . The numbers next to the protons are labeled to identify the peaks

The vinylic protons corresponding to the AA monomer are labeled at positions **14** and **15** in the monomer impurity. The concentration of AA groups of the monomer from the integrated area is thus $(6.04 + 9.65)/3H = 5.23$. It is known that the peaks at $\delta = 3.42\text{--}3.43$ correspond to the methylene protons of the AA monomer and the AA units involving into the copolymer, which corresponds to a concentration AA in the monomer and copolymer from the integrated areas of $= 20.22/2H = 10.11$. To get the concentration from the units only in the polymer, we subtract $10.11 - 5.23 = 4.88$ units. Thus, we can determine the corrected composition using $F_{\text{AMPS, corrected}} = (34.8/2H)/[(34.8/2) + 4.88] = 78.1\%$.

Thus, on the basis of the ^1H NMR spectrum, it can be concluded that the AMPS-AA copolymer obtained from the mixture of the monomers with mole ratio = 60:40 mol% has a composition of 78.1:21.9 mol%. However, it should be noted that the copolymer can contain a small amount of the non-polymerized AA monomers, which may be linked to the sulfonic groups of the copolymer by the acid–base (electrostatic) mechanism according to the following scheme:



Determination of the monomer reactivity ratios

Monomer reactivity ratios were determined by appropriate linearization from the Mayo-Lewis equation and given in Table 1. Taking into consideration of non-polymerized AA monomers linked to the sulfonic groups by the acid–base (electrostatic) mechanism, the polymerized AA in the copolymer was calculated. Taking into account the values of r_{AMPS} , r_{AA} , and $r_{\text{AMPS}} \times r_{\text{AA}}$, we can conclude that like the other acrylamide derivatives, AMPS is more active than AA and the monomers copolymerize essentially randomly [47, 48].

Determination of the mole composition of AMPS-AA copolymers by elemental analysis

Elemental analysis of copolymer samples for S, H, C and N was performed on a Vario El cube instrument (Germany). Table 2 presents the results of element analysis of the compositions of AMPS-AA copolymers.

As can be seen from Table 2, that the mole content of AA in the AMPS-AA copolymer is not dramatically different from the feed composition. This seems to

Table 1 Comonomer reactivity ratios of AMPS-AA copolymers

Method	r_{AMPS}	r_{AA}	$1/r_{\text{AMPS}}$	$1/r_{\text{AA}}$	$r_{\text{AMPS}} \times r_{\text{AA}}$
Fineman-Ross	0.91 ± 0.01	0.40 ± 0.02	1.10	2.50	0.36
Inverted Fineman-Ross	0.85 ± 0.01	0.31 ± 0.03	1.18	3.23	0.26
Kelen-Tudos	1.10 ± 0.02	0.45 ± 0.01	0.91	2.22	0.50

contradict the literature [36–40], according to which the reactivity of AA should be much lower than that of AMPS, *N*-vinylpyrrolidone, acrylic and methacrylic acids. This “unusual” behavior of AA in a mixture with AMPS can be explained by the interaction of unpolymerized AA monomers with sulfonic acid groups of AMPS in the copolymer on the acid–base (electrostatic) mechanism, according to Eq. (1).

Studying the viscosity of aqueous solutions of AMPS-AA copolymers

Rheology measurements were performed on the AMPS-AA polymers aqueous solution using an Anton Paar MCR302 double-gap measuring systems rheometer at room temperature. Rotation rate was varied between 0.01 and 10 s^{−1}. Figure 5 shows the effect of the concentration and mole composition of the AMPS-AA copolymer on the viscosity of its aqueous solution.

From Fig. 5, the following conclusions can be made:

1. Viscosity of copolymer solution decreases with lower AMPS composition in the copolymer; this can be attributed to the electrostatic repulsion between negatively charged sulfonic groups in the macromolecules that leads to stretching of the chains and subsequent orientation.
2. In the copolymer with mole composition AMPS:AA = 59:41, the viscosity of the polymer at different concentrations is nearly identical. When the main chain of the copolymer contains a relatively low concentration of AMPS units, the repulsive force between the negatively charged sulfonic groups becomes minimal. In addition, sulfonic groups can be neutralized via intramolecular acid–base interaction with the amino groups of the AA units (Fig. 1). As a result, the copolymer behaves like a non-ionic polymer. Consequently, viscosity can be expressed as a power series in concentration, and graphs of viscosity versus concentration become linear [49–52].

Studies of flocculation properties

The flocculation properties of the AMPS-AA copolymer were studied by using a Fe(OH)₃ hydrosol. The results are presented in Fig. 6. We have taken Fe(OH)₃ hydrosol as a model system to study the flocculating properties of AMPS-AA copolymer for the following reasons:

- (a) The particles of this hydrosol are positively charged, and the macromolecules of the AMPS-AA copolymer have a total negative charge. The flocculating effect of a negatively charged flocculant is more pronounced for flocculation of positively charged particles. Therefore, it is advisable to use the AMPS-AA copolymer for the purification of wastewater from positively charged colloidal particles.
- (b) In metallurgical and ore processing factories, the industrial waste water is often contaminated with iron ions (Fe²⁺ and Fe³⁺), and these ions, as a result of hydrolysis in an aqueous solution, easily pass into hydroxides and then into hydrosols. Thus, iron ions presented in industrial wastewater are usually in the

Table 2 Results of elemental analysis of the AMPS-AA copolymers

Content of monomers in feed, mol% [AMPS]: [AA]	Content of elements in the copolymer, wt%			Average mole composition of the copolymer from the results of elemental analysis, mol% [AMPS]:[AA]	Average mole composition of the copolymer from the ¹ H NMR spectroscopy, mol% [AMPS]:[AA]	Yield of the copolymer, %
	N	C	H			
50:50	10.0	49.6	7.5	59:41	55:45	42 ± 0.5
60:40	9.7	44.9	7.3	64:36	63:37	54 ± 0.6
80:20	7.4	41.6	6.6	89:11	86:14	76 ± 0.6
100:0	6.6	39.8	6.2	98	98	94 ± 0.3

form of colloidal particles. Therefore, in order to purify waste water from iron ions, it is necessary to destabilize (coagulate) the colloidal particles of $\text{Fe}(\text{OH})_3$. In principle, our copolymer (flocculant) can be used to purify wastewater from any positively charged colloidal particles.

The temporal dependences of the optical density of the hydrosol in the presence of 0.2% of the AMPS-AA copolymer can be conditionally divided into three phases. In the first phase, turbidity occurs, i.e., an increase in the optical density of the hydrosol, which can be explained as the commencement of flocculation of the particles of $\text{Fe}(\text{OH})_3$ hydrosol due to the action of the copolymers. Then, the hydrosol particles flocculate and precipitate. As a result, a transparent layer forms in the upper part of the mixture. The second and third phases of Fig. 6 correspond to these latter two stages of the process.

We also determined the effect of the copolymer concentration on the degree of water purification from colloidal particles $\text{Fe}(\text{OH})_3$, i.e., on the concentration of Fe^{3+} ions in water. The results are presented in Fig. 7.

From Fig. 7, it can be seen that the intense precipitation of iron (III) ions leads to the purification of water from metal ions, starting from a concentration of the $\text{Fe}^{3+} = 160$ mg/L. Moreover, AMPS:AA = 89:11 is a more effective mole composition for the deposition of Fe^{3+} ions from hydrosol. At the optimum concentration of the copolymer, the degree of purification of the water from iron (III) ions reaches 94 wt. %.

The precipitation of iron (III) ions from the hydrosol in the presence of the AMPS-AA copolymer can be explained by the adsorption of macromolecules on the surface of the hydrosol particles by the electrostatic mechanism. (The negatively charged functional groups of the copolymer are attracted to positively charged particles of the hydrosol $\text{Fe}(\text{OH})_3$.) As a result of this, a decrease in the charge density on the surface of iron particles occurs, as evidenced by the drop in the electrokinetic (zeta) potential of the hydrosol particles with increasing copolymer concentration (Fig. 8). When the zeta potential reaches +22 mV, the attractive forces between colloidal particles will dominate the repulsive forces, which as a result the particles lose stability and begin to aggregate, forming flocs. The floccule formation stage corresponds to a sharp increase in the average particle size of the hydrosol under

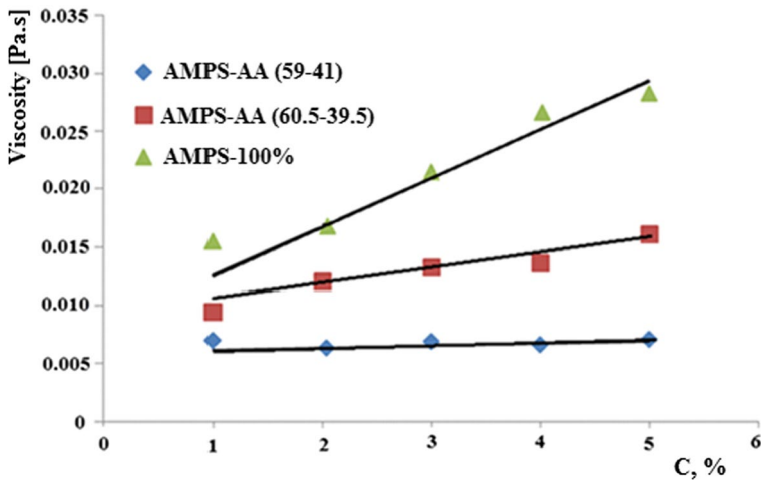


Fig. 5 The effect of the concentration and mole composition of the AMPS-AA copolymer on the viscosity of its aqueous solution

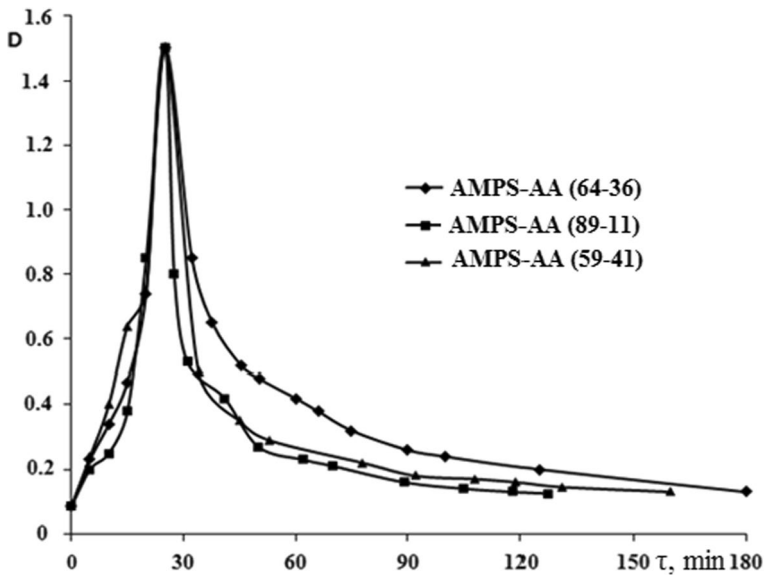


Fig. 6 Kinetics of changes in the optical density of the hydrosol of $\text{Fe}(\text{OH})_3$ in the presence of 0.2% AMPS-AA copolymer with different mole composition

the action of the copolymer macromolecules in the concentration range $> 15 \text{ mg/L}$ (Fig. 9). Average particle size was determined with a Zetasizer Nano ZS Malvern at room temperature.

In this concentration range, colloidal particles will begin to aggregate, forming flocs which lead to a sharp increase in the average particle size of the hydrosol. The particle size of the hydrosol increases approximately 30 times. Further, under the action of gravity, the flocs precipitate and consequently the upper part of the suspension becomes transparent.

So, based on the results obtained, we can state that electrostatic interaction is found to be the dominant force in the flocculation of $\text{Fe}(\text{OH})_3$ colloidal particles by AMPS-AA copolymer. When the copolymer is added to the hydrosol, negatively charged macromolecules of the polymer are adsorbed on the surface of colloidal particles. As a result, the surface charge of the $\text{Fe}(\text{OH})_3$ particles decreases, and when the critical value of the zeta potential ($< +40$ mV) is reached, the colloidal particles lose their stability and they flocculate and precipitate.

In the reported work [53], the flocculation of the particles of aluminum hydroxide suspension by the lignin-g-AMPS copolymer was studied. The electrokinetic potentials of the lignin-g-AMPS copolymer, poly-AMPS and aluminum hydroxide were determined, which were -52.6 , -48.6 , and $+30.0$ mV, respectively. It was found that the lignin-g-AMPS copolymer may be used to flocculate aluminum hydroxide particles and to achieve the relative turbidity of 0.2, about 0.40 mg/g lignin-g-AMPS copolymer was needed. The relatively lower consumption of lignin-g-AMPS copolymer for flocculation in comparison with AMPS-AA copolymer can be explained by the fact that the stability of the aluminum hydroxide suspension is much lower than that of the $\text{Fe}(\text{OH})_3$ hydrosol. This is evidenced by the data of zeta potentials of the systems: $+58$ mV for $\text{Fe}(\text{OH})_3$ hydrosol and $+30$ mV for the aluminum hydroxide particles. Therefore, less amount of flocculant is required to destabilize a less stable suspension. Unfortunately, in the literature, in most cases, the flocculation of negatively charged particles (for example, suspensions of clays, aluminosilicates, etc.) by polymers is considered. Only in some of the reported literature, the flocculation of positively charged suspension particles was discussed. There is practically no work on the flocculation of positively charged colloidal particles. Therefore,

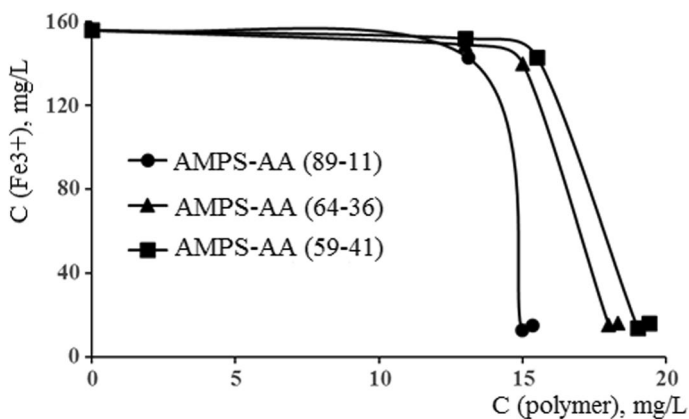


Fig. 7 The effect of the concentration of AMPS-AA copolymer in the $\text{Fe}(\text{OH})_3$ hydrosol on the concentration of Fe^{3+} ions in the solution

for comparison, we took the flocculation of particles of an aluminum hydroxide suspension.

We assume that in the future, AMPS-AA copolymers with active sulfonic and amine groups can be also used in the paper industry [1, 2], in water treatment for the removal of metal ions [3, 32], positively charged dyes and polyelectrolytes [6, 7, 30, 54], and also as a biocidal polymer to suppress the growth of microorganisms and to protect metal constructions from microbiological corrosion [28, 42].

Conclusion

AMPS-AA copolymers with different mole composition were synthesized by radical copolymerization of AMPS and AA monomers in water at 70 °C using ammonium persulfate as an initiator. Mole composition and structure of the copolymers were determined by elemental analysis, FTIR and ^1H NMR spectrometers. It was found that in all cases, the AMPS monomer had a higher reactivity than AA. The monomer reactivity ratios were determined by Fineman-Ross ($r_{\text{AMPS}} = 0.91 \pm 0.01$ and $r_{\text{AA}} = 0.40 \pm 0.02$), Kelen-Tudos ($r_{\text{AMPS}} = 1.10 \pm 0.02$ and $r_{\text{AA}} = 0.45 \pm 0.01$) and inverted Fineman-Ross ($r_{\text{AMPS}} = 0.85 \pm 0.01$ and $r_{\text{AA}} = 0.31 \pm 0.03$) methods. The flocculating ability of the AMPS-AA copolymer with different mole composition was studied in $\text{Fe}(\text{OH})_3$ hydrosol. It was found that the AMPS-AA copolymers had good flocculating properties and can be used for purification of the industrial water from colloidal particles of $\text{Fe}(\text{OH})_3$. At the optimum copolymer concentration ($> 15 \text{ mg/L}$), the degree of the water purification from colloidal particles of iron hydroxide reached 94%. The flocculating agreed with a charge neutralization

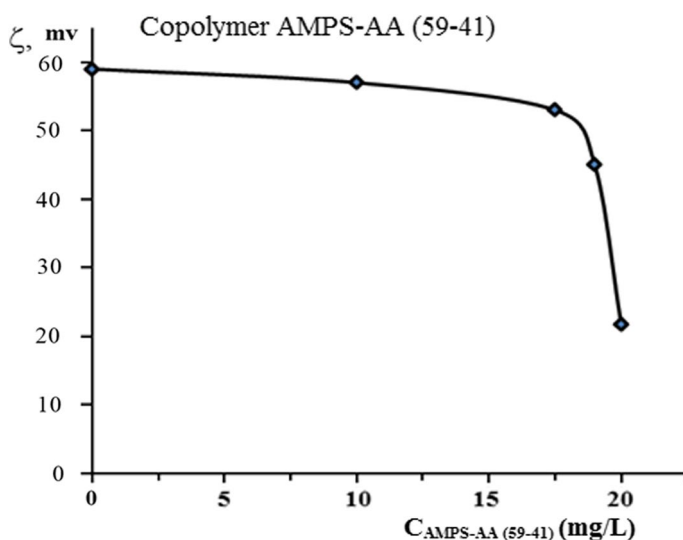


Fig. 8 Effect of the AMPS-AA (59–41) copolymer concentration on the electrokinetic potential of the particles of $\text{Fe}(\text{OH})_3$ hydrosol

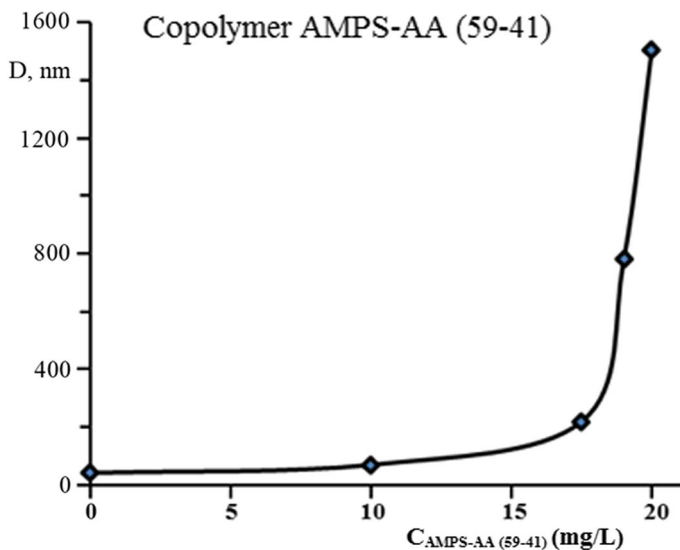


Fig. 9 Effect of the AMPS-AA (59–41) copolymer concentration on the average particle size of $\text{Fe}(\text{OH})_3$ hydrosol

mechanism according to electrokinetic potential and particle size measurements. Particle size of the hydrosol was determined with a Zetasizer Nano ZS Malvern at room temperature.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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