

Heat-Resistant Polymeric Modifier of Drilling Fluid Based on Potassium Salt of Acrylamide Copolymer

Khuzhanazarova Sarvigul, Bukhorov Shukhrat

PhD student, Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan

Doctor of Technical Sciences, Associate Professor, Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan.

ABSTRACT: The article presents the results of synthesis and research of a new polymer modifier of drilling mud based on potassium salt of a copolymer of acrylamide and acrylic acid. The objective of the work is to increase heat resistance and inhibitory properties of aqueous drilling muds at high temperatures due to the introduction of partially hydrolyzed polyacrylamide. It is shown that the synthesized copolymer has a high-molecular structure and resistance to thermal decomposition. Optimum conditions for obtaining the polymer - a neutral environment (pH ~ 7-8) and a polymerization temperature of about 70 ° C - provide the maximum molecular weight and efficiency of the reagent. Laboratory tests demonstrate that the addition of 0.5-1.0% of this polymer significantly improves the rheological characteristics of the drilling mud at 120-150 ° C, reduces water loss and suppresses swelling of clay particles. Due to the presence of potassium in the polymer, an additional inhibitory effect is achieved compared to traditional polyacrylamide reagents. The obtained results confirm the potential of using the developed modifier for stabilizing drilling fluids in complex geological and technical conditions.

KEYWORDS: potassium salt of polyacrylamide copolymer, drilling fluids, heat resistance, inhibiting properties, rheological properties, filtration.

I. INTRODUCTION

Modern well drilling technologies place increased demands on the stability of drilling fluids under high temperature and pressure conditions. When drilling deep and high-temperature wells, standard aqueous drilling fluids are subject to deterioration of rheological properties and increased filtration, as well as intensive swelling and dispersion of clay rocks. This can lead to complications - loss of circulation, collapse of the well walls and reduced drilling efficiency. In this regard, the development of special drilling fluid modifiers is relevant, capable of preserving its properties under extreme temperature and speed loads and inhibiting undesirable processes of interaction of the solution with the rock. One of the promising areas for improving the properties of drilling fluids is the use of water-soluble organic polymers. Both natural and synthetic polymers are used in practice. Natural biopolymers (starch, cellulose, xanthan gum, etc.) are environmentally friendly, but their heat resistance is limited (~90–120°C), and at higher temperatures they are subject to destruction [9]. Synthetic polymer reagents, on the contrary, can be adapted for harsh conditions: thus, heat-resistant drilling fluids based on esters are known, which have high biodegradability and low toxicity [1]. Polymers based on acrylic monomers are widely used due to their high molecular weight and availability [2]. For example, partially hydrolyzed polyacrylamide (PHPA) has long established itself as an effective clay inhibitor in fresh and low-mineralized solutions. PHPA forms adsorption layers on clay particles, preventing their hydration and dispersion, and also increases the viscosity of the solution, improving the bearing capacity [2, 5]. To enhance the inhibitory effect, potassium salts (KCl), cationic polymers or other additives are often introduced simultaneously [5]. In particular, a combination of polyacrylamide reagents with potassium can significantly reduce clay swelling and strengthen the wellbore walls due to the exchange of Na⁺ ions for K⁺ in the structure of clay minerals. It is known that modification of the polymer structure or introduction of functional groups can improve their efficiency. Thus, works [3] show the possibility of using modified starches as filtration reducers in oil-containing drilling fluids, and in [4] the synthesis of polyacrylamide gel with surface-active fragments (CTAB) is described, which increased the thermal stability and viscosity of the drilling fluid. It is also reported that polymer reagents are combined with nanoparticles to impart additional properties. In one study, the introduction of nano-SiO₂ into an acrylate polymer contributed to an increase in the thermal stability and strength of the structure of the resulting material [4]. These approaches indicate wide possibilities for improving polymer inhibitors and

stabilizers of drilling fluids. Based on the literature review, it can be concluded that the urgent task is to create a polymer reagent that combines high thermal stability and pronounced inhibitory properties. The aim of this work was to synthesize such a modifier based on the potassium salt of a copolymer of acrylamide and acrylic acid (analog of partially hydrolyzed polyacrylamide) and to study its effect on the rheological, filtration and inhibition characteristics of aqueous drilling fluids at high temperatures.

II. SIGNIFICANCE OF THE SYSTEM

The article presents the results of synthesis and research of a new polymer modifier of drilling mud based on potassium salt of a copolymer of acrylamide and acrylic acid. In this study, the methodology is explained in Section III, the experimental results are presented in Section IV, and future research and conclusions are discussed in Section V.

III. METHODOLOGY

Acrylamide (AAm, $\text{CH}_2=\text{CH}-\text{CONH}_2$) and acrylic acid (AA, $\text{CH}_2=\text{CH}-\text{COOH}$) were selected as monomers for the synthesis of the copolymer. Before polymerization, acrylic acid was neutralized with 10% KOH solution to pH ~7–8 to obtain potassium salt of acrylate ($\text{CH}_2=\text{CH}-\text{COOK}$) in the reaction mixture. As a result, copolymerization led to the formation of poly(acrylamide-co-potassium acrylate) chains. Ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, chemically pure) was used to initiate the radical reaction. All reagents were of laboratory quality and were used without additional purification. To test the resulting polymer, a model drilling mud was prepared on fresh water with bentonite clay. Sodium bentonite from the Navbakhor deposit (Uzbekistan) was used as a dispersion medium - 4% suspension in water, conditioned at room temperature for 24 hours. This base solution had a nominal viscosity of ~35–40 s (according to a VZ-246 viscometer) and a filtration of ~18 ml/30 min (according to API). A 5% KCl solution (for comparative inhibition tests) and buffer solutions for pH adjustment were also used when assessing the polymer stability to different acidity values. Synthesis methods. A copolymer of acrylamide and potassium acrylate was synthesized by radical polymerization in an aqueous solution. 0.1 mol (about 7.1 g) of acrylamide and the corresponding calculated amount of acrylic acid (from 0.01 to 0.05 mol) in 200 ml of deionized water were loaded into a 500 ml three-necked flask equipped with a stirrer, thermometer, and gas inlet tube. The flask was cooled with an ice bath, and the KOH solution was gradually added with continuous stirring until the pH reached ~7. The reaction mixture was then purged with purified nitrogen for 30 min to remove oxygen (an inert atmosphere prevents inhibition of radical polymerization). The flask was then heated in a water bath to 50°C and 0.5 g of ammonium persulfate dissolved in 20 ml of water was added. The temperature was raised to 70°C and maintained at this level for 4 hours. Polymerization proceeded with moderate heat evolution; the mixture was thoroughly stirred (300 rpm) to ensure uniformity of the reaction. The resulting viscous polymer solution was cooled to room temperature. To isolate the product, the polymer was precipitated by slowly adding the reaction mass to 1 l of ethanol with vigorous stirring. The resulting white precipitate was filtered, washed with ethanol and dried in a vacuum oven at 50°C to constant weight. The polymer yield was 90–95%. The content of acrylate units in the copolymer was estimated titrimetrically by the content of carboxyl groups and varied in a series of samples from 10 to 50% (mole fraction) by changing the ratio of AAm:AA monomers. Test methods. The resulting polymer powder was dissolved in water or drilling mud to the required concentration immediately before testing. Rheological properties were estimated at different temperatures and polymer concentrations. Viscosity was measured with a VZ-246 viscometer (nozzle diameter 4 mm) and a Fann 35A rotational viscometer (modeling of plastic viscosity and dynamic shear stress) in the temperature range from 20 to 120°C. To study the effect of pH on the efficiency of the modifier, 0.5% aqueous solutions of the polymer with different pH values (3, 7, 10) were prepared using hydrochloric acid or sodium hydroxide for adjustment, and their viscosity and stability were measured for 24 hours at 90°C. The thermal stability of the polymer was estimated in two ways: (1) by thermogravimetric analysis (TGA) on a TA Instruments device by heating a polymer sample from 30 to 600°C (rate 10°C/min) in a nitrogen atmosphere, with registration of weight loss and characteristic decomposition temperatures; (2) a test for thermal stability of rheological properties, consisting of thermostating samples of drilling mud with polymer at 150°C in sealed autoclaves for 16 hours, followed by measuring their viscosity and filtration after cooling. The inhibitory properties were estimated by the bentonite swelling test and clay slurry dispersion. The swelling test was carried out in a PT (OFI Testing) device at 90°C: a pressed sample of sodium bentonite was kept in the test liquid (distilled water, KCl solution, polymer solution of a given concentration) and the relative increase in volume (height) of the sample was measured after 2 hours. The degree of dispersion was determined by the hot rolling method: samples of the argillite model (pressed clay balls) were placed in a cell with the test solution and kept on a roller at 120°C for 16 hours, after which they were sifted through a 2 mm sieve and the percentage of retained large particles (sludge recovery



coefficient) was determined. These tests made it possible to quantitatively compare the inhibiting capacity of various compositions.

IV. EXPERIMENTAL RESULTS

Radical copolymerization of acrylamide with potassium acrylate under the selected conditions proceeded efficiently, as evidenced by the high yield of the product (>90%). The resulting copolymer is highly soluble in water, forming transparent viscous solutions. The average molecular weight (estimated by the reduced viscosity of the solutions) is about 106 Da. A series of syntheses with different molar contents of acrylic acid showed that an increase in the proportion of acrylate units leads to an increase in the degree of ionization of the polymer, but an excessive content (>40%) reduces the molecular weight of the product. It was found that the optimal composition of the copolymer in terms of the combination of properties is about 30% acrylate and 70% acrylamide. With this ratio, a high molecular weight of the chains is achieved with a sufficient number of charged groups, providing good solubility and the ability to inhibit clays. Infrared spectral analysis of the product confirmed the structure of the copolymer: characteristic bands are observed at $\sim 1670\text{ cm}^{-1}$ (stretching vibrations of the C=O amide group) and $\sim 1560\text{ cm}^{-1}$ (symmetric stretching vibrations of the carboxylate ions CO-O-K^+), which are absent in the original polyacrylamide. This indicates the presence of a significant number of carboxylate units in the potassium form in the chain. Effect of pH and temperature on polymer rheology. The resulting copolymer is sensitive to extreme pH values. At room temperature, a 0.5% polymer solution has the highest viscosity at neutral $\text{pH} \approx 7$, whereas in an acidic medium ($\text{pH} 3$) its viscosity decreases by about 30%, and in an alkaline medium ($\text{pH} 10$) — by 20%. The decrease in viscosity in an acidic medium is due to partial protonation of carboxylate groups and folding of macromolecules, whereas at $\text{pH} > 9$ alkaline hydrolysis of amide bonds and some destruction of chains are possible. Thus, for maximum efficiency of the reagent, the pH range of 7–9 is desirable, which coincides with the typical pH level of water-based drilling fluids. Temperature tests have shown that the viscosity of an aqueous polymer solution decreases moderately with increasing temperature, following the expected rheological behavior of thin polymer solutions. For example, when heated from 20 to 120°C , the conventional viscosity of a 0.5% solution decreases from ~ 40 to ~ 20 s. However, after cooling to 20°C , the viscosity is almost completely restored, indicating the absence of irreversible thermal decomposition in this range. More severe heating (up to 150°C) leads to a slight irreversible decrease in viscosity ($\sim 10\%$ of the initial value) — probably due to the onset of hydrolysis of amide groups or the rupture of individual chains. Fig. 1 shows the nature of the change in viscosity of a 0.5% copolymer solution depending on temperature. It is evident that up to $120\text{--}130^\circ\text{C}$ (the usual application threshold for most water-soluble polymers), the solution retains sufficient viscosity, and with a further increase in temperature, a noticeable drop is observed due to the thermal destruction of polymer chains. The subsequent redistribution of potassium cations during the adsorption of additional carbonyl sulfide molecules is also indicated. The amount of adsorption corresponding to a decrease in Gibbs energy to 10 kJ/mol is ten times lower than the total amount of potassium cations in the zeolite, suggesting that, like the differential heat, carbonyl sulfide molecules form up to 10-layer structures on the surface of the zeolite. In the region between 0.1 mmol/g and the experimental maximum of 0.3 mmol/g adsorption, the change in Gibbs energy is 2 kJ/mol, which is also equal to the 2 kJ/mol variation in differential heat. This indicates that the subsequent carbonyl sulfide molecules are adsorbed via weak Van der Waals forces through adsorbate–adsorbate interactions.

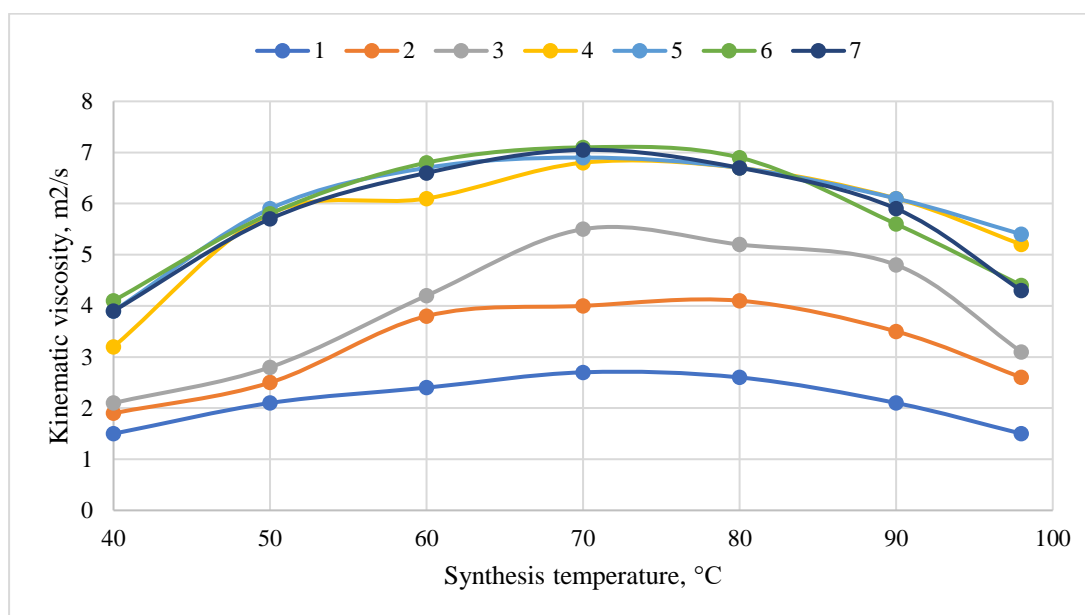


Figure 1. Dependence of the viscosity of a 0.5% aqueous solution of the copolymer on the reaction temperature (°C) at AA:AA ratios: 1) 0/100; 2) 10/90; 3) 30/70; 4) 50/50; 5) 60/40; 6) 70/30; 7) 90/10

TGA of the polymer samples confirmed its high thermal stability in the dry state. The onset of noticeable weight loss is noted at a temperature of about 200°C, which corresponds to the evaporation of residual moisture and the onset of decomposition of side groups. The main stage of thermal decomposition of macromolecules occurs in the range of 350–450°C with a weight loss of ~50%. The temperature at which the weight loss reaches 10% is ~250°C. These values are significantly higher than those of unionized polyacrylamide (for which the onset of decomposition is observed at ~170°C), which can be explained by the stabilizing effect of potassium cations and greater thermooxidative stability of the ionic copolymer. Thus, the thermal stability of the synthesized reagent is sufficient for use at high temperatures (up to ~150°C) without significant degradation.

Effect of polymer concentration on drilling fluid properties. The effect of copolymer additives in various dosages on the rheological and filtration characteristics of bentonite solution was studied. Addition of only 0.2% polymer already significantly increases drilling mud viscosity (conditional viscosity increases from 40 to 50–55 s) and reduces fluid loss by 15–20%. At a concentration of 0.5%, the optimal effect is achieved: further increase in dosage to 1.0% provides only a slight additional improvement. Probably, at a polymer content of >0.5%, the active positions on clay particles are already saturated with polymer, and excess molecules remain in the solution, increasing viscosity, but not affecting inhibition. After thermal exposure (heating the suspension at 120°C for 16 h), samples with polymer retain satisfactory rheological properties: the viscosity of a 0.5% solution decreases by only ~10%, whereas without polymer, the bentonite solution almost completely loses its structural and mechanical properties (liquefies). This confirms that the copolymer effectively stabilizes the structure of the clay suspension upon heating, preventing liquefaction by retaining water and strengthening the framework of aggregated particles.

Inhibitory properties of the copolymer. The polymer additive demonstrated high efficiency in suppressing swelling and destructibility of clay rocks. In tests of bentonite swelling at 90°C, samples in distilled water increased their volume conditionally to 100% of the initial volume, whereas in the presence of 0.5% copolymer, swelling was only ~60%. Increasing the polymer concentration to 1.0% reduced swelling to ~40% of the control value. For comparison, the traditional inhibitor KCl (5% solution) provided ~50% swelling, i.e. the potassium salt of polyacrylamide is comparable in efficiency to potassium chloride. Moreover, the combined use of 0.5% polymer and 5% KCl almost completely suppresses swelling (≤15%). The results are summarized in Table 1. It is obvious that the copolymer provides a dual inhibition mechanism: sodium exchange for potassium in the interlayer positions of the clay mineral and simultaneous adsorption shielding of particles by the polymer chain. In addition, a significant decrease in clay dispersibility was observed: in the hot rolling test, samples with 0.5% polymer had a recovery coefficient of ~80%, while without the reagent it did not exceed 40%. This means that the polyacrylamide chain not only prevents water from penetrating the clay crystal lattice, but also glues the particles together, preventing them from disintegrating during circulation. Taken together, the inhibiting properties of the

developed modifier make it possible to significantly increase the stability of the wellbore when drilling in sections rich in clays and water-sensitive shales.

Table 1.
Results of the bentonite swelling test (90°C, 2 hours) in various modeling liquids

Composition of the liquid	Relative swelling, %
Distilled water (control)	100
5% aqueous solution of KCl	50
0.5% aqueous solution of copolymer	60
1.0% aqueous solution of copolymer	40
0.5% copolymer + 5% KCl (solution)	15

The test results show that the synthesized potassium polyacrylamide copolymer successfully performs the functions of a reagent-stabilizer: it increases the viscosity and structure of the drilling fluid, reduces filtration during heating and simultaneously serves as an effective inhibitor of clay rocks. This distinguishes it favorably from traditional potassium-free polyacrylamides, which provide either a predominantly rheological effect or require the addition of individual salt components for inhibition. Based on the combination of properties, the new modifier can be classified as a multifunctional additive for drilling fluids.

V. CONCLUSION AND FUTURE WORK

A new polymer modifier for drilling fluid based on the potassium salt of a copolymer of acrylamide and acrylic acid has been developed. It has high heat resistance and pronounced inhibitory properties. The studies have revealed the following main results.

Polymer heat resistance. The copolymer maintains a stable molecular structure at temperatures up to 150°C in an aqueous medium. Thermogravimetric analysis revealed a shift in the onset of destruction to 200°C, which is due to the presence of carboxylate groups and potassium ions stabilizing the polymer chain. This allows the modifier to be used in high-temperature drilling conditions, where biopolymer reagents lose activity.

Rheological action. The introduction of 0.5–1.0% of the copolymer into the drilling fluid contributes to a significant increase in viscosity and stability of its structure, especially after exposure to temperature. Polymer macromolecules form a spatial network, enhancing the structural and mechanical properties of the solution, preventing sludge settling and improving the transportation of drilled rock. **Inhibitory properties.** The synthesized copolymer effectively suppresses swelling and dispersion of clay particles. In laboratory tests, its concentration of 0.5–1.0% reduced the degree of swelling of bentonite by 1.5–2.5 times compared to distilled water. The mechanism of action is associated with the cation-exchange replacement of Na⁺ with K⁺ in the interlayers of minerals and the formation of a protective adsorption film on the surface of clays. This increases the stability of the well walls and reduces the risk of accidents when drilling water-sensitive sections. As a result, the synthesized potassium-acrylamide copolymer is a promising multifunctional reagent for aqueous drilling fluids intended for drilling in complex geological and technical conditions. Its use will improve drilling stability by maintaining the rheological parameters of the solution at high temperatures and preventing swelling of clay rocks. In the future, it is planned to expand the research: optimization of the molecular characteristics of the polymer, testing in the presence of drilling contaminants (CO₂, Ca²⁺) and pilot tests in real wells.

REFERENCES

1. Dardir, M.M.; Ibrahime, S.; Soliman, M.; Desouky, S.D.; Hafiz, A.A. Preparation and evaluation of some esteramides as synthetic based drilling fluids. *Egypt. J. Petrol.* 2014, 23, 34–43.
2. Vipulanandan, C.; Mohammed, A.S. Hyperbolic rheological model with shear stress limit for acrylamide polymer modified bentonite drilling muds. *J. Pet. Sci. Eng.* 2014, 122, 38–47.
3. Dias, F.T.G.; Souza, R.R.; Lucas, E.F. Influence of modified starches composition on their performance as fluid loss additives in invert-emulsion drilling fluids. *Fuel* 2015, 140, 711–716.
4. Shettigar, R.R.; Misra, N.M.; Patel, K. CTAB grafted PAM gel and its application in drilling fluid. *J. Pet. Sci. Eng.* 2018, 163, 280–286.
5. Blinov, P.A.; Dvoynikov, M.V. Rheological and filtration parameters of the polymer salt drilling fluids based on xanthan gum. *J. Eng. Appl. Sci.* 2018, 13, 5661–5664.
6. Menezes, R.R.; Campos, L.; Ferreira, H.S.; Marques, L.N. Use of statistical design to study the influence of CMC on the rheological properties of bentonite dispersions for water-based drilling fluids. *Appl. Clay Sci.* 2010, 49, 13–20.
7. Hamed, S.B.; Belhadri, M. Rheological properties of biopolymer drilling fluids. *J. Pet. Sci. Eng.* 2009, 67, 84–90.