Eng. Sci., 2024, **31**, 1260

Engineered Science
DOI: https://dx.doi.org/10.30919/es1260

Polymerization Dynamics of Zwitterionic Monomers with Polyacrylamide for Enhanced Oil Recovery

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Abstract

In this paper, the synthesis of zwitterionic copolymers for enhanced oil recovery (EOR) was studied in detail. The copolymers were synthesized via free-radical copolymerization. Different molar ratios (2:98, 10:90, 20:80, 30:70) of zwitterionic sulfobetaine-N-(3-dimethylamino)propyl methacrylamide (P(SB-DMAPMA)) copolymerized with acrylamide (AM). Resulted in copolymers characterized by nuclear magnetic resonance (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). The molecular weight of copolymers was measured with the Static Light Scattering method. Reactivity ratios of the monomers were calculated using three methods: Fineman-Ross, Kelen-Tudos, and Mayo-Lewis. The study also discussed the thermal stability of zwitterionic copolymers and rheological properties in pure water and in high-salinity conditions with different charges. Increased viscosity after adding different salts was analyzed by rheological measurements, and the images of structures of molecules were taken by Transmission Electronic Microscope (TEM). The findings of this study can be useful to enhance the efficiency of EOR processes, paving the way for more advanced oil recovery techniques.

Keywords: Enhanced oil recovery; Zwitterionic polymers; Reactivity ratios; Sulfobetaine-N-(3-dimethylamino)propyl methacrylamide; Polyacrylamide.
Received: 10 August 2024; Revised: 10 September 2024; Accepted: 21 September 2024.
Article type: Research article.

1. Introduction

Zwitterionic polymers are a group of polymers that contained both positive and negative charges on a molecule. These unique properties make the zwitterionic polymers important for various applications which has triggered an increased interest in the synthesis of Zwitterionic copolymers. Zwitterionic polymers are regarded as a new class of non-adherent materials which can be applied in biomedical and biconical uses.[1] The zwitterionic-copolymer synthesis proceeds by conventional copolymerization techniques, which is the incorporation of hydrophilic monomers with both positive and negative charges on polymer chains. Due to improved biocompatibility, antimicrobial and antifouling properties of these copolymers become suitable for use in biomaterials, drug delivery systems and as well as membrane technologies. Many studies have demonstrated the broad applicability and efficacy of zwitterionic copolymers. It has been noted that the zwitterionic block copolymers greatly improved the stability of colloids and surfaces, making them suitable for application in nanotechnology and materials science.[2]

Additionally, zwitterionic copolymers have been used as crosslinking materials for effective application in organic electronics and may uncover novel chances in device fabrication and improving performance.[3] Furthermore, multi-shape memory effects in zwitterionic copolymers have opened novel possibilities in materials science. These materials found many other applications due to their adjustable properties and stimuli-responsive behavior.[4] Various research has outlined the possibilities of the use of these copolymers in various areas. For example, Bengani-Lutz *et al.* (2017) reported self-assembling zwitterionic copolymers as membrane selective layers with higher fouling resistance, demonstrating their potential application in membranes, drug delivery systems,

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and sensors.[5] Zhu *et al.* (2017) developed a superhydrophilic zwitterionic polyelectrolyte/PVDF-blend membrane for efficient separation of oil from water in the emulsion.[6] With this research, they highlighted the potential of zwitterionic copolymers in developing advanced membranes for environmental applications like water purification. Sathyan *et al.* (2023) used catechol and zwitterion-functionalized copolymers to prevent dental bacterial adherence, emphasizing the antifouling capabilities and hydrolytic stability of zwitterionic polymers for biomedical purposes.[7] Walker *et al.* (2019) also studied surface modified zwitterionic networks and their resistance to bovine serum albumin adsorption, highlighting the potential of zwitterionic copolymers in the development of bioinert environments.[8]

Despite their wide range of applications, zwitterionic polymers are widely used in Enhanced Oil Recovery (EOR) due to their favorable properties of dual charge, which improves water solubility and reduces adsorption on rock surfaces. These properties of zwitterionic polymers allow for increased oil displacement efficiency, while increasing the viscosity of pumped fluids and providing stability under high salinity and temperature conditions. Experimental studies of scientists like Kamal *et al.* evaluated the thermal stability and rheological properties of various terpolymers with and without zwitterionic amidosulfobetaine surfactants. Rheological measurements showed that polyacrylamide, the most widely used polymer in EOR, decreased viscosity due to charge screening under saline conditions. However, the addition of a small amount of zwitterionic surfactant increased the stability of polyacrylamide in saline media, increased viscosity and improved oil displacement efficiency.[9] In addition, Alcázar-Vara *et al.* studied the multifunctional properties of zwitterionic polymers and showed that zwitterionic molecules even inhibit asphaltene aggregation. Thus, it should be emphasized that zwitterionic molecules are of great importance in solving problems in oil extraction processes.[10]

One of the key mechanisms of action of zwitter-ion polymers in EOR is their ability to significantly reduce the interfacial tension between oil and water, thereby contributing to the release of oil droplets from the porous medium of the formation.[11] Another important advantage of these polymers is their high chemical compatibility with other reagents commonly used in enhanced oil recovery processes, such as surfactants and alkaline solutions.[12] This opens up the possibility of developing complex methods using multicomponent mixtures that simultaneously improve the dispersion of oil and prevent its re-capture in porous media. In addition, zwitter-ion polymers exhibit resistance to hydrolysis and oxidation, which increases their service life in the reservoir and reduces the need for frequent re-injection of the polymer. This factor is important for the economic efficiency and overall sustainability of the EOR process.[13]

Other studies have investigated the surface and interfacial properties of five zwitterionic surfactants at air–water and oil-water interfaces. The results of the study showed that longer alkyl chains decrease the critical micelle concentration and surface tension. And hydroxyl groups increase the critical micelle concentration and decrease the surface tension at the critical micelle concentration. Hydroxypropyl sulfobetaine surfactant C_{14}HSB significantly reduced the interfacial tension (IFT) between oil and water under high temperature and salinity conditions, indicating that zwitterionic molecules are very promising candidates for oil production.[14]

In a different study, the monomers phenylsulfonamide N-allyl-4-methylbenzenesulfonamide and N,N-diallyl-4-methylbenzenesulfonamide were copolymerized with acrylamide, acrylic acid, and zwitterionic 3-(3-methacrylamidopropyl-dimethylammonio)-propane-1-sulfonate via free-radical micellar copolymerization in deionized water for enhanced oil recovery (EOR). The zwitterionic copolymers demonstrated exceptional salt tolerance compared to HPAM. Core flooding experiments revealed significantly higher EOR values for the two zwitterionic copolymers, at 11.4% and 13.8%, versus 3.5% for HPAM. These findings suggest that zwitterionic copolymers outperform HPAM and gas injection methods in EOR under harsh conditions.[15-19]

Based on the above references, we can say that zwitterionic molecules can lower the surface tension at the oil-water interface and reduce the interfacial tension by breaking the cohesive forces. They also increase the viscosity through electrostatic interaction and hydration, form a stable network that thickens the solution, and increases the efficiency of oil recovery. Therefore, we can see that zwitterionic polymers are new polymers that can be used in the field of oil production. However, the large charge density of zwitterionic molecules can reduce their reactivity, which can reduce the rate of polymerization and the molecular weight of the resulting polymers.Hence, in this study, we investigated the reactivity of zwitterionic monomers and their effect on the molecular weight of the polymer when reacted with polyacrylamide, which is widely used in EOR.

2. Materials and methods

2.1 Materials

N-(3-dimethylaminopropyl)methacrylamide (DMAPMA) (99%, contains MEHQ as inhibitor), 1,3-propane sultone (1,3-PS), ammonium persulfate, acrylamide, ethanol, acetone

(≥99.5%), sodium chloride, calcium chloride, aluminium chloride, deuterium oxide were purchased from Sigma Aldrich. All reagents were used without additional purification and had an analytical or higher degree of purity.

2.2 Synthesis of zwitterionic monomers

The monomer sulfobetaine-N-(3-dimethylamino)propyl methacrylamide (SB-DMAPMA) was synthesized through the reaction of DMAPMA and 1,3-PS. A mixture of 1,3-PS (6.41 g, 0.05 mol) and acetone (15 g) was added dropwise to a three-neck flask containing a mixture of DMAPMA (8.51 g, 0.05 mol) and acetone (15 g), with stirring over a total period of 0.5 hours. The reaction mixture was then stirred at room temperature for 24 hours. The resulting white powder product was filtered, washed with acetone, and dried under reduced pressure for 24 hours at 40 °C, the synthetic pathway of the reaction is given in Fig. 1.

2.3 Synthesis of copolymers

For the synthesis of the copolymer P(SB-DMAPMA):AM, the total mass of AM was fixed at 20 g, and the calculated volume of water was used to dilute the reagents to monomer concentrations of 2 and 30 mol%. In a typical process, the specified amounts of AM and the zwitterionic monomer were dissolved in water. All solutions were added to a 500 mL round-bottomed three-neck flask. The reaction solution was then placed in a water bath at 60 °C and purged with pure nitrogen while stirring for at least 30 minutes to remove dissolved oxygen. Subsequently, 10 ml of an aqueous solution of ammonium persulfate (0.57% of the total monomer mass) was added to initiate free-radical polymerization. The reaction mixture was stirred under a nitrogen atmosphere for 6 hours until a viscous copolymer solution formed. After the reaction was completed, the resulting copolymer was repeatedly washed with acetone. Acetone washing was necessary to remove unreacted monomers, reaction byproducts and catalyst residues that could negatively affect the properties of the final material. After washing, a viscous copolymer solution was deposited in the form of white crystals. These crystals were then dried in a vacuum system at a temperature of 40 °C to completely remove the remaining traces of solvents, which ensured the high purity and stability of the resulting polymer. The synthesis pathway of the copolymer P(SB-DMAPMA) is shown in Fig. 2.

2.4 Infrared Fourier spectroscopy (IR Fourier)

Identification of functional groups in the obtained polymers was carried out using FTIR spectroscopy, a Nicolet iS10 FT-IR spectrometer.

2.5 ^{1}H NMR Spectroscopy

The JNM-ECA 500 MHz nuclear magnetic resonance (NMR) spectrometer was used to perform ^{1}H NMR spectroscopy. To determine the chemical structure and composition, the polymer was dissolved in deuterium oxide (D2O).

2.6 Molecular weight measurement

To measure the molecular weight of polymers, the Zetasizer Nano ZS device was used, providing data on both the size distribution and the molecular weight of samples.

2.7 Elemental analysis of CHNS-O UNICUBE

Elemental analysis was performed using an organic elemental analyzer to accurately quantify carbon, hydrogen, nitrogen,

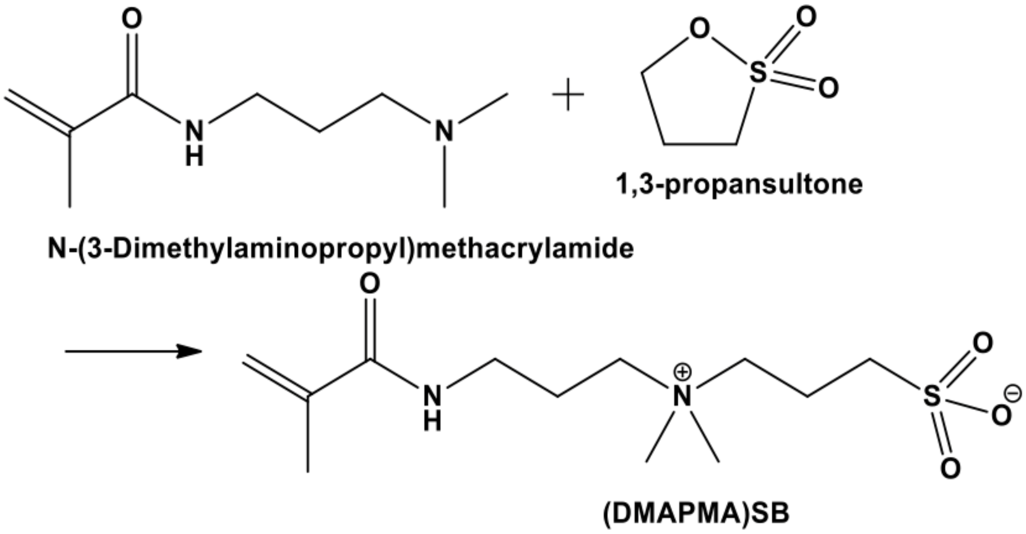

Fig. 1 Synthetic pathway of sulfobetaine-N-(3-dimethylamino)propyl methacrylamide monomer.

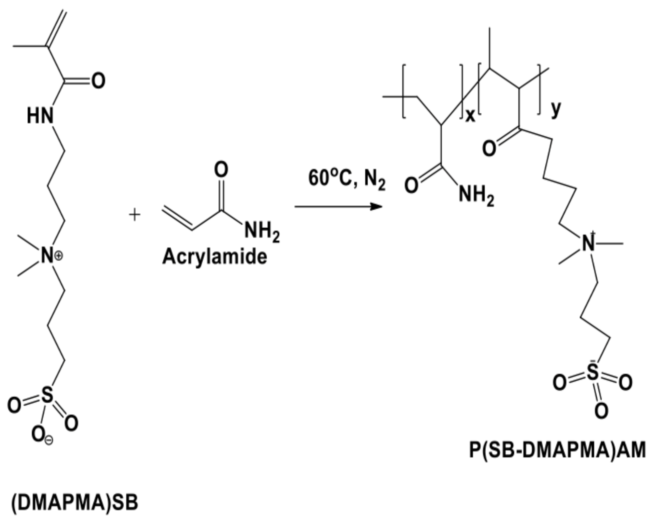

Fig. 2 Synthetic pathway of zwitterionic copolymer P(SB-DMAPMA):AM.

oxygen and sulfur content. This method guarantees an accurate quantitative measurement of these components in copolymer samples.

2.8 Viscosity measurement

The viscosity of the polymers was measured using an MCT 302 hydrometer. This technique evaluates rheological characteristics and intermolecular associations within a polymer solution.

2.9 Analysis of the polymer structure

The composition of the obtained polymers was analyzed using a transmission electron microscope JEM-1400 Plus. This method allows you to obtain high-resolution photographs of the morphology and structural organization of the polymer.

3. Results and discussion

3.1 FTIR studies of zwitterionic P(SB-DMAPMA):AM copolymers

Figure 3 shows the results of the FTIR spectra of acrylamide, sulfobetaine-DMAPMA and synthesized copolymers in their various molar ratios. Characteristic NH_2 peaks for acrylamide at 3328 and 3150 cm can be observed in all 4 copolymers and the peaks of the SO group characteristic of sulfobetaine-DMAPMA are observed at 1173 and 1033 cm. Copolymer peaks were identified at the same wavelength, which indicates the successful synthesis of copolymerization of acrylamide and sulfobetainimidazole. The successful synthesis of polymerization is also indicated by the fact that the pronounced peak of the C = C bond at 1610 cm of acrylamide is not observed in all four copolymer samples.

3.2 ^{1}H NMR studies of zwitterionic P(SB-DMAPMA):AM copolymers

Figure 4 shows the ^{1}H NMR spectrum characterizing zwitterionic copolymers based on acrylamide (AM) and sulfobetaine-N-(3-dimethylamino) propyl methacrylamide (SB-DMAPMA). The spectra show a change in chemical shifts depending on the ratio of monomers in the polymer chain (30:70, 20:80, 10:90 and 2:98). The main peaks correspond to different protons in the polymer structure and can be identified by the following characteristics. Peaks in the range from 1.0 to 2.0 ppm correspond to methyl and

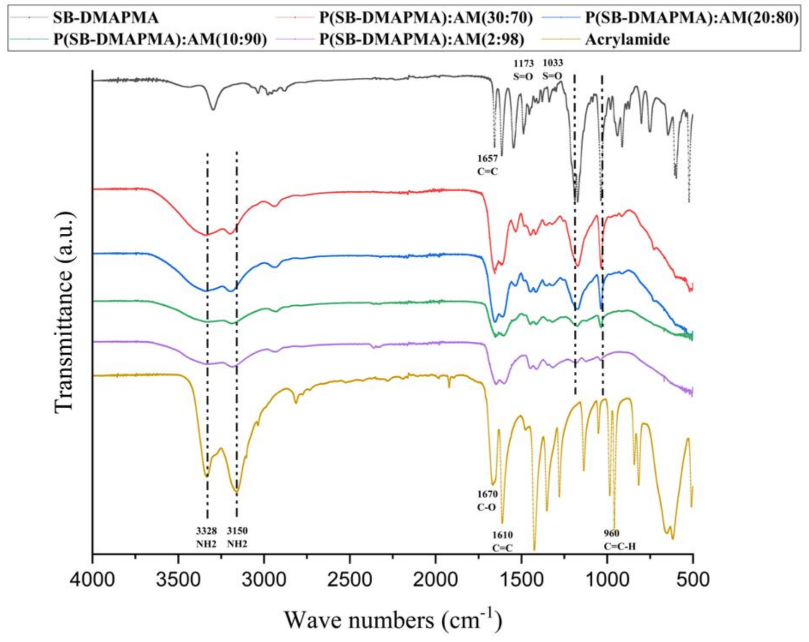

Fig. 3 FTIR spectra of monomers and zwitterionic polymers.

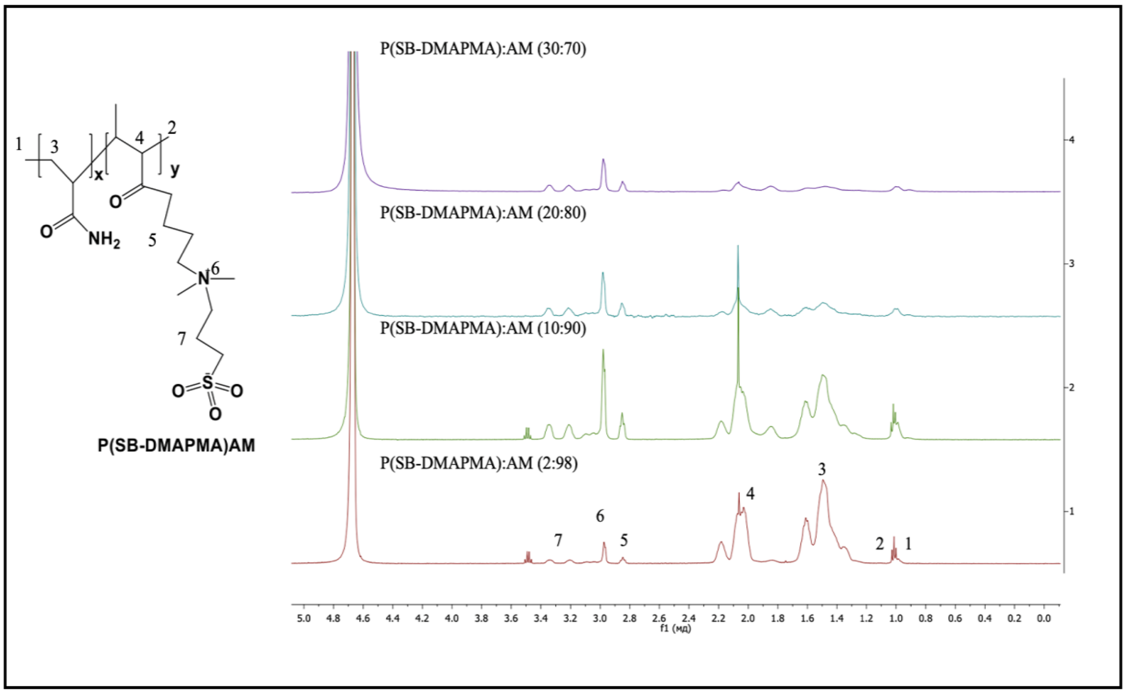

Fig. 4 ^{1}H NMR spectra of zwitterionic polymers.

methylene groups in the side chains of acrylamide and sulfobetaine. The presence of these signals indicates that the side chain is structurally correct. The region of 2.0-2.8 ppm is associated with protons of methylene groups located next to amino groups in the DMAPMA structure. The intensity of these peaks increases with an increase in the content of SB-DMAPMA in the composition of the copolymer, which can be observed when comparing spectra at different molar ratios.[20] Peaks in the range of 2.6-3.8 ppm is associated with methylene groups in the structure of sulfobetaine and dimethylamine fragments, characteristic of zwitterionic polymers such as P(SB-DMAPMA). Polymers containing sulfobetaine groups tend to exhibit noticeable peaks due to the high polarity and ionic interactions in the system.[21]

3.3 Molecular weight determination

To determine the molecular weight of zwitterionic copolymers, the process of static light scattering (SLS) was used. This method is non-invasive and is used to characterize molecules in solution. The laser installed in the Zetasizer Nano ZS equipment illuminates the particles and scatters light in all directions. After static light scattering uses the average intensity of the scattered light over time, the light intensity is measured over a period of 10 to 30 seconds and the accumulation is calculated for a series of concentrations of the polymer sample. This time averaging eliminates the inherent fluctuations in the signal, hence the term "static light scattering".[22] Based on this, we can determine the molecular weight (M_n) of zwitterionic polymers and the results are presented in Table 1.

Table 1. Molecular weight of zwitterionic copolymers.

Polymers	M_n average (kDa)
P(SB-DMAPMA):AM (2:98)	746±141.5
P(SB-DMAPMA):AM (10:90)	576±67.5
P(SB-DMAPMA):AM (20:80)	452±20.5
P(SB-DMAPMA):AM (30:70)	402±25.75

With the increase of the proportion of the second monomer (DMAPMA) in the copolymer, the average molecular weight decreases. This may be due to the change in the molecular and chain structure of the polymer with the increase of the content of the second monomer. For example, P(SB-DMAPMA):AM(2:98) has the highest molecular weight of 746 ± 141.5 kDa, and P(SB-DMAPMA):AM(30:70) has the highest molecular weight of 746 ± 141.5. kDa, whereas P(SB-DMAPMA):AM(30:70) has the highest and lowest atom 402 ± 25.75 kDa. Higher molecular weight values indicate longer polymer chains or more repeating bonds in the chain. The decrease in molecular weight with increasing content of the second monomer may indicate that the inclusion of more DMAPMA results in the shortening of the polymer chains or a change in the polymerization mechanism, which prevents the formation of long chains.

3.4 Elemental analysis

The data in Table 2 shows that with an increase in the sulfobetaine content in the copolymer, the sulfur (S) and hydrogen (H) content, as well as the nitrogen (N) content, also increased. This is due to the fact that the chemical composition of sulfobetaine contains sulfur and acrylamide, which mainly contribute to the nitrogen content in the polymer. The lowest sulfur content was observed in the copolymer with a monomer ratio of (2:98), which is explained by the minimum amount of sulfobetaine in the composition. As a result, with an increase in the proportion of sulfobetaine to 30%, the sulfur content will increase more than 24 times.

Table 2. The elemental composition of zwitterionic copolymers.

Name	N (%)	C (%)	H (%)	S (%)
P(SB-DMAPMA):AM (2:98)	16,485	43,745	7,2505	0,188
P(SB-DMAPMA):AM (10:90)	15,22	44,04	7,462	1,6375
P(SB-DMAPMA):AM (20:80)	13,81	44,165	7,87	3,3245
P(SB-DMAPMA):AM (30:70)	12,605	44,495	8,065	4,5665

The change in the carbon (C) and hydrogen (H) content with an increase in the sulfobetaine ratio is also associated with differences in the molecular structure of the monomers used. Consequently, with an increase in the sulfobetaine content, the amount of H increases due to the presence of hydrophilic groups in its composition. After determining the quantitative elemental composition of the copolymer, the actual ratio of the polarities of acrylamide and sulfobetaine is calculated based on the sulfur content. Calculations were carried out for each of the four copolymers and the results are presented in the Table 3.

Table 3. Molar fractions of monomers in the feed and copolymer.

Molar fractions of monomers in the feed, %		Molar fractions of monomers in the copolymer, %	
M_1 (AM)	M_2 (SB)	m_1 (AM)	m_2 (SB)
98	2	98,8	1,2
90	10	95,9	4,1
80	20	90,35	9,65
70	30	85	15

Table 3 shows that the actual monomer ratio in the copolymer differs from the initial ratio in the blend. The copolymer has a lower content of sulfobetaine than the initial monomer mixture. This may be due to differences in the reactivity of the monomers or their different solubility in the polymerization medium. Thus, with an initial monomer ratio of 98:2 (acrylamide:sulfobetaine), the actual ratio in the copolymer is 98.8:1.2, which indicates a slight decrease in the sulfobetaine content. As the sulfobetaine content in the initial blend increases, the difference between the initial and actual ratios increases. For example, with a monomer ratio of 70:30, the actual ratio is 85:15. These data are important for understanding the polymerization process and accurately controlling the composition of the resulting copolymer. The difference between the theoretical and actual monomer ratios must be taken into account when developing polymer materials for a specific application to ensure the required properties of the final product.

3.5 Calculation of reactivity ratios

Determining the practical molar ratio of acrylamide to sulfobetaine allowed us to calculate the reactivity coefficients of the monomers. Three calculation methods were used: Fineman-Ross, Kelen-Tudos, and Mayo-Lewis. The results are shown in the Table 4.

Table 4. Comparison of the reactivity ratios determined by various methods.

Methods	r_1	r_2	$1/r_1$	$1/r_2$	r_1*r_2
Fineman Ross	1,61	1,35	0,62	0,74	2,1735
Mayo- Lewis	1,66	1,25	0,60	0,8	2,075
Kelen-Tudos	1,36	0,912	0,73	1,09	1,24

3.6 Methods for calculating reactivity ratios

1. Fineman-Ross: This method is based on linear regression in which the initial monomer concentration ratio is used to determine the reaction rate response. This involves plotting a graph in which the slope of the regression line gives the r_1 and r_2 values.[23]

2. Kelen-Tudos: This modified version of the Fineman-Ross method aims to reduce mistakes in determining the initial monomer concentration. This approach linearizes the copolymer composition equation, accounting for the degree of dispersion in experimental data.[24]

3. The Mayo-Lewis technique employs experimental data on copolymer composition to calculate r_1 and r_2 dependences based on polymer kinetic principles. This approach is regarded as one of the most accurate methods for determining the reaction rate of monomers during copolymerization.[25]

The reactivity ratios of the monomers r_1 (acrylamide) and r_2 (sulfobetaine) were calculated using three methods, and the results show that the values of r1 and r_2 vary depending on the method:

According to the Fineman-Ross method, the values for r_1 and r_2 are 1.61 and 1.35 respectively, indicating a high reactivity and a strong tendency for monopolymerization of the two monomers. On other hand, the Mayo-Lewis method demonstrates a slightly higher value of 1.66 for r_1 and a lower value of 1.25 for r_2, which confirms the high reactivity of

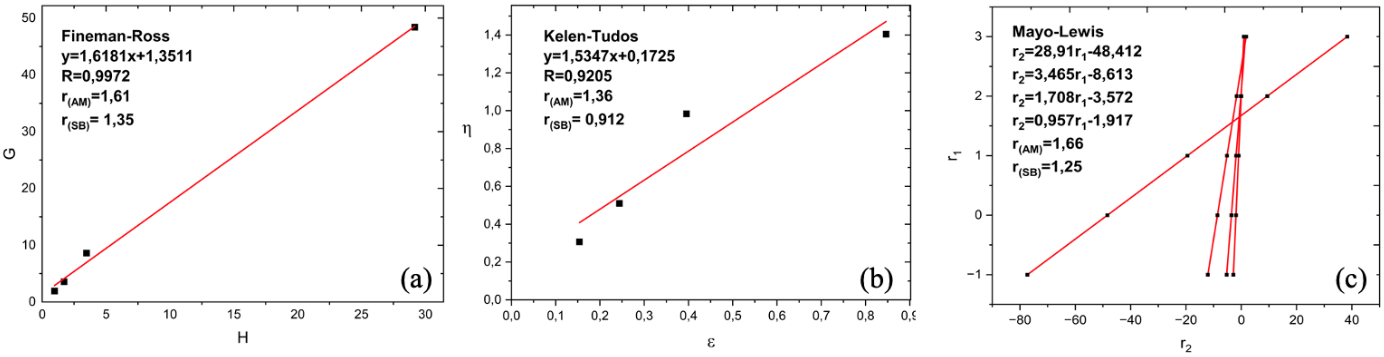

Fig. 5 Fineman-Ross (a), Kelen-Tudos (b), and Mayo-Lewis (c) plots for P(SB-DMAPMA)AM system.

acrylamide. In contrast, the Kelen-Tudos method yields the lowest values for r_1 and r_2, specifically 1.36 and 0.912 respectively. These values suggest a more accurate assessment of the reactivity of sulfobetaine and acrylamide, which can mean that the interaction between monomers is stronger and the tendency to copolymerization is higher.

In summary, all three methods exhibit high monomer reactivity coefficients (Fig. 5), but the Kelen-Tudos method probably provides the most accurate representation of monomer interactions during copolymerization, considering that the product $r_1 \times r_2$ values are lower and the reactivity coefficient values are more balanced.

3.7 Rheological experiments

From the Fig. 6 it can be seen that, the viscosities of zwitterionic polymer solutions are significantly influenced by the presence of salts such as NaCl, $CaCl_2$ and $AlCl_3$. The viscosity of P(SB-DMAPMA):AM (2:98) increased after the addition of sodium and calcium salts, becoming more viscous than polyacrylamide in these salt environments. This increase can be attributed to the interactions between the zwitterionic groups and salt ions due to the antipolyelectrolyte effect, which enhances the hydrodynamic volume of the polymer chains, leading to higher viscosity. This phenomenon has been observed in multiple studies. For example, Chen *et al.* (2014) investigated the solution behavior of hydrophobically associating zwitterionic polymers in saltwater and found that the addition of sodium salts increases the viscosity of

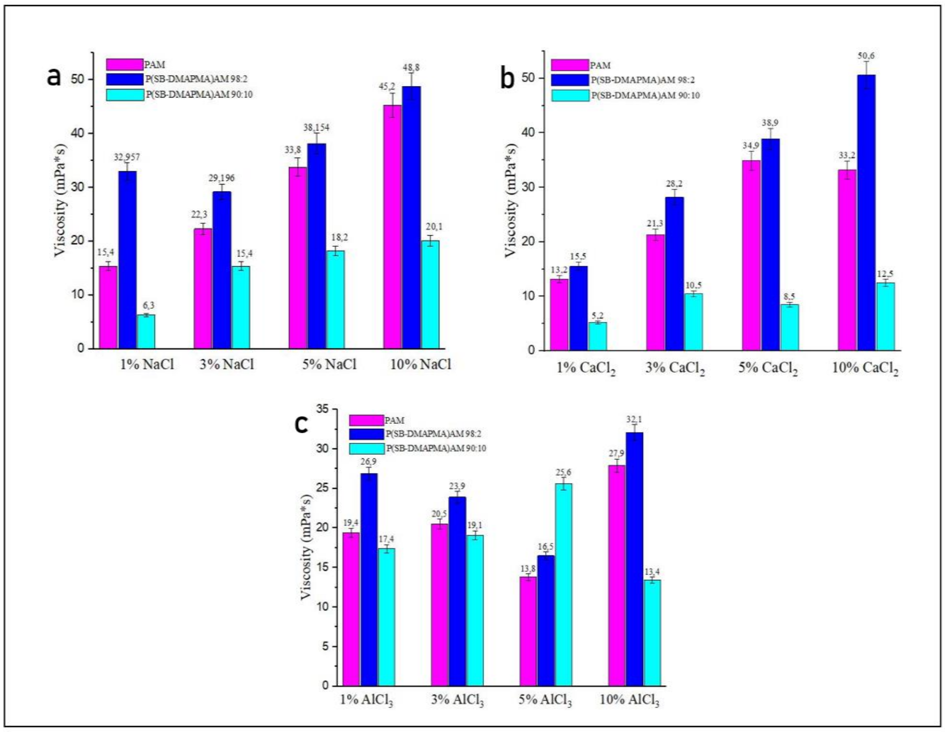

Fig. 6 Variation in viscosities of polymer solutions with increasing concentrations of Sodium (a), Calcium (b), and Aluminum (c) salts (Cp = 5000 mg/L).

zwitterionic polymer solutions.[26] Similarly, Dsouza and Parthiban (2019) explored the behavior of polysulfobetaines in the presence of calcium salts and indicated that calcium ions have a complex effect on the viscosity of zwitterionic polymer solutions.[27]

However, the viscosities of P(SB-DMAPMA):AM (10:90) were lower than those of polyacrylamide, likely due to the lower molecular weight of P(SB-DMAPMA):AM (10:90). As shown in Table 1, the molecular weight of P(SB-DMAPMA):AM (10:90) is 576 ± 67.5 kD, which is significantly lower than that of P(SB-DMAPMA):AM (2:98) (746 ± 141.5 kDa). Studies have shown that polymers with high charge density tend to have low molecular weights, whereas polyacrylamide, which has no charge, typically has a molecular weight higher than 1 million kDa.[28-30] The findings indicate that both charge effects and molecular mass significantly affect polymer viscosity where higher molecular weight zwitterionic polymers generally exhibit increased viscosity due to the greater entanglement of polymer chains, which leads to substantial resistance to flow.

Interestingly, at higher concentrations of aluminum salt solutions, the viscosity of P(SB-DMAPMA):AM (2:98) decreased, whereas the viscosity of P(SB-DMAPMA):AM (10:90) increased. This may be due to the lower molecular mass of P(SB-DMAPMA):AM (10:90), allowing aluminum ions to more easily interact with the polymer chains, especially given the higher content of the charged monomer (SB-DMAPMA), which increases the overall charge density of the polymer. At higher concentrations of aluminum salts, P(SB-DMAPMA):AM (10:90) interacts strongly with multivalent aluminum ions through electrostatic interactions, resulting in a significant increase in viscosity due to enhanced ion bridging and network formation. The influence of aluminum salts on the viscosity of zwitterionic polymer solutions is less frequently studied, and specific references supporting this behavior were not found. Although it is known that multivalent cations can alter the viscosity of polymer solutions, further research is needed to draw definitive conclusions regarding the effects of aluminum salts.

3.8 Thermogravimetric Analysis (TGA) analysis of polyacrylamide (PAM) and P(SB-DMAPMA):AM copolymers

Thermal stability of polymers is one of the very important parameters for the polymers used in EOR because the temperature range of many oil reservoirs between 20 - 200 °C. Therefore, the polymers used in EOR must exhibit thermal stability to maintain their quality and performance under such temperatures without degradation. On the other hand, polymers with good thermal stability can retain their viscosifying properties and rheological behavior at high temperatures, leading to improved oil recovery efficiency. Polymers that lack thermal stability may degrade or lose their effectiveness over time, leading to reduced oil recovery efficiency. In our research, we tested thermal stability of P(SB-DMAPMA): AM copolymers and compared with PAM. The thermal stability of the polymer P(SB-DMAPMA):AM demonstrates weight loss in several stages. In Fig.7, the first loss is at temperatures up to 150 °C, the second at about 200-250 °C and 330-370 °C is associated with a sulfogroup and a quaternary ammonium group associated with a polymer base, respectively (25% by weight). The final significant mass loss was observed at temperatures above 440 °C. From the graphs, it can be seen that at the critical coking temperature, the mass loss increases very little with a decrease in the molar amount of acrylamide in the copolymer. This is also due to the fact that the molecular weight of the copolymers is also decreasing.

3.9 TEM analysis of P(SB-DMAPMA):AM copolymers in salts with different oxidation states

To investigate how different salt media affect the polymer structure at the nanoscale, we examined the morphologies of

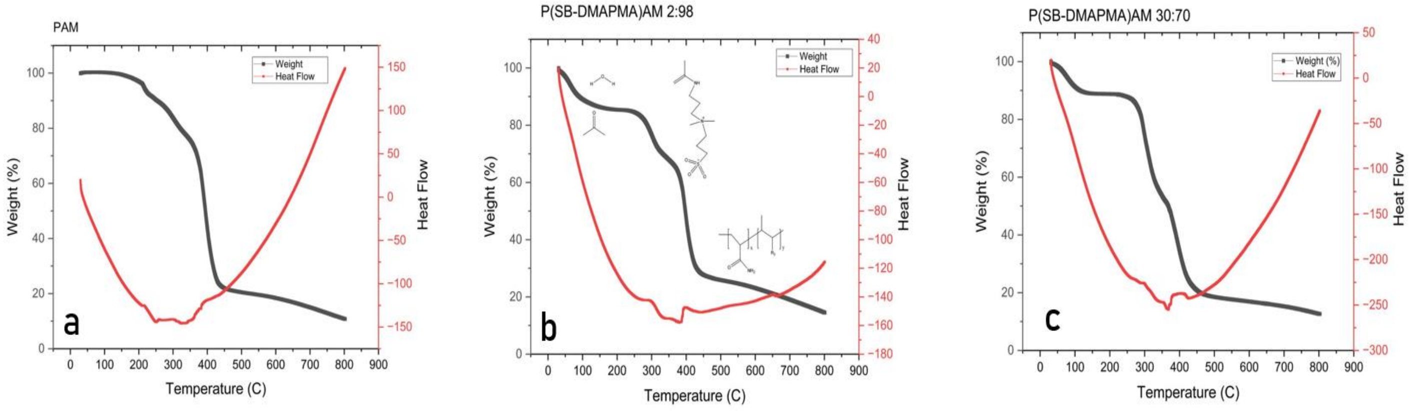

Fig. 7 The thermal stability of PAM (a) and P(SB-DMAPMA):AM copolymers (b and c).

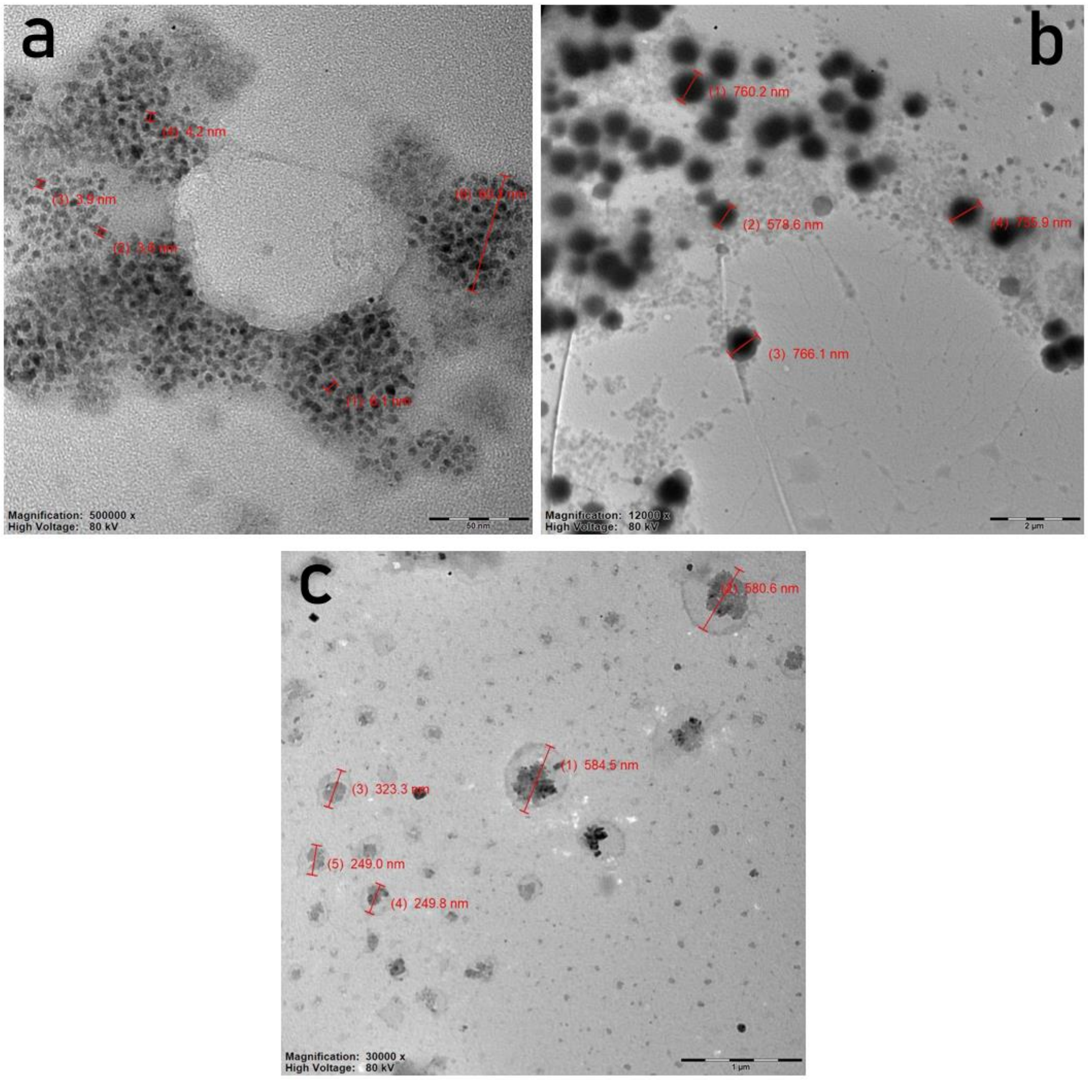

Fig. 8 TEM images of (a) P(SB-DMAPMA)AM 98:2 in 5% NaCl, (b)P(SB-DMAPMA)AM 98:2 in 5% $CaCl_2$, (c) P(SB-DMAPMA)AM 98:2 in 5% $AlCl_3$.

synthesized *P(SB-DMAPMA):AM* copolymers in different salt solutions. Fig. 8 provides TEM images of *P(SB-DMAPMA):AM* copolymers with a 2:98 ratio in different salt solutions: (a) 5% NaCl, (b) 5% $CaCl_2$, and (c) 5% $AlCl_3$. The TEM image in the NaCl medium shows relatively dispersed polymer particles with diameters ranging from approximately 50 nm to over 200 nm. The particle sizes are relatively small, but moderate aggregation can already be observed at some points in Fig. 8. This indicates that Na^+ interacts with the polymer and, due to the screening effect, allows the polymer chains to aggregate, which results in an increase in the viscosity of the polymer solutions. The TEM image of the $CaCl_2$ medium shows larger and more aggregated polymer particles, with sizes ranging from approximately 578 nm to 786 nm. The particles appear more densely packed and aggregated compared to the NaCl medium. Ca^{2+}, being divalent, has a stronger interaction with the polymer chains compared to monovalent sodium ions. The divalent nature of Ca^{2+} allows it to bridge between different polymer chains, leading to increased cross-linking and aggregation. This results in larger particle sizes and more pronounced aggregation in the TEM image. The higher degree of cross-linking due to Ca^{2+} ions contributes to an increase in viscosity, as previously discussed, by forming a more interconnected polymer network. Unlike the TEM images of polymers in sodium and calcium solutions, the addition of $AlCl_3$ resulted in a decrease in particle size by approximately 30 nm. Aggregation occurred only at some points, forming particles with a wide range of sizes, from approximately 248 nm to 586 nm. This is likely due to the high charge density of aluminum ions, which can lead to strong interactions with multiple negatively charged groups on the polymer. This strong cross-linking may result in the formation of a tightly bound network or cause the polymer chains to collapse and aggregate. Instead of just increasing the viscosity, excessive cross-linking leads to a reduction in viscosity.[31-33] This could be the reason for the viscosity differences observed in polymer solutions with different salts in Fig. 6. Based on the salt tolerance and viscosity studies in this research, zwitterionic polymers offer several advantages over traditional methods such as acrylamide-based polymers and gas injection, including better thermal stability, lower toxicity, and enhanced performance in challenging reservoir conditions. These unique properties make zwitterionic surfactants a viable alternative for EOR applications.[34-38]

4. Conclusions

The research presents a detailed analysis of the synthesis and application of zwitterionic copolymers in enhanced oil recovery. The copolymers exhibited superior thermal stability and rheological properties, particularly in saline environments. The inclusion of zwitterionic surfactants improved viscosity and enhanced oil displacement efficiency, outperforming traditional hydrolyzed polyacrylamides. The study's findings highlight the potential of these copolymers to address the challenges of EOR in harsh reservoir conditions, offering a promising solution for sustainable oil extraction. Future work should focus on optimizing the polymerization process and exploring the long-term stability and environmental impact of these materials in real-world applications.

Acknowledgments

This work was supported by the Ministry of Science and Higher Education of the Republic of Kazakhstan under the project AP13068466 “Novel Concept to Design the ASP flooding System Using Zwitteronic Polymer and Investigation on Its Mechanism”. The authors also would like to acknowledge the assistance from the Targeted Program of the MHES of the Republic of Kazakhstan, Grant No. BR21882439, “Advancement of the Green Energy: Foundational Research of Solar Fuel Technologies for Sustainable Production and Advanced Storage”.

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

References

[1] L. Mi, S. Jiang, Integrated antimicrobial and nonfouling zwitterionic polymers, *Angewandte Chemie International Edition*, 2014, **53**, 1746-1754, doi: 10.1002/anie.201304060.

[2] M. G. Petroff, E. A. Garcia, R. A. Dengler, M. Herrera-Alonso, M. A. Bevan, *kT*-scale interactions and stability of colloids with adsorbed zwitterionic and ethylene oxide copolymers, *Macromolecules*, 2018, **51**, 9156-9164, doi: 10.1021/acs.macromol.8b01792.

[3] Y. Liu, V. V. Duzhko, Z. A. Page, T. Emrick, T. P. Russell, Conjugated polymer zwitterions: efficient interlayer materials in organic electronics, *Accounts of Chemical Research*, 2016, **49**, 2478-2488, doi: 10.1021/acs.accounts.6b00402.

[4] S. Chen, F. Mo, F. J. Stadler, S. Chen, Z. Ge, H. Zhuo, Development of zwitterionic copolymers with multi-shape memory effects and moisture-sensitive shape memory effects, *Journal of Materials Chemistry B*, 2015, **3**, 6645-6655, doi: 10.1039/c5tb01075f.

[5] P. Bengani-Lutz, E. Converse, P. Cebe, A. Asatekin, Self-assembling zwitterionic copolymers as membrane selective layers with excellent fouling resistance: effect of zwitterion chemistry, *ACS Applied Materials & Interfaces*, 2017, **9**, 20859-20872, doi: 10.1021/acsami.7b04884.

[6] Y. Zhu, W. Xie, F. Zhang, T. Xing, J. Jin, Superhydrophilic In-situ-cross-linked zwitterionic polyelectrolyte/PVDF-blend membrane for highly efficient oil/water emulsion separation, *ACS Applied Materials & Interfaces*, 2017, **9**, 9603-9613, doi: 10.1021/acsami.6b15682.

[7] A. Sathyan, I. Kurtz, P. Rathore, T. Emrick, J. D. Schiffman, Using catechol and zwitterion-functionalized copolymers to prevent dental bacterial adhesion, *ACS Applied Bio Materials*, 2023, **6**, 2905-2915, doi: 10.1021/acsabm.3c00371.

[8] E. J. Walker Jr, C. K. Pandiyarajan, K. Efimenko, J. Genzer, Generating surface-anchored zwitterionic networks and studying their resistance to bovine serum albumin adsorption, *ACS Applied Polymer Materials*, 2019, **1**, 3323-3333, doi: 10.1021/acsapm.9b00772.

[9] M. S. Kamal, S. M. Shakil Hussain, A. S. Sultan, Development of novel amidosulfobetaine surfactant–polymer systems for EOR applications, *Journal of Surfactants and Detergents*, 2016, **19**, 989-997, doi: 10.1007/s11743-016-1848-1.

[10] L. A. Alcázar-Vara, L. S. Zamudio-Rivera, E. Buenrostro-González, R. Hernández-Altamirano, V. Y. Mena-Cervantes, J. F. Ramírez-Pérez, Multifunctional properties of zwitterionic liquids. application in enhanced oil recovery and asphaltene aggregation phenomena, *Industrial & Engineering Chemistry Research*, 2015, **54**, 2868-2878, doi: 10.1021/ie504837h.

[11] Z. Li, D. Xu, Y. Yuan, H. Wu, J. Hou, W. Kang, B. Bai, Advances of spontaneous emulsification and its important applications in enhanced oil recovery process, *Advances in Colloid and Interface Science*, 2020, **277**, 102119, doi: 10.1016/j.cis.2020.102119.

[12] X. F. Geng, X. Q. Hu, J. J. Xia, X. C. Jia, Synthesis and surface activities of a novel di-hydroxyl-sulfate-betaine-type zwitterionic gemini surfactants, *Applied Surface Science*, 2013, **271**, 284-290, doi: 10.1016/j.apsusc.2013.01.185.

[13] A. Gbadamosi, S. Patil, M. S. Kamal, A. A. Adewunmi, A. S. Yusuff, A. Agi, J. Oseh, Application of polymers for chemical enhanced oil recovery: a review, *Polymers*, 2022, **14**, 1433, doi: 10.3390/polym14071433.

[14] J. Zhao, C. Dai, Q. Ding, M. Du, H. Feng, Z. Wei, A. Chen, M. Zhao, The structure effect on the surface and interfacial properties of zwitterionic sulfobetaine surfactants for enhanced oil recovery, *RSC Advances*, 2015, **5**, 13993-14001, doi: 10.1039/c4ra16235h.

[15] H. Zhang, S. Gou, L. Zhou, Y. Fei, C. Peng, J. Huang, L. Chen, Modified polyacrylamide containing phenylsulfonamide and betaine sulfonate with excellent viscoelasticity for EOR, *Journal of Applied Polymer Science*, 2019, **136**, 47971, doi: 10.1002/app.47971.

[16] D. Karimov, Z. Toktarbay, Enhanced oil recovery: techniques, strategies, and advances, *ES Materials & Manufacturing*, 2023, **23**, 1005, doi: 10.30919/esmm1005.

[17] I. Gussenov, S. Bakytzhan, S. Amangaliyev, Y. Abba, HPAM-Cr (III) gel syneresis in bulk volume, *Eurasian Chemico-Technological Journal*, 2024, **26**, 61-66, doi: 10.18321/ectj1608.

[18] I. Gussenov, The effect of polymer mixing time on the strength of HPAM-Cr(III) gels, *Eurasian Chemico-Technological Journal*, 2023, **25**, 157-163, doi: 10.18321/ectj1518.

[19] N. Tileuberdi, M. Mashrapova, Z. Toktarbay, A review on nitrogen flooding for enhanced oil recovery, *ES Materials & Manufacturing*, 2023, **22**, 968, doi: 10.30919/esmm968.

[20] H. Abdollahi, V. Najafi, F. Amiri, Determination of monomer reactivity ratios and thermal properties of poly(GMA-co-MMA) copolymers, *Polymer Bulletin*, 2021, **78**, 493-511, doi: 10.1007/s00289-020-03123-5.

[21] Z.-H. Liu, Y.-H. Xiao, X.-Y. Ma, X. Geng, L. Ye, A.-Y. Zhang, Z.-G. Feng, Preparation and characterisation of zwitterionic sulfobetaine containing siloxane-based biostable polyurethanes, *Materials Advances*, 2022, **3**, 4608-4621, doi: 10.1039/d2ma00049k.

[22] N. P. Truong, M. V. Dussert, M. R. Whittaker, J. F. Quinn, T. P. Davis, Rapid synthesis of ultrahigh molecular weight and low polydispersity polystyrene diblock copolymers by RAFT-mediated emulsion polymerization, *Polymer Chemistry*, 2015, **6**, 3865-3874, doi: 10.1039/c5py00166h.

[23] M. Fineman, S. D. Ross, Linear method for determining monomer reactivity ratios in copolymerization, *Journal of Polymer Science*, 1950, **5**, 259-262, doi: 10.1002/pol.1950.120050210.

[24] T. Kelen, F. TÜdOtildes, Analysis of the linear methods for determining copolymerization reactivity ratios. I. A new improved linear graphic method, *Journal of Macromolecular Science: Part A - Chemistry*, 1975, **9**, 1-27, doi: 10.1080/00222337508068644.

[25] F. R. Mayo, F. M. Lewis, Copolymerization. I. A basis for comparing the behavior of monomers in copolymerization; the copolymerization of styrene and methyl methacrylate, *Journal of the American Chemical Society*, 1944, **66**, 1594-1601, doi: 10.1021/ja01237a052.

[26] H. Chen, Z. M. Wang, Z. B. Ye, L. J. Han, The solution behavior of hydrophobically associating zwitterionic polymer in salt water, *Journal of Applied Polymer Science*, 2014, **131**, 39707, doi: 10.1002/app.39707.

[27] R. F. Dsouza, A. Parthiban, Polymaleimide-based polysulfobetaines bearing functional and nonfunctional hydrophobic units and its aggregation behavior in aqueous media, *Langmuir*, 2019, **35**, 13942-13949, doi: 10.1021/acs.langmuir.9b02290.

[28] K. Z. Abdiyev, Z. Toktarbay, A. Z. Zhenissova, M. B. Zhursumbaeva, R. N. Kainazarova, Copolymerization of N, N-dimethyl-N, N-diallylammonium chloride with N, N-dimethylacrylamide, *Polymer Science Series B*, 2015, **57**, 217-223, doi: 10.1134/s156009041503001x.

[29] K. Abdiyev, M. Marić, B. Orynbaev, M. Zhursumbaeva, N. Seitkaliyeva, Z. Toktarbay, A novel cationic polymer surfactant for regulation of the rheological and biocidal properties of the water-based drilling muds, *Polymers*, 2023, **15**, 330, doi: 10.3390/polym15020330.

[30] Y. Dauletov, K. Abdiyev, Z. Toktarbay, N. Nuraje, M. Zhursumbaeva, B. Kenzhaliyev, Radical polymerization and kinetics of N, N-diallyl-N, N-dimethylammonium chloride and vinyl ether of monoethanolamine, *Fibers and Polymers*, 2018, **19**, 2023-2029, doi: 10.1007/s12221-018-6947-3.

[31] H. Khattab, A. A. Gawish, S. Gomaa, A. Hamdy, A. N. El-hoshoudy, Assessment of modified chitosan composite in acidic reservoirs through pilot and field-scale simulation studies, *Scientific Reports*, 2024, **14**, 10634, doi: 10.1038/s41598-024-60559-9.

[32] H. Khattab, A. A. Gawish, A. Hamdy, S. Gomaa, A. N. El-hoshoudy, Assessment of a novel xanthan gum-based composite for oil recovery improvement at reservoir conditions; assisted with simulation and economic studies, *Journal of Polymers and the Environment*, 2024, **32**, 3363-3391, doi: 10.1007/s10924-023-03153-w.

[33] K. G. Salem, M. A. Tantawy, A. A. Gawish, S. Gomaa, A. N. El-hoshoudy, Nanoparticles assisted polymer flooding: comprehensive assessment and empirical correlation, *Geoenergy Science and Engineering*, 2023, **226**, 211753, doi: 10.1016/j.geoen.2023.211753.

[34] S. Ozdoyev, V. Popov, N. Tileuberdi, H. Ma, The balkhash depression sediment paleogeology and oil-gas prospectsSGEM International Multidisciplinary Scientific GeoConference EXPO Proceedings, *International Multidisciplinary Scientific GeoConference: SGEM*, 2020, **20**, 799-804, doi: 10.5593/sgem2020/1.2/s06.102.

[35] N. Tileuberdi, A. N. AL-Dujaili, M. Mashrapova, K. Togizov, M. Sanatbekov, A. Yergali, Optimizing oil recovery by low-pressure nitrogen injection: an experiment case study, *ES Materials & Manufacturing*, 2024, **25**, 1189, doi: 10.30919/esmm1189.

[36] N. Tileuberdi, I. Gussenov, Review on miscible, immiscible, and progressive nitrogen injection for enhanced

oil recovery, *Energy Reports*, 2024, **12**, 360-367, doi: 10.1016/j.egyr.2024.06.004.
[37] A. B. L. «kmge», G. B. Duzbayeva, R. N. Uteev, A. B. L. «kmge», V. Z. Khazhitov, A. B. L. «kmge», A. S. Mardanov, A. B. L. «kmge», Estimation of recoverable reserves of carbonate reservoirs at the early development stage, *Engineering Journal of Satbayev University*, 2022, **144**, 36-42, doi: 10.51301/ejsu.2022.i5.05.
[38], B. S. Kelamanov, O. V. Zayakin, D. A. Yessengaliev, Y. Kobegen, R. A. Adaybayeva, A. Z. Temirbekov, Study of the Fe-Si-Al-Ba system using the thermodynamic-diagrammatic analyses method, *Engineering Journal of Satbayev University*, 2023, **145**, 20-24, doi: 10.51301/ejsu.2023.i2.03.