

ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD)
in the educational PROGRAM 6D073900 – “Petrochemistry”

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NEW BIOCIDAL FLOCCULANTS BASED ON VINYL MONOMERS FOR APPLICATION IN OIL FIELD TECHNOLOGIES

The main goal of the dissertation work is to synthesize new polymeric surfactants (poly-SAS) based on vinyl monomers that can be used in oilfield technologies. These compounds provide deep processing of petrochemical raw materials and expand the possibility of their transformation into value-added products. The synthesized poly-SAS can be used as flocculants to purify industrial and natural wastewaters generated at oil production and refining enterprises from fine dispersed polluting particles. In addition, they can be used as biocidal compounds that effectively inhibit the growth of sulfate-reducing and thiobacteria that cause microbiological corrosion.

Relevance of the research topic. Nowadays, the oil industry is not limited only to fuel production, but is becoming an important part of scientific and technological progress, which allows obtaining multifunctional chemical products that are widely used in various industries. The synthesis of new polymeric surfactants (poly-SAS) based on monomers obtained from petroleum products opens the way to obtaining affordable effective flocculants, structuring agent, biocides and polymeric compounds that allow regulating the stability of dispersion systems, thereby expanding their range. This in turn allows replacing foreign (imported) poly-SAS with domestic products.

Nowadays, cleaning natural and industrial wastewater from fine dispersed particles of harmful mechanical impurities and protecting metal, reinforced concrete installations from microbiological corrosion is considered one of the most complex environmental problems of industry. In addition, another important problem that has not been fully resolved in the oil production and refining processes is the separation of solid waste from used mud drilling fluids, drilling wastewater and sludge. After all, drilling waste belongs to the 4th hazard class. Therefore, dumping used drilling fluids into the sea without preliminary treatment or collecting them in underground reservoirs (sludge pits) causes enormous harm to the environment.

Poly-SAS allows you to regulate the rheological (thixotropic) properties of drilling fluids, separate harmful solid particles from their composition and inhibit microbiological corrosion. This, in turn, helps to increase the productivity of wells and inhibit corrosive wear of equipment.

From this point of view, polymeric surfactants synthesized based on the monomers obtained from available petrochemical products are of particular interest. The reason is that such compounds, due to their structural features (diphilic properties), can perform several functions at the same time: they allow separating

solid waste from drilling muds, regulating the rheological properties of drilling fluids, purifying wastewater from finely dispersed particles of pollutants by flocculation, and inhibiting the growth of microorganisms that cause microbiological corrosion. In general, the use of the studied polymer compounds in the petrochemical and oil and gas industries is an urgent scientific and practical task aimed at ensuring environmental safety, as well as the efficient use of resources and increasing the potential of local raw materials.

The purpose of the research work. Using derivatives of vinyl monomers based on petrochemical products, to synthesize new polymeric surfactants with flocculating and biocidal properties, to propose a technology for their production, as well as to justify the possibility of their effective use in oilfield technologies by studying their physicochemical, surface, flocculating and biocidal properties.

To achieve this goal, the following **tasks** were defined:

- to synthesize new effective polymeric surfactants of various molar compositions, which can be used in the field of oil production and refining, using the radical copolymerization method using industrial monomers containing the necessary functional groups, to determine their functional and molar composition using modern methods (elemental analysis, IR and NMR spectroscopy, conductometric titration); to determine the influence of various factors on the yield of the copolymerization reaction;

- determination of surface and thermogravimetric properties of synthesized copolymers, ensuring their stability in various temperature and chemical environments, as well as determination of biocidal properties that allow reducing microbiological corrosion of drilling and oilfield equipment and pipelines;

- studying the flocculation and demulsification properties of synthesized poly-SAS, justifying their use for cleaning used drilling muds from rocks and production waters from harmful dispersed particles, as well as for dewatering crude oil;

- development of a basic technological scheme for the production of synthesized new polymeric surfactants and their use as flocculants in oil industry technologies using the Aspen Hysys computer modeling program and calculation of the estimated material and energy balance of the process and justification of the possibility of their use as flocculants with biocidal and demulsifying properties in oil industry technologies.

Objects of study: N-[3-(methacryloylamino)propyl] trimethylammonium chloride, N,N-dimethylacrylamide, itaconic acid and synthesized new polymeric surfactants – copolymer of [(3-methacryloylamino)propyl] trimethylammonium chloride and N,N-dimethylacrylamide (TMAPMAX-DMAA) and copolymer of [(3-methacryloylamino)propyl] trimethylammonium chloride and itaconic acid (TMAPMAX-IA).

Subject of study: oilfield chemistry, polymer chemistry, colloid chemistry. Applied research.

Research methods: In this dissertation, new polymer biocidal compounds were synthesized by radical copolymerization of commercially available monomers in an aqueous medium. Radical copolymerization is currently considered the most convenient and effective method for synthesizing polymeric surfactants. Since no

by-products are formed during the reaction, there is no need to purify the main product from by-products. Elemental, functional and molar compositions and structures of the synthesized polymeric surfactants are determined using modern methods such as IR, ¹H-NMR, ¹³C-NMR spectroscopy, elemental analysis, thermogravimetric analysis and conductometric titration. Bactericidal (biocidal) properties were proven by determining the ability to suppress the growth of sulfate-reducing bacteria (SRB) and Thiobacillus ferrooxidans thiobacilli (TB) in the Scientific and Production Center for Microbiology and Virology (Almaty). Surface and flocculating properties of poly-surfactants were determined using modern methods in the field of colloidal and surface chemistry (turbidimetry, measurement of surface tension and adsorption capacity of solutions, electro kinetic analysis, etc.).

Scientific novelty of the study:

1. The cationic poly-SAS – copolymer of [(3-methacryloylamino) propyl]trimethyl ammonium chloride with N,N-dimethylacrylamide (TMAPMAX-DMAA) and the ampholyte poly-SAS - copolymer of [(3-methacryloylamino) propyl]trimethyl ammonium chloride with itaconic acid (TMAPMAX-IA) were synthesized by radical copolymerization reaction, the molar composition, surface-active and biocidal properties of which can be adjusted by changing the relative amounts of monomers in the initial mixture.

2. The adsorption of TMAPMAX -DMAA and TMAPMAX -IA copolymers on the water-air interface were studied, and it was proved that the copolymers are poly-bases. It was found that the synthesized cationic and ampholyte copolymers have biocidal properties, i.e. they inhibit the growth of Thiobacillus ferrooxidans (TB) and sulfate-reducing bacteria (SRB). This allows these compounds can be used as biocidal compounds against microbiological corrosion.

3. The synthesized new poly-SAS have flocculating properties and their flocculating ability can be regulated by changing the hydrophilic-lipophilic balance (molar composition) of the copolymer macromolecules. This opens the way to using these copolymers in oilfield technologies for the purpose of cleaning mud drilling fluids and wastewater from dispersed particles.

4. Technological schemes for the production of copolymers and their use as flocculants were developed using the Aspen HYSYS computer program. The material and energy balance of the processes was calculated, and the efficiency and suitability of the flocculation process for industrial implementation in production and oil industry technologies were scientifically substantiated.

Reliability and accuracy of the obtained data. The reliability and accuracy of the obtained research results are beyond doubt, since they were obtained using modern methods in the field of polymer chemistry, colloidal and surface chemistry (radical copolymerization reaction, IR, NMR spectroscopy, conductometry, turbidimetry, measurement of surface tension of a solution, calculation of the adsorption value using the Gibbs equation, study of the kinetics of the copolymerization reaction using the Mayo-Lewis and Feynman-Ross equations, measurement of the electro kinetic potential (Z-sizer), etc.). The obtained experimental values were analyzed by comparing them with the latest data published in the literature in this field. Certified methods and state standards were used in the

research. The equipment and materials used comply with the requirements of regulatory documents.

The connection of the research topic with the plan of scientific research and various state programs

The research part of the dissertation was carried out within the framework of scientific project N° AR14870286 "New polymeric biocidal compounds: synthesis and study of properties" (2022-2024) funded by the Science Committee under the Ministry of Science and Higher Education of the Republic of Kazakhstan.

The provisions submitted for defense:

1. The cationic poly-SAS copolymer of [(3-methacryloylamino) propyl]trimethyl ammonium chloride with N,N-dimethylacrylamide (TMAPMAX-DMAA) and the ampholyte poly-SAS copolymer of [(3-methacryloylamino) propyl]trimethyl ammonium chloride with itaconic acid (TMAPMAX-IA), the molar composition, surface-active and biocidal properties of which can be adjusted by changing the relative amounts of monomers in the initial mixture, were obtained by radical copolymerization reaction.

2. The biocidal properties of the new poly-SAS were studied and it was proven that they have biocidal properties that inhibit the growth of *Thiobacillus ferrooxidans* and sulfate-reducing bacteria.

3. The synthesized copolymers can be used as flocculants with biocidal and demulsifying properties in oil industry technologies. Their flocculation ability can be adjusted by changing the hydrophilic-lipophilic balance (molar composition) of the copolymer macromolecules.

4. Using the Aspen HYSYS computer-modeling program, process flow diagrams for flocculant production and wastewater treatment processes using them were developed, material and energy balances were calculated. The efficiency of the flocculation process in industrial oil production and refining technologies, as well as its suitability for industrial application, were scientifically substantiated.

Practical significance of the research results. The multifunctional properties of the polymeric surfactants (poly-SAS) synthesized during the study - TMAPMAC-DMAA and TMAPMAC-IA copolymers - expand the scope of their practical application in industrial conditions. In particular, the obtained poly-surfactant samples can be used:

- as effective flocculants for the efficient sedimentation of finely dispersed pollutant particles in industrial and wastewater treatment;

- as biocidal compounds that inhibit the growth of SRB and TB bacteria, which cause microbiological corrosion;

- in oil and gas production, specifically for stabilizing the structure of drilling fluids, regulating thixotropic properties, suppressing microbiological corrosion of metal and reinforced concrete structures, and improving drilling efficiency. The use of these compounds not only improves the environmental safety of production processes, but also reduces the overall consumption of reagents, provides a comprehensive effect of the substances used, and reduces dependence on foreign analogues.

In addition, the research results are a concrete step towards creating a new generation of reagent technology for the domestic petrochemical and oil and gas industries, substantiation of the possibilities of their production based on local raw materials, development of the domestic scientific and technical base.

The results of testing the obtained poly-surfactant compounds in specific technological processes show their suitability and efficiency for industrial use, which in the future can serve as the basis for their production and commercialization on an industrial scale.

Approbation of the results of the dissertation:

The main results of the dissertation were published at the following scientific conferences:

Satbayev International Conference 2023, April 12, 2023, Almaty, Satbayev University;

Satbayev International Conference 2024, April 12, 2024, Almaty, Satbayev University;

Publications. The main results of the dissertation work were published in 7 co-authored works, including 1 article in the journal "ES Materials and Manufacturing" (quartile Q2, percentile 92%), included in the Scopus database, 1 article in the journal "Engineered Science" (quartile Q1, percentile 96%); 1 article in the "Chemical Journal" recommended by the "Committee for Quality Assurance in Science and Higher Education" of the Ministry of Education and Science of the Republic of Kazakhstan; Published in the form of materials and abstracts of 2 reports at international and republican scientific conferences. Received 2 patents of the Republic of Kazakhstan for methods of producing new polymeric biocidal compounds.

Personal contribution of the author. The dissertation author read articles published in the press on the topic of the research, conducted a literature review, participated in the experimental part of the work, selected physicochemical research methods, conducted research, participated in the analysis of the obtained experimental values and drawing conclusions. Participated in the publication of the experimental results in print.

Structure and volume of the dissertation. The dissertation consists of an introduction, three chapters, a conclusion and a list of references. The dissertation consists of 119 pages, 27 tables and 41 figures. The list of references includes 116 sources.