SYNTHESIS AND RHEOLOGICAL PROPERTIES OF WATER-SOLUBLE ACRYLAMIDE–METHACRYLIC ACID COPOLYMERS FOR HIGH-SALINITY WATER SYSTEMS

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Abstract. Water-soluble copolymers based on acrylamide (AAM) and methacrylic acid (MAA) were synthesized as highly efficient flocculants, and their composition–structure characteristics were investigated. The effects of monomer ratio, polymerization temperature, and ionic strength on the viscosity properties were analyzed using 0.1% solutions. According to the results, a maximum in relative viscosity was observed at 30–35 mol% MAA, which was attributed to the optimal balance between hydrophilic and hydrophobic fragments. Under conditions of high ionic strength, the viscosity of the copolymers decreased due to charge screening; however, chains containing MAA retained higher stability. The optimal polymerization conditions (45–50 °C, 0.2% initiator) provided the highest viscosity and yield. The obtained results confirm the potential applicability of these copolymers in real high-salinity water systems.

Keywords: acrylamide, methacrylic acid, copolymer, viscosity, flocculant.

Аннотация. Акрилламид (AAM) ва метакрил кислота (MAA) асосидаги сувда эрийдиган сополимерлар юқори самарали флокулянтлар сифатида синтез қилинди ва уларнинг таркиб–тузилма хусусиятлари тадқиқ қилинди. Мономерлар нисбати, полимеризация ҳарорати ва ионлилик кучининг қовушқоқлик хусусиятларига таъсири 0,1% эритмаларда таҳлил қилинди. Натичаларга кўра, нисбий қовушқоқлик 30–35 мол.% MAA да максимал қийматга эришди, бу гидрофил ва гидрофоб фрагментлар ўртасидаги оптимал мувозанат билан изоҳланади. Юқори ионлилик кучи шароитида сополимерларнинг қовушқоқлиги зарядларнинг экранланиши сабабли камайди; бироқ MAA ни ўз ичига олган занжирлар юқори барқарорликни

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сақлаб қолди. Оптимал полимеризация шароитлари (45–50 °C, 0,2% инициатор) энг юқори қовушқоқлик ва унумдорликни таъминлади. Олинган натижалар ушбу сополимерларни амалдаги юқори туз миқдорига эга сув тизимларида қўллаш потенциалини тасдиқлайди.

Калит сўзлар: акрилламид, метакрил кислота, сополимер, қовушқоқлик, флокулянт.

Аннотация. Были синтезированы водорастворимые сополимеры на основе акриламида (AAM) и метакриловой кислоты (MAA) в качестве высокоэффективных флокулянтов, а также изучены их композиционно-структурные характеристики. Влияние соотношения мономеров, температуры полимеризации и ионной силы на вязкостные свойства анализировалось с использованием 0,1% растворов. Согласно результатам, максимальное значение относительной вязкости наблюдалось при 30–35 моль.% MAA, что объясняется оптимальным балансом между гидрофильными и гидрофобными фрагментами. При высоких значениях ионной силы вязкость сополимеров снижалась из-за экранирования зарядов; однако цепи, содержащие MAA, сохраняли более высокую стабильность. Оптимальные условия полимеризации (45–50 °C, 0,2% инициатор) обеспечивали наивысшую вязкость и выход. Полученные результаты подтверждают потенциальную применимость этих сополимеров в реальных водных системах с высокой солёностью.

Ключевые слова: акриламид, метакриловая кислота, сополимер, вязкость, флокулянт.

Introduction

Globally, the problem of pollution in natural and wastewater is increasing due to intensive industrial development, widespread use of synthetic materials, and improper waste management. This leads to the accumulation of organic and mineral substances, deterioration of water quality, and a decline in the ecological stability of aquatic ecosystems. Therefore, it is particularly important to develop new, efficient, and environmentally safe polymeric materials that can simultaneously remove colloidal, organic, and ionic pollutants, while maintaining stability under high-mineral conditions of water systems. To address these challenges, it is necessary to synthesize water-soluble copolymers based on acrylamide and methacrylic acid, study their colloid-chemical fundamentals, and investigate their structural parameters.

Copolymers based on acrylamide and MAA are considered promising for the development of highly efficient reagents for water purification. The balance between hydrophilic and hydrophobic fragments allows for controlling the physicochemical and functional properties of the polymer and ensures optimal

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interactions with various pollutants. Studying the influence of copolymerization conditions on composition and structure is essential for obtaining stable and effective flocculants in real water environments.

LITERATURE REVIEW

In colloid chemistry, flocculation is defined as the process in which dispersed particles aggregate into larger assemblies—flocs—under the action of high-molecular-weight substances, known as flocculants. A key feature of this process is that polymer molecules act as specific "bridges" between dispersed phase particles. Adsorption of individual segments of the macromolecule onto the surfaces of colloidal particles allows simultaneous linking of different particles, resulting in aggregates with increased mass and size. Such aggregates are relatively unstable and can easily settle or be separated by mechanical methods [1-5].

Anionic copolymers such as AAM/AA and AAM/MAA are widely used in negatively charged colloidal systems; they are capable of forming effective bridges even in the presence of repulsion at moderate ionic strength. The carboxyl groups provide controllable negative charges depending on the degree of neutralization. As noted by Duis and colleagues, such copolymers are applied in large-scale wastewater treatment facilities, and their ecological stability and toxicity remain key directions in current research [6].

Copolymers based on acrylamide and methacrylic acid (MAA) are considered a promising approach for developing highly efficient reagents for water purification. The balance between hydrophilic and hydrophobic fragments in the structure of these copolymers allows for targeted control of their physicochemical and functional properties, thereby ensuring optimal interactions with various types of pollutants. Furthermore, studying the effects of copolymerization conditions on the composition and structure of these polymers is essential for elucidating the underlying patterns, which is crucial for producing flocculants with predictable and stable performance in real water environments.

RESULTS AND DISCUSSION

Analytical-grade reagents were used for the synthesis of water-soluble copolymers based on acrylamide (AAM) (CH_2=CH($CONH_2$)) and methacrylic acid (MAA) (CH_2=C(CH_3)(COOH)). The main monomer, AAM (>99.5 %), forms the hydrophilic matrix of the polymer and is incorporated into the linear chains. As the copolymerization component, MAA with >99 % purity was used, introducing carboxyl groups into the polymer and controlling the charge density. The trace amount of MEHQ inhibitor present protects against premature self-polymerization.

Ammonium persulfate (APS) >98 % was used as a radical polymerization initiator in the form of a 10 % aqueous solution, with its concentration varying from 0.1 to 0.6 % of the monomer mass. For low-temperature polymerization, a redox

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system consisting of PSA and sodium metabisulfite ($Na_2S_2O_5$) >98 % was employed in a molar ratio of 1:1–1.5.

The copolymers were synthesized in an aqueous medium without hydrolysis by radical polymerization in a thermostated glass reactor with mechanical stirring. The reaction system was washed with deionized water to remove oxygen and purged with nitrogen.

Acrylamide and MAA copolymers were synthesized in a 500 cm^3 three-necked flask equipped with a stirrer, thermometer, and nitrogen distributor. A mixture of 100 cm^3 of deionized water and 5 g of monomers was added, with the molar ratio of acrylamide to MAA varied as 1:0.1, 1:0.3, 1:0.5, 1:0.7, and 1:1. The monomers were dissolved and stirred continuously until a homogeneous, transparent solution was obtained.

After complete dissolution of the monomers, the mixture was degassed under nitrogen for 20 minutes. Then, under a nitrogen, the initiator comprising ammonium persulfate and sodium metabisulfite (molar ratio 1:1–1.5) was added. The redox system allows the polymerization to proceed under mild conditions at 25–30 °C, ensuring a high degree of monomer conversion. Polymerization was carried out at 300 rpm for 60–120 minutes and was considered complete when the viscosity stabilized and no heat evolution was observed. At the end of the reaction, the system was cooled to room temperature, the inert atmosphere was maintained, and the product was isolated.

The data in Figure 1 show the relationship between the relative viscosity of aqueous solutions of acrylamide copolymers with acrylic acid (AAM–AA) and methacrylic acid (AAM–MAA) and the molar fraction of the acidic monomer.

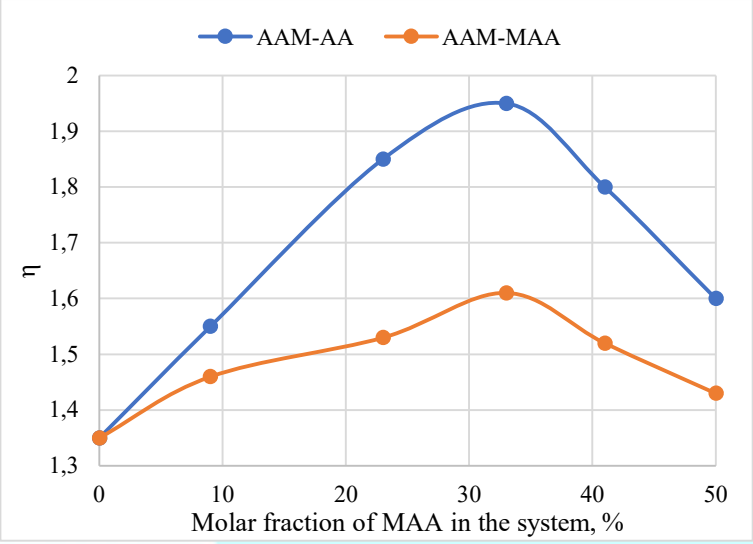


Figure 1. Dependence of the viscosity properties of 0.1 % solutions of the synthesized copolymers on the monomer ratio (synthesized at 50 °C for 2 hours)

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Both series show a typical dependence for copolymers with ionizable groups, but the maximum value and its position differ. In the AAM–AA system, the relative viscosity increases from 1.35 in the absence of acidic chains to 1.95 at 33 mol % acrylic acid, then decreases to 1.6 at 50 mol %. This curve is associated with an increase in charge density and electrostatic expansion of the chains, leading to an increase in hydrodynamic volume at moderate acid concentrations. As the acid fraction increases further, ionic strength and screening effects induce partial chain folding, resulting in a decrease in viscosity.

A similar trend is observed for the AAM–MAA copolymer, although the viscosity values are significantly lower at all points. The maximum value (1.61 at 33 mol % MAA) is less pronounced and shifted to a lower concentration. This is explained by the presence of a methyl group at the α-position, the lower ionization of the carboxyl groups, and the hydrophobicity of the methacrylate fragments, which lead to partial chain folding and a reduction in hydrodynamic volume.

To further investigate the effect of ionic strength on the viscosity properties of acrylamide copolymers with acrylic and methacrylic acids, measurements were carried out at high electrolyte concentrations. Increasing the ionic strength is an important stage of the analysis because real wastewater, particularly from industrial and energy sectors, contains high levels of dissolved salts, which can significantly affect the conformation and behavior of polymer chains. It is known that in ionic copolymers, electrostatic interactions depend on the degree of charge screening; as ionic strength increases, macromolecules lose their extended conformation and adopt a more compact state. This results in a reduction of the hydrodynamic volume and a decrease in the solution viscosity.

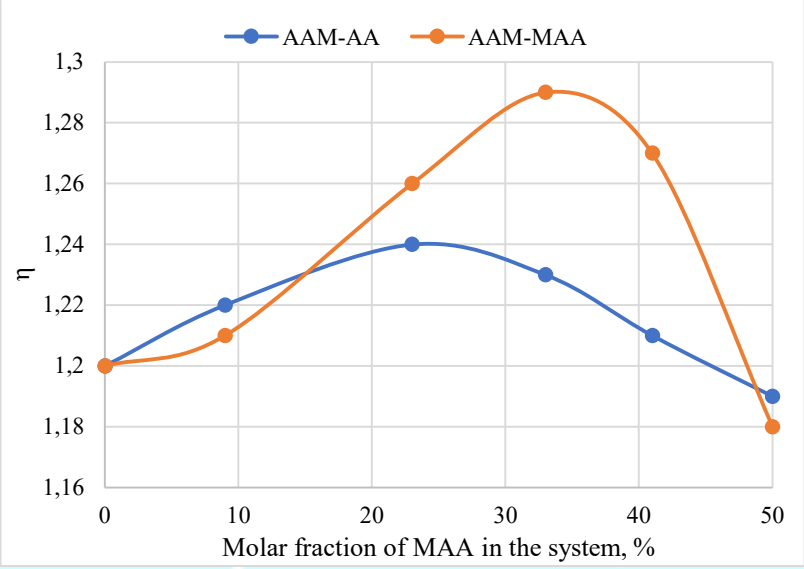


Figure 2. Variation of the viscosity properties of solutions of the synthesized copolymers (C = 0.1 g/L, 0.50 M $NaNO_3$) with the monomer ratio (synthesized at 50 °C for 2 hours).

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Under high ionic strength conditions (0.50 M $NaNO_3$; for comparison, the initial solution ~10 mM), the relative viscosity of the solutions is significantly reduced due to charge screening and densification of polyelectrolyte coils. For AAM–AA copolymers, in the 0–50 mol % acid range, the relative viscosity varies within a narrow interval: starting from 1.20 at 0 % acid, it slightly increases to 1.24 at 23 % and then gradually decreases to 1.19 at 50 %. Under the same conditions, AAM–MAA copolymers exhibit a more pronounced "plateau-maximum": increasing from 1.20 in the absence of acid to 1.26 at 23 % and 1.29 at 33 %, followed by a decrease to 1.18 at 50 %.

The selected compositions (0; 9; 23; 33; 41; 50 mol % acid) cover the full range of monomer ratios, from 0 % pure polyacrylamide to 50 % highly anionic copolymer. In the 20–40 % range, the hydrodynamic volume reaches a maximum. In saline media, this maximum is smoothed for AAM–AA copolymers, whereas for AAM–MAA copolymers it remains shifted to 30–35 %, which is attributed to the effect of the methyl group in MAA. The additional stiffness of the chains and moderate hydrophobicity reduce folding and partially compensate for charge screening. As a result, under high-salinity conditions, AAM–MAA copolymers maintain stable viscosity in the 23–41 mol % acid range, demonstrating high robustness.

Subsequently, the effect of polymerization temperature on the viscosity properties of the obtained copolymers was investigated. The resulting data are presented in Figure 3.

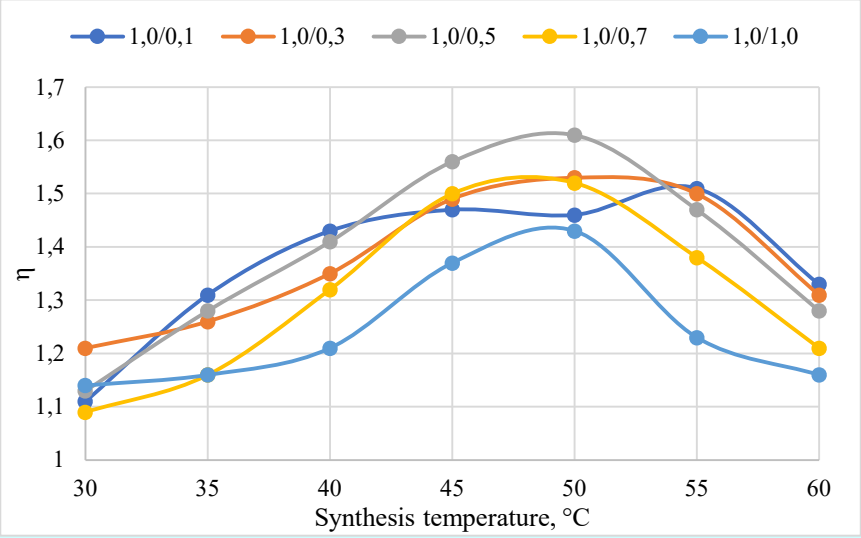


Figure 3. Dependence of the viscosity of 0.1 g/L copolymer solutions on the polymerization temperature (synthesis duration: 2 hours).

Figure 3 shows the dependence of the relative viscosity of 0.1 g/L solutions of AAM and MAA copolymers on the polymerization temperature; the reaction duration was 2 hours. All samples exhibit a distinct extremum, confirming the

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complex influence of temperature on the kinetics of radical copolymerization and the structural characteristics of the macromolecules.

An increase in viscosity is observed in the temperature range of 30–45 °C, which is attributed to enhanced monomer mobility and an optimal ratio between radical initiation and chain termination rates, resulting in chain extension. At temperatures below 35 °C, polymerization proceeds slowly, producing low-molecular-weight chains; therefore, viscosity values do not exceed 1.2–1.3. Raising the temperature to 45–50 °C increases the degree of polymerization, manifesting in maximum relative viscosity values of 1.47–1.61. At temperatures above 50 °C, rapid decomposition of ammonium persulfate begins, and chain termination is accelerated, leading to a decrease in molecular weight and a reduction in solution viscosity.

The highest viscosity is observed at a monomer ratio of 1.0/0.5 (33 mol % MAA), where the optimal balance between hydrophilic and hydrophobic fragments ensures an extended chain conformation. When the acid fraction increases to 0.7–1.0, the hydrophobic interactions of the methacrylate units intensify, leading to enhanced interchain associations and a subsequent decrease in viscosity.

CONCLUSION

The conducted studies established the synthesis of AAM and MAA copolymers and the regularities in their structure–functional properties. Viscosity investigations revealed that the relationship between hydrodynamic properties and the monomer ratio is of an extremal nature: the relative viscosity reaches a maximum at 30–35 mol % methacrylic acid, which is explained by the optimal balance between hydrophilic and hydrophobic fragments and the uniform distribution of charges along the chain. With increasing ionic strength, viscosity decreases due to charge screening and densification of the macromolecular coil structures; however, copolymers based on methacrylic acid exhibit high robustness, indicating the structural stability of these polymers in saline solutions.

Copolymer formation proceeds with an increase in viscosity and molecular weight up to a certain limit; excessive initiator or prolonged reaction leads to chain scission, reducing the properties. The optimal conditions were determined to be 45–50 °C, 2.5 hours, and 0.2 % initiator, under which the viscosity (1.61) and product yield reach their maximum.

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