



Structure formation in suspensions and biocidal properties of copolymer of 2-acrylamido-2-methylpropanesulfonic acid and allylamine

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ABSTRACT

Bentonite is a type of montmorillonite clay that used in many places in the industry. It has been widely used for drilling fluid for many decades. Reducing the friction and lubricating the drilling the bentonite fluid has to be smooth and viscos. In this work, the structure-formation of bentonite clay suspensions in the presence of the 2-acrylamido-2-methylpropanesulfonic acid – allylamine (AMPS-AA) copolymer was studied. The static shear stress (SSS) of the bentonite suspension was investigated at different polymer concentration and monomer molar ratio. The antimicrobial activity of the copolymer AMPS-AA against sulfate-reducing bacteria (SRB) with different molar composition was studied. Based on the research results AMPS-AA copolymer was suggested to be a structuring and antibacterial agent for bentonite clay. Copyright © 2022 Elsevier Ltd. All rights reserved.

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1. Introduction

During the drilling of oil and gas wells, in order to improve the rheological and filtration properties, bentonite clays are often added to the water-based drilling fluids [1–3]. Bentonite clays give drilling fluids the necessary viscosity and thixotropic properties, provide the formation of a three-dimensional structure in suspension and a thin filtration layer on the surface of the borehole wall. Due to this, the rock particles do not settle to the bottom of the well when the drilling is stopped, water filtration through the walls of the well into the formation (water absorption) is reduced, and the risk of collapse of the well wall is decreased [4–6]. However, the known polymeric structurants are not always effective for use, due to their high cost and difficulty in synthesis. Therefore, the formation of new effective polymeric structurants is an urgent task.

Another serious problem in the oil and gas industry is the microbiological corrosion of processing and drilling equipments. As a result, several thousand tons of metal constructions fail every year. Usually, metal constructions are not susceptible to the effects of microorganisms. However, during the vital activity (metabolism) of microorganisms, some corrosion-active substances (hy-

drogen sulfide, acids, bases) can be released into the environment. Among the bacteria, sulfate-reducing (SRB) and thionic bacteria are more dangerous in terms of corrosion [7–10].

For inhibition of SRB, biocidal polymers are often used. However, these polymers are not always effective. According to [11,12] regular inhibition of SRB by certain compounds can promote the development of biocide-resistant mutants. For this reason, mixtures of biocides are often used to prevent the development of mutant strains. Today, despite the many biocidal compounds, biocorrosion of equipments and materials remains one of the unsolved problems. In this regard, the synthesis of new effective polymeric biocidal compounds is one of the most urgent issues.

The increasing interest of the researchers in the synthesis of (co)polymers based on 2-acrylamido-2-methyl-propanesulfonic acid (AMPS) is due to the possibilities of the use of these compounds as polyelectrolytes and catalytic membranes in fuel cells [13] and in the production of biodiesel [14,15], complexing agents [16], flocculants [17], as well as in the production of cosmetics, coatings, adhesives [18] and antimicrobial materials [19]. The AMPS monomer is highly soluble in water (~150 g /100 g water, at 25 °C), stable to the action of divalent cations and has hydrolytic and thermal stability. The introduction of allylamine (AA) as a second monomer into the poly-AMPS structure should enhance the interaction of macromolecules of the resulting copolymer with

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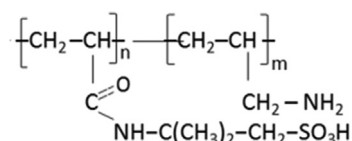
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metal cations due to the formation of coordination bonds between nitrogen atoms of AA monomers and metal cations.

In this paper, we observe the study of the structure formation in bentonite suspension and biocidal properties of a new polymer surfactant - the AMPS-AA copolymer. The synthesis procedure and flocculating properties of this copolymer are presented in [17]. It has been shown that the AMPS-AA copolymer has flocculating properties and can be used to treat wastewater from colloidal particles of iron (III) hydroxide.

2. Experimental

Copolymer of 2-acrylamido-2-methylpropanesulfonic acid and allylamine (AMPS-AA).



was synthesized in a three-necked flask by radical copolymerization of AMPS with AA in an aqueous medium at 343 K and constant stirring of the mixture in the presence of ammonium persulfate ((NH₄)₂S₂O₈) as an initiator for 2 ÷ 3 h in argon gas atmosphere at different molar ratios of monomers [17]. The resulting copolymers were precipitated from the reaction medium and purified with a mixture of dioxane and acetone (50:50 vol%) and then dried under vacuum at 313 K to the constant weight.

Poly-2-acrylamido-2-methylpropanesulfonic acid (poly-AMPS) was also synthesized by radical polymerization of AMPS monomer under the same conditions as the AMS-AA copolymer.

The structure and molar composition of AMPS-AA copolymer were determined by FTIR and ¹H NMR spectroscopy, elemental analysis for H, C, and N (Vario El cube instrument, Germany). The yield of the copolymerization reaction was determined gravimetrically. The synthesis condition and determination of the molar composition of the copolymer are described in detail in [17]. Table 1 shows the results of determining the composition and yield of the AMPS-AA copolymer.

Bentonite clay from the Tagan deposit (East Kazakhstan) was used to study the structure formation properties of the AMPS-AA copolymer. Structure formation in suspensions in the presence of a copolymer was determined using a rotational viscometer with manual control of 6 speeds RC-35D (China). The static shear stress (SSS) of the bentonite suspension was measured at room temperature in 1 min (SSS-1) and 10 min (SSS-10) after preparation of the suspension treated with copolymer. The SSS is one of the most important drilling fluid parameters. It indicates the rate of formation and strength of the gel forming in suspension at rest. The higher the SSS, the larger the size of the particles that are in suspension and which do not settle to the bottom of the well.

Table 1
Composition and yield of the AMPS-AA copolymer.

Content of monomers in feed, mol. % [AMPS]:[AA]	Average mole composition of the copolymer from the results of elemental analysis, mol. % [AMPS]:[AA]	Yield of the copolymer, %
50:50	59:41	42 ± 0.5
60:40	64:36	54 ± 0.6
80:20	89:11	76 ± 0.6

Chemical analysis of the used bentonite sample was carried out by X-ray fluorescence spectroscopy (XRF) using PANalytical Axios PW400. Bentonite clay had the following composition, wt. %: Na₂O – 1.00; MgO – 3.59; Al₂O₃ – 22.46; SiO₂ – 58.78; SO₃ – 0.06; Cl – 0.02; K₂O – 0.59; CaO – 3.99; TiO₂ – 0.79; Cr₂O₃ – 0.01; Fe₂O₃ 8.60 and others – 0.2 [20].

Before use, the bentonite clay was grounded in a ball mill at 300 rpm for 15 min and then sieved through a sieve with a pore diameter of 0.01 mm. For this study, a sample with a particle diameter of not more than 0.01 mm was used.

The specific surface area of the bentonite clay was determined in liquid N₂ by the Brunauer–Emmett–Teller (BET) approach using a Micromeritics ASAP 2020 instrument at – 196 °C (77 K). The approximate total pore volume of clay was calculated from the amount of adsorbed liquid at 0.99 relative pressures. Distribution of pore sizes was calculated from the desorption part of the N₂ adsorption/desorption isotherms, using the Barrett–Joyner–Halenda (BJH) method [20].

Bentonite clay particles had the following characteristics: BET surface area – 59 m²/g; Langmuir surface area – 74 m²/g; t-Plot micropore area – 2 m²/g; t-Plot external surface area – 57 m²/g; BJH desorption cumulative surface area of pores with diameter 2–100 nm – 57 m²/g; Single point adsorption total volume of pores with diameter less than 141 nm at P/P₀ = 0.99 – 0.39 cm³/g; t-Plot micropore volume – 0.0003 cm³/g; BJH Desorption cumulative volume of pores with diameter 2–100 nm – 0.38 cm³/g; Adsorption average pore width (4 V/A) by BET) – 26 nm and BJH desorption average pore diameter (4 V/A) – 27 nm.

30 wt% suspension of the bentonite clay was prepared by stirring at 300 rpm for 10 min in water. Then, the prepared suspension was left for 24 h for the complete swelling of bentonite clay. The next day the suspension was treated with required volume of copolymer solution and stirred at 100 rpm for 3 min. After treating it with copolymer the concentration of the suspension was always equal to 20 wt%. A copolymer solution with a concentration of 0.1 wt% was prepared the day before. The desired copolymer concentration was prepared by diluting the stock solution.

The antimicrobial activity of the copolymer AMPS-AA with different molar composition against sulfate-reducing bacteria (SRB) was studied at the Institute of Microbiology and Virology (IMB&V) of the Ministry of Education and Science of the Republic of Kazakhstan. The effect of the copolymer on the growth of SRB was studied at three concentrations (wt. %): 0.01, 0.05, and 0.1. In the control variant, SRB was cultured without copolymer. When SRB grows, a black film with a metallic outflow on the inner surface of the tube was observed.

3. Results and discussion

3.1. Structure formation in the suspensions of bentonite clay in the presence of AMPS-AA copolymer

Fig. 1–3 show the results of a study of structure formation in the bentonite clay suspensions in the presence of homopolymer (poly-AMPS) and AMPS-AA copolymer.

It can be seen from the figures that poly-AMPS does not effect on the SSS of suspension while with an increase in the concentration of the copolymer in the suspension, SSS increases and the copolymer with the molar composition AMPS:AA = 89:11 has the highest structure formation property. It should also be noted that at a copolymer concentration of 516 g/t suspension, SSS increases by 2.7 ÷ 2.8 times.

An analysis of the effect of the pH on the suspension's SSS in the presence of the AMPS-AA copolymer (Fig. 3) showed that the largest structure formation in the suspension occurs in an acidic med-

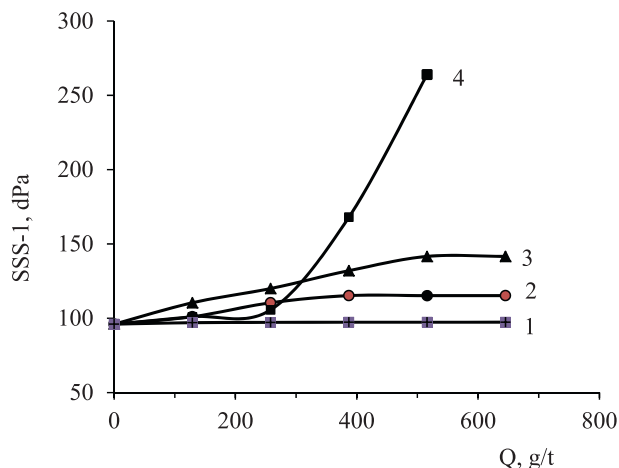


Fig. 1. Dependence of SSS-1 of the bentonite clay suspensions treated with poly-AMPS (1) and AMPS-AA copolymer (2 - 4) on the molar composition and concentration of the polymer.

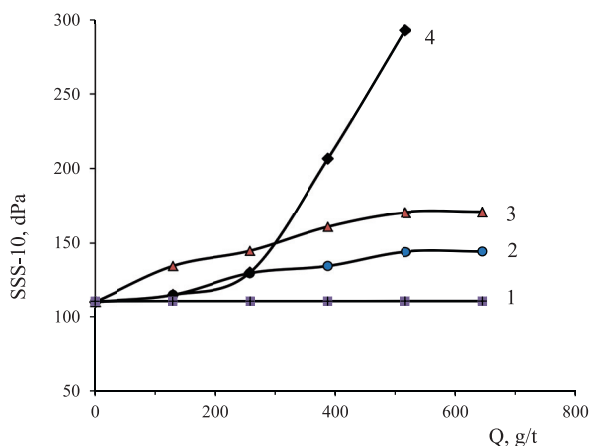


Fig. 2. Dependence of SSS-10 of the bentonite clay suspensions treated with poly-AMPS (1) and AMPS-AA copolymer (2-4) on the molar composition and concentration of the polymer.

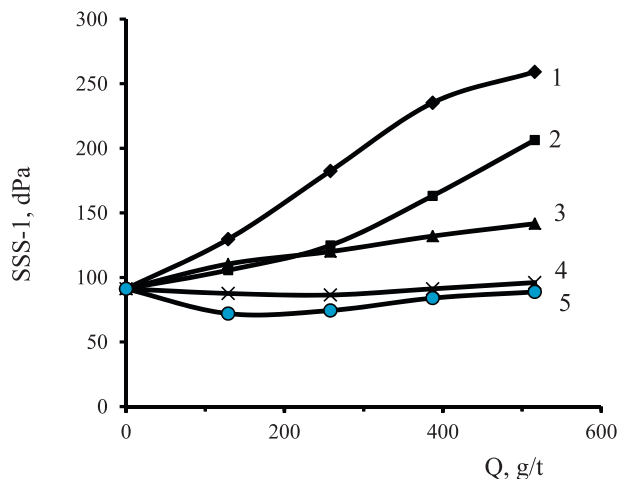


Fig. 3. Dependence of SSS-1 of the bentonite clay suspensions treated with AMPS-AA copolymer (molar composition of 76:24) on pH and copolymer concentration.

ium. The increasing of SSS in the acidic environment can be explained by the protonization of copolymer's amino groups. As a result, the specific positive charge along the copolymer chain increases. Increase of the positive charge along the macromolecule chain enhances the electrostatic interaction of the copolymer with negatively charged clay particles in suspension [21].

In the presence of poly-AMPS in suspension both macromolecules and clay particles have the same (negative) charge that's why they don't interact with each other.

The interaction of copolymer macromolecules with the surface of suspension particles occurs according to the mechanism of polymer complex formation [16,22]. This interaction ultimately leads to an increase in structure formation in the bentonite clay suspensions and an increase in SSS.

3.2. Biocidal properties of the AMPS-AA copolymer against the growth of SRB

In this work, the biocidal properties of the AMPS-AA copolymer with the molar composition [AMPS]:[AA] = 89:11; 76:24 and 64:36 were studied. In order to do this, 1 ml of the SRB culture liquid was added to the test tubes and filled with a nutrient medium with a copolymer at the required concentration. In the control variant, SRB was cultivated without copolymer (4th tubes, Fig. 4).

The development of SRB was noticed on the 5th day of cultivation. With the growth of SRB, the development of a black film with a metallic sheen is observed on the inner surface of the tube. From the test results, it can be stated that all the studied samples of the AMPS-AA copolymer have a biocidal effect against SRB. When samples of the AMPS-AA copolymer interact with the nutrient medium, the latter acquires a color changing from gray to black without the formation of a black film with a metallic sheen. This indicates suppression of SRB growth. Microscopic studies also showed the absence of SRB cells in the test samples.

The biocidal effect of the copolymer was observed during the entire test period. The optimal concentration of the copolymer at which SRB growth was inhibited is ≥ 0.01 wt%. It should also be noted that the AMPS-AA copolymer with a molar composition of 89:11 has the highest biocidal effect.

4. Conclusion

1. In this work, the structure formation and biocidal properties of AMPS-AA copolymers against sulfate-reducing bacteria were studied. It was found that structure formation properties of the AMPS-AA copolymer in bentonite clay depend on its molar composition, concentration and pH of the medium. It was shown that the largest structure formation occurs at the molar composition of the copolymer AMPS:AA = 89:11 and in the acid environment. It has been also found that at a concentration of AMPS-AA copolymer 516 g/t, SSS increased by a factor of $2.7 \div 2.8$.
2. It was shown that samples of the AMPS-AA copolymer (with a molar composition of 89:11; 76:24 and 64:36) had a biocidal effect against SRB and at a concentration not less than 0.01 wt% complete inhibition of bacterial growth occurs.

CRediT authorship contribution statement

K.Zh. Abdiyev: Conceptualization, Methodology, Writing – review & editing, Supervision, Validation. **Zh. Toktarbay:** Writing – original draft. **B.Ye. Orynbayev:** Data curation. **M.B. Zhursumbayeva:** Visualization, Investigation. **N.Zh. Seitkaliyeva:** Visualization, Investigation. **U. Nakan:** Data curation.

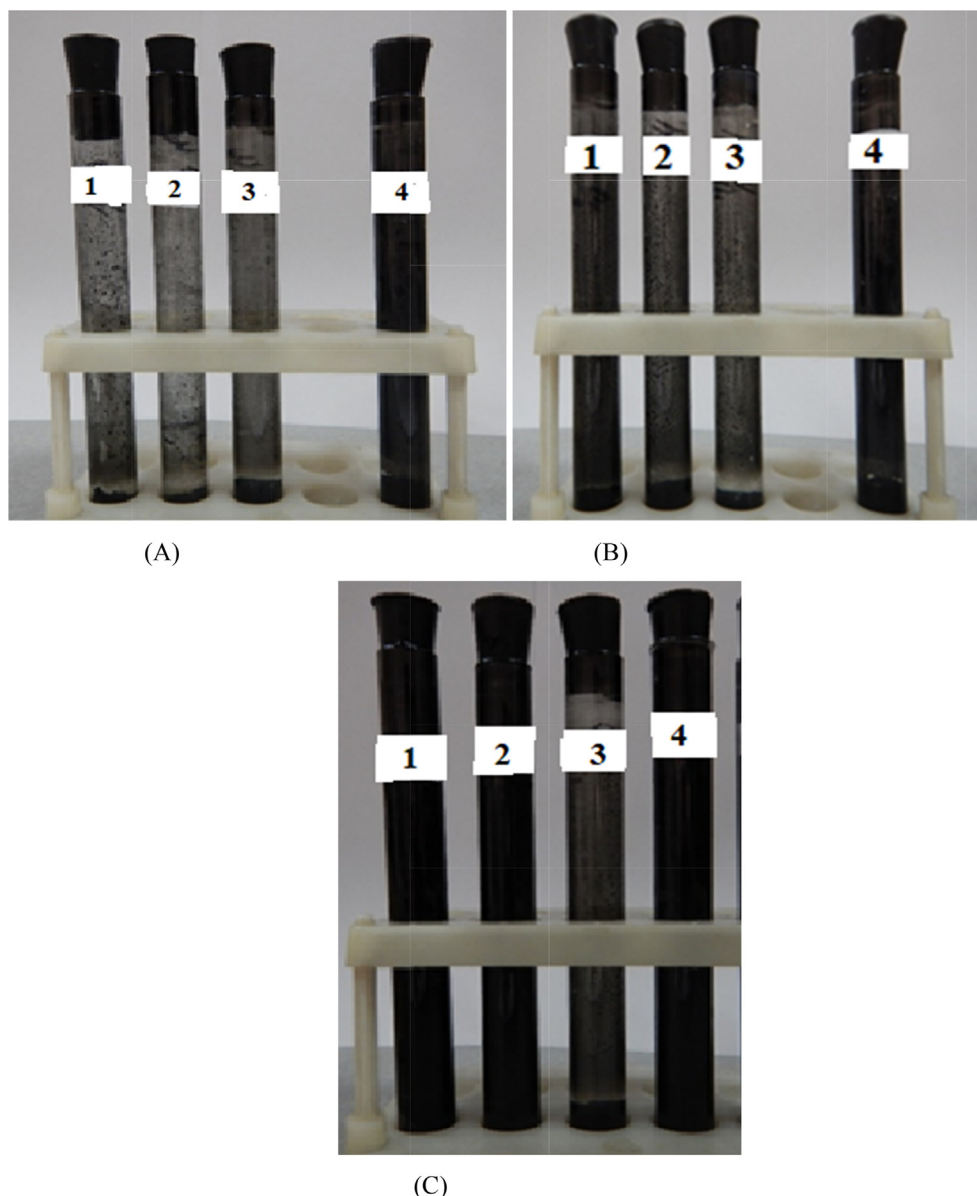


Fig. 4. Growth of SRB in the presence of AMPS-AA copolymer.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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