ANNOTATION

of the dissertation thesis on the requirements for the degree of Doctor of Philosophy (Ph.D.) in the specialty 6D073900 - "Petrochemistry"

by **Nurbatyr Mukhametgazy**

on the topic "**Synthesis and characterization of acrylamide-based polyampholytes for EOR, drilling of wells and tracer applications**"

Characterization of the research.

In this study, acrylamide-based polyampholytes were synthesized, characterized, and tested as additives for oil recovery-drive fluid, drilling fluid, and tracer fluid agents.

The relevance of the research.

Water is usually used to displace oil from matrix rocks. However, because of the unstable displacement front due to the differences in oil and water viscosities and heterogeneous nature of matrix rocks the oil production rates are often decline accompanied by the increase of water production.

Injection of polymer solutions into wells is one of the most efficient processes in oil production. In world practice the HPAM found the widest application due to its low cost and commercial availability. However, the main disadvantage of HPAM is its intolerance with respect to high salinity of oil reservoir. With an increase in salinity the HPAM chains tend to coil, because the electrostatic repulsion between negatively charged carboxylic groups is screened by the added salts. Moreover, the bivalent cations (Ca^{2+} and Mg^{2+}) present in saline water can bridge the carboxylic ions in the HPAM, effectively shrinking the macromolecules leading to precipitation. In fact, relatively high oil viscosity and brine salinity are common phenomena for Kazakhstani oil reservoirs. For example, the viscosity of Karazhanbas field oil may be higher than 350 cp, while brine salinity of Zhetibay and Moldabek fields may exceed 150 $g \cdot L^{-1}$. In this connection the oil industry of Kazakhstan needs the salt tolerant polymers that are able to viscosify the brine solution.

The ability of amphoteric polyelectrolytes to swell and be effective viscosity enhancers in high salinity and high-temperature reservoirs plays a crucial role in enhanced oil recovery (EOR) processes. Strongly charged (or quenched) polyampholytes due to salt- and temperature resistance can serve as viscosifying agents in EOR where thickeners are required in brine solution. In this regard, amphoteric polyelectrolytes – polymers which have both positively and negatively charged monomers, are promising, because in high saline water the anions and cations of salts screen the electrostatic attraction between positively and negatively charged groups of the polymer chain and increases the viscosity of the brine water.

Water-based drilling fluids (WBDF) play an important role in oil well drilling operations, including cleaning of the wellbore, carrying and suspending cuttings, cooling and lubricating drilling tools, and maintaining stability of the wellbore and formation. Conventional polymer additives, such as HPAM, polyanionic cellulose, and carboxymethyl (or ethyl) cellulose, exhibit low efficiency in a saline environment due to the polyelectrolyte effect. When expanded (or swollen) in pure water, polyelectrolyte chains shrink in a salt solution due to the screened electrostatic repulsion between uniformly charged macroions (polyelectrolyte effect) and adopt a coil conformation. This, in turn, leads to worse maintenance of the hydration dispersion, resulting in poorer performance and even insolubility. To overcome this problem, a WBDF containing salt-tolerant polyampholyte, bentonite, and inorganic salt NaCl was developed for wells with high salinity.

Many inter-well tracers have been widely used to obtain information on the interaction between producer and injector, evaluation of interwell and interlayer connections, as well as heterogeneities of oil reservoirs. The fluorescence-detection technology attracts considerable interest in oilfield operations due to many advantages over radioactive isotopes, ionic and organic tracers. For

evaluation of interwell permeability and porosity the fluorescent polyacrylamide microspheres, which fluoresce under ultraviolet irradiation, were applied. However, some parts of polymer-based fluorescent tracers, including microspheres, are absorbed onto the surface of rocks in the stratum, and it is difficult to detect them precisely. In the frame of this thesis the trace amount of fluorescent monomer – acrylamide Nile Blue (1 mol.%) was introduced into the composition of previously developed quenched polyampholyte to prepare globular and fully electroneutral macromolecular chains to minimize or exclude its adsorption to the rock. The advantage of proposed approach is that the quenched polyampholyte of equimolar composition containing fluorescent dye – Nile Blue is insoluble in oil, but water-soluble, salt tolerant, detectable in very low concentrations, and does not adsorb on the rock or clay minerals. The ternary polyampholyte based on acrylamide derivatives through the core sample was demonstrated for monitoring of well-to-well connections.

The aim of the study. develop the synthesis and characterization of acrylamide-based ternary polyampholytes (AAm-*co*-AMPS-*co*-APTAC) and determine their potential applications in the oil industry, such as enhanced oil recovery (EOR), drilling fluids, and tracer agents. To achieve this goal, we have outlined the following main tasks:

1. Synthesis and characterization of high molecular weight water-soluble ternary polyampholytes possessing high viscosity in high salinity brine (200-300 $g.L^{-1}$) and temperature.
2. Investigation the rheological characteristics of chosen polyampholyte in high salinity brine at 25°C and 60°C.
3. Conducting of laboratory oil displacement experiments through the sand pack model and core samples using aqueous solutions of TPA for evaluation the potential application of polymer flooding technology in EOR.
4. Comparison of the enhanced oil recovery efficiency of the high molecular weight TPA with HPAM, traditionally used polymer-flooding agent in oilfields of Kazakhstan.
5. Studying of TPA as a rheology enhancer and fluid-loss additive for the preparation of salt-tolerant water-based drilling fluids (WBDFs).
6. Synthesis and characterization of fluorescently labeled novel ternary polyampholyte (AMPS-*co*-APTAC-*co*-ANB=50:49:1 mol. %) to test as a tracer agent in core flooding experiments.

Objects of the study: is the synthesis and characterization of strongly charged linear acrylamide-based polyampholytes (AAm-*co*-AMPS-*co*-APTAC) composed of a nonionic monomer - acrylamide (AAm), an anionic monomer - 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), and a cationic monomer - (3-acrylamidopropyl) trimethylammonium chloride (APTAC). As well as a fluorescently labeled novel ternary polyampholyte (AMPS-*co*-APTAC-*co*-ANB) containing a fluorescent dye, acrylamide nile blue (ANB).

The subjects of the research: determination of optimal molar composition of acrylamide-based polyampholytes with the highest viscosity value in a wide range of brine and temperature for use in oil recovery, oil well drilling and as tracer agent.

The methods of the research

The dissertation work introduces a novel high molecular weight ternary polyampholyte (TPA) synthesized through conventional free radical copolymerization in an aqueous solution. Various analytical techniques were employed for comprehensive characterization:

1. FTIR spectroscopy
2. ^{1}H and ^{13}C-NMR spectroscopy
3. UV-Vis and fluorescence spectroscopy
4. Dynamic light scattering (DLS) and zeta-potential measurements
5. Gel-permeable chromatography (GPC)
6. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)
7. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)
8. Chemical analysis (XRF)
9. Elemental analysis (C,H,S,N)
10. Rheological study
11. Permeability and porosity measurements of sand pack and core samples

12. Core/sand pack flooding experiments
13. Preparation of bentonite/water and bentonite/polymer dispersion
14. Fluid loss tests
15. Permeability of filter cake and SEM analysis

The main research results

1. The dynamic viscosity of ternary polyampholytes (AAm-*co*-AMPS-*co*-APTAC) in water depends on the composition of the terpolymers and increases in the following series: 80:10:10 > 60:20:20 > 70:15:15 > 50:25:25 > 90:5:5 mol.%. In this regard, for the comprehensive study of the behavior of TPA in saline solutions, the optimal composition [AAm]:[AMPS]:[APTAC] = 80:10:10 mol% was chosen. Initially, injecting the low-molecular weight TPA solution during the core flooding tests resulted in a 4.8-5 % increase in the oil recovery factor (ORF).

2. Rheological studies of high-molecular-weight TPA (AAm-*co*-AMPS-*co*-APTAC in an 80:10:10 ratios solution showed improved viscosifying behavior in high-salinity brine (200-300 $g \cdot L^{-1}$) at both 24 and 60 °C.

3. The injection of 0.25% amphoteric terpolymer and HPAM solutions prepared in 200 g/L brine into the 0.62 and 1.77 Darcy sand packs resulted in the increase of the oil recovery factor by 28 and 18%, respectively. Incremental 10% oil recovery by AAm-*co*-AMPS-*co*-APTAC confirms that the amphoteric terpolymer has a higher oil displacement capacity than HPAM.

4. The addition of TPA not only improved rheological properties and reduced fluid loss of WBDFs but also increased salt resistance of the drilling fluids and gel stregnth, providing excellent performance in a wide range of high salinity brine and shear rate under room temperature geothermal conditions.

5. A novel ternary polyampholyte (AMPS-*co*-APTAC-*co*-ANB=50:49:1 mol. %) in both water and saline solutions effectively reduces rock adsorption, resulting in a 90% recovery factor when injecting a 0.1 wt.% solution into the core sample.

The novelty of the thesis.

The novelty of the PhD thesis is that the high molecular weight ternary polyampholytes (TPA) based on AAm-*co*-AMPS-*co*-APTAC were synthesized for the first time and they have a superior oil displacement capability in high-saline reservoirs compared to hydrolyzed polyacrylamide (HPAM) traditionally used in EOR.

Moreover, the salt-tolerant ternary polyampholyte AAm-*co*-AMPS-*co*-APTAC was applied for preparation of water-based drilling fluid. The novel amphoteric terpolymer possessed not only to boost its salt tolerance but also to enhance drilling mud performance (viscosity and filtration properties) under lower temperature geothermal conditions.

For the first time, a trace amount of fluorescent monomer – Acrylamide Nile Blue (ANB) was introduced into the composition of AMPS-*co*-APTAC copolymer. As a result, a novel ternary polyampholyte [AMPS]:[APTAC]:[ANB] = 50:49:1 mol.%, featuring a globular structure and fully electroneutral macromolecular chains, was obtained to minimize or prevent its adsorption on to the rock.

The practical significance of the thesis

TPA emerges as a novel alternative to HPAM for application in enhanced oil recovery under high salinity conditions in Kazakhstan. It also serves as a crucial polymeric additive, enhancing the rheological properties of salt-tolerant WBDF while minimizing fluid loss. Additionally, its application extends to interwell connections via core analysis, leveraging fluorescence detection technology within oil well monitoring. Its important role as a tracer agent in polymer flooding tests further underscores the significance and practical relevance of this study.

The validity and reliability of the results. the obtained data were confirmed using selective, accurate, and modern analysis methods, as well as the scientific methods. To ensure reliability and reproducibility, all experiments were conducted in several parallels.

Relation of the thesis with research and government programs

The research work was performed in the framework of several grant projects funded by the Ministry of Education and Science of the Republic of Kazakhstan. The first project, titled "Synthesis and Study of Thermo- and Salt-Sensitive Polyampholyte Nano- and Microgels" for the period 2020-2022 (AP08855552), aimed to develop new materials. The second project, ongoing from 2021 to 2023 (AP09260574), focused on the "Development of New Thermal and Salt-Resistant Amphoteric Terpolymers for Enhanced Oil Recovery". The third project, the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan provided funding to support the research under the project "Zhas Galym" for the period 2022-2024 (AP14972771), focusing on the title of "Synthesis and Study of New Modified Complexes Based on Synthetic and Natural Polyampholytes for Water-Based Drilling Fluids". Therefore, the author of the dissertation deserves the degree of Doctor of Philosophy (Ph.D.) in the specialty 6D073900-Petrochemistry.

Main provisions to be defended:

1. Novel high molecular weight TPA were successfully synthesized and characterized, comprising 50-90 mol.% acrylamide (AAm) as a nonionic monomer, 5-25 mol. % 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS) as an anionic monomer, and 5-25 mol. % (3-acrylamidopropyl) trimethylammonium chloride (APTAC) as a cationic monomer. The sample AAm-*co*-AMPS-*co*-APTAC=80:10:10 mol. % was chosen for the further sand pack and core flooding tests due to its highest viscosifying ability in high salinity (200-300 $g.L^{-1}$) brine.

2. The injection of 0.25 % TPA and HPAM solutions, prepared in 200 $g \cdot L^{-1}$ brine, into the 0.62 and 1.77 Darcy sand pack models saturated with viscous Karazhanbas oil (420 cp) at 30 , resulted in an increase of the IOR by 28 % and 18 %, respectively. These results show that the TPA has a higher oil displacement capacity than HPAM in high salinity conditions.

3. Adding 2 wt.% of a novel ternary polyampholyte (AAm-*co*-AMPS-*co*-APTAC=80:10:10 mol. %) to a high salinity (35 wt.%) NaCl brine with bentonite (4 wt.%) drilling fluid formulation significantly reduced the filter cake thickness to 0.09 cm. This reduction in filter cake thickness surpassed the thickness achieved with BT/PAC-LV (0.18 cm) and bentonite alone (0.41 cm). Additionally, the BT/TPA drilling fluid showed the lowest permeability/thickness ratio at 13 mD/cm, indicating its potential as a rheology enhancer and fluid loss additive for salt-resistant WBDF. Furthermore, the BT/TPA drilling fluid exhibited remarkably low fluid loss, measuring only 3.5 ml, well below the API standard limit of 12 ml.

4. A novel ternary polyampholyte composition (AMPS-*co*-APTAC-*co*-ANB = 50:49:1 mol. %) was synthesized and found to be efficient at minimizing adsorption on rock surfaces. When injected a 0.1 wt.% (or 1.3×10^{-3} $mol \cdot L^{-1}$) aqueous solution into a core, it achieved a 90% recovery factor, making it a promising polymer tracer for monitoring oil wells in oil industry.

Approval of practical results of the work. The main results of the work were presented at the following international conferences and symposia: 8th International Symposium on Specialty Polymers (Karaganda, Kazakhstan, August 23-25, 2019); AIP Conference Proceedings, (Conference paper, Scopus/WoS CiteScore 0.7 Percentile 17%, Q 4,Volume 2167, Page 020236-Pages 1-3, Nov 19, 2019); VIII All-Russian Conference "Recovery, Preparation, and Transportation of Oil and Gas" (Tomsk, Russia, October 1-3, 2019); VIII All-Russian Kargin Conference "Polymers in the Strategy of Scientific and Technological Development in the Russian Federation, Polymers-2020" (Tver, Russia, September 20-24, 2020); Uzbek-Kazakh Symposium "Modern Problems of Polymer Science" (Tashkent, Uzbekistan, November 24, 2020); and 13th International Symposium on Polyelectrolytes (Shanghai, China, June 21-25, 2021);

Publications.

Results of the research work are reflected in 12 publications: 1 article – in the Scientific Journal cited in the Scopus data base (Q1, 77 percentile), 1 article in AIP Conference Proceedings (Q4, 17 percentile), 4 articles – in the Scientific Journals listed in the recommended by the Committee for Quality Assurance in the Sphere of Education and Science of the Ministry of Science and Higher

Education of the Republic of Kazakhstan, and 1 publication in other scientific journals and publications (Kazakhstan Journal for the Oil & Gas Industry). Scientific results were also reported at 5 International Conferences and Symposiums.

The personal contribution of the Ph.D candidate to the preparation of each article was as follows:

In the article "Comparative Study of Oil Recovery Using Amphoteric Terpolymer and Hydrolyzed Polyacrylamide" (Polymers 2022, 14(15), 3095; ISSN: 2073-4360. Q1 Scopus/WoS CiteScore 5.7 Percentile 77%), Nurbatyr M. is the corresponding author. The Ph.D candidate participated in conducting all experiments, interpreting the results, and preparing the initial drafts of the article, including descriptions of the introduction, methodology, results, conclusion, and graphics. Additionally, he was involved in formatting the article according to the journal's requirements and improving it after each stage of peer review.

In the article "Salt-Tolerant Acrylamide-Based Quenched Polyampholytes for Polymer Flooding" (Bulletin of Karaganda University, Chemistry Series, №4 (100)/2020, pages 119-127), and "Oil Recovery at High Brine Salinity Conditions Using Amphoteric Terpolymer" (Bulletin of the University of Karaganda – Chemistry Series. No. 3(107)/2022, pages 141-149), Nurbatyr .M is the first author. In these articles including "Synthesis and Characterization of a Novel Acrylamide-Based Ternary Polyampholyte as a Tracer Agent" (Chemical Bulletin of Kazakh National University, 100(1): 22-29, 2021), "Synthesis and Characterization of High Molecular Weight Amphoteric Terpolymer Based on Acrylamide, 2-Acrylamido-2-Methyl-1-Propanesulfonic Acid Sodium Salt, and (3-Acrylamidopropyl) Trimethylammonium Chloride for Oil Recovery" (Chem. Bull. Kazakh Natl. Univ. 2021, 103, 12-20), and "Synthetic Polyampholytes Based on Acrylamide Derivatives – A New Polymer for Enhanced Oil Recovery" (Kazakhstan Journal for Oil & Gas Industry, 4(4), 104-116), Nurbatyr M. is the corresponding author. Additionally, Nurbatyr M. participated in formatting the articles according to the journal's requirements, submitting the articles to the journals, and improving the articles after each stage of peer review.

Dissertation structure. The dissertation includes a review of applicable literature, an explantion of methodology, and a discussion of the results, a conclusion, and a list of available sources. The total volume is 109 pages, including 67 figures, 14 tables, and a bibliography of 206 titles.