# ANNOTATION

dissertation work of Issa Aziza Bakytzhankyzy on the topic: “Development of obtaining technology of composite surface-active acrylate polymers for increase of oil recovery” submitted for the degree of Doctor of Philosophy (PhD) on specialty 6D072100 - “Chemical technology of organic substances”

**The relevance of the topic.** Most of Kazakhstan's oil fields are at a late stage of development, which is characterized by a constant decline in oil production. Continuous production of oil from the reservoir reduces the operational reserve of the well.

To increase oil recovery, polymer flooding methods have become widespread. Polymer flooding uses predominantly imported polymer reagents, which in turn leads to significant financial costs for companies involved in oil production and treatment. Therefore, the search for accessible secondary chemical raw materials to obtain polymer reagents that can be used for polymer flooding is a relevant and cost-effective solution.

Most wells of the Kyzylorda fields are operated under conditions of high waterflooding of well products, since the produced oil is highly paraffinic, highly emulsified and low-sulfur. In this regard, to increase oil recovery from oil and gas fields, it is necessary to select available raw materials, as well as new technologies based on the use of effective modified polymer reagents.

This dissertation presents the results of obtaining composite surface-active acrylate polymers to enhance oil recovery from underground formations and research on their activity in relation to the Kumkol oil and gas field.

**The purpose of the research** is to develop a technology for producing composite surfactant acrylate polymers to enhance oil recovery.

**The research objectives:**

- determination of the possibility of using the polymer flooding process to increase the production of residual oil from reservoirs;
- development of technology and selection of optimal conditions for the production of high-molecular surface-active composite polymers, resistant to aggressive environments and high temperatures, by modifying polyacrylamide with fatty acids of gossypol resin to impart surface-active properties;
- research of the physicochemical properties of synthesized composite polymers;
- testing of the resulting composite polymers during oil displacement by testing on rock samples using the UIK-S(2) installation;
-mathematical optimization of technology and assessment of the economic efficiency of oil displacement from flooded formations of the Kumkol field using synthesized composite surfactant polyelectrolytes;

- conducting field tests of the resulting composite surfactant acrylate polymers to increase oil recovery.

**Objects and methods of research.** The objects of research of the dissertation work are oil from the Kumkol field, polyacrylamide, gossypol resin, sodium hydroxide, glycerin, formalin, potassium persulfate, sodium bisulfite, core.

To achieve the goals of the research work, the following physicochemical and analytical research methods were chosen: saponification; infrared spectroscopy (IR-Fourier spectrophotometer ShimadzuYRPrestige-21); elemental analysis (EM); electron microscopy; capillary viscometry method; differential thermogravimetry (DTA) method; polymer flooding method to increase oil displacement efficiency (UIK-S(2)).

**The main provisions submitted for defense:**

- development of a technology for producing composite surfactant polymers of the MPAA series, resistant to aggressive environments and high temperatures, based on polyacrylamide by hydrolysis with sodium hydroxide followed by modification in the presence of formaldehyde, sodium thiosulfate or fatty acids of gossypol resin, at a temperature of 353-363 K, time 4 ,0-4.5 hours, reagent ratio 1:0.8;

- production of gel polymers based on synthesized polymers by cross-linking in the presence of initiators potassium persulfate and sodium bisulfite at a temperature of 60-80°C for 1.0 hour to increase the efficiency of displacement of high-viscosity oils;

- physico-chemical properties of the obtained composite polymers, as well as their aqueous solutions, study of the influence of temperature, concentration, pH of the environment, degree of water mineralization on the process of obtaining a polymer reagent, where it was established that these polymers belong to amphoteric polyfunctional (amide, imide, carboxyl, hydroxyl, sulfomethyl, ether) surfactant polyelectrolytes;

- results of the influence of the concentration of MPAA-3 in formation water, which contains salts (100 g/l) on the kinematic viscosity of Kumkol oil, a study on the laboratory installation UIK-S (2) of rock samples (core), with an optimal concentration of MPAA-3 equal to 0.4%;

- resistance of composite surfactant polymers to high temperatures (180°C);

- mathematical optimization of the main parameters of the process of obtaining composite surfactant polymers based on hydrolyzed and modified polyacrylamide (PAA);

- economic efficiency from the use of the resulting composite polymers, at which the profit will be 25,696,689 tenge per year, profitability - 20%.

**The main research results**:

- a technology has been developed for the production of new composite surfactant polymers of the MPAA series based on polyacrylamide by hydrolysis with sodium hydroxide followed by modification in the presence of formaldehyde, sodium thiosulfate or fatty acids of gossypol resin, at a temperature of 353-363 K, time 4.0-4.5 hours, the ratio of reagents is 1:0.8, resistant to aggressive environments and high temperatures. As a result of the modification, the ability to regulate the

surface-active properties of composite polymers in the presence of fatty acids of gossypol resin or technical glycerin obtained on their basis has been achieved. In this case, the surface tension of the modified PAA was σ=43.6 N/m;

-production of gel polymers by crosslinking in the presence of initiators potassium persulfate and sodium bisulfite at a temperature of 60-80°C for 1.0 hours in order to use them to increase the efficiency of displacement of highly paraffinic and highly viscous oils;

- the results of the physicochemical properties of the obtained composite polymers, as well as their aqueous solutions, established that these polymers belong to amphoteric polyfunctional (amide, imide, carboxyl, hydroxyl, sulfomethyl, ether) surface-active polyelectrolytes;

- research results on the effect of MPAA-3 concentration (formation water 100 g/l) on the kinematic viscosity of Kumkol oil. In this case, the kinematic viscosity decreases to 13-14 $mm^2/s$, and the concentration of the composite polymer is C = 0.4%;

- a study was carried out on the laboratory installation UIK-S (2) of rock samples (core) of a 0.4% aqueous solution of MPAA-3, as a result of which the displacement coefficient of Kumkol oil from soil layers was established to be K = 7%;

- determination by DTA method of resistance of composite surfactant polymers to high temperatures (180°C);

-mathematical optimization of the main parameters of the process of obtaining composite surfactant polymers based on hydrolyzed and modified PAA;

- field tests and economic efficiency from the use of the resulting composite polymers, at which the profit will be 25,696,689 tenge per year, profitability is 20%.

**Justification of the novelty and importance of the obtained results:**

- the possibility of obtaining new composite surfactant polymers based on polyacrylamide by hydrolysis with sodium hydroxide with subsequent modification in the presence of formaldehyde, sodium thiosulfate or fatty acids of gossypol resin has been proven and justified, at a temperature of 353-363K, time 4.0-4.5hours, reagent ratio 1:0.8;

- a method has been proposed for producing gel polymers based on synthesized polymers by cross-linking in the presence of initiators potassium persulfate and sodium bisulfite at a temperature of 60-80°C for 1.0 hour to increase the efficiency of oil displacement;

- established that the synthesized composite polymers belong to amphoteric polyfunctional (amide, imide, carboxyl, hydroxyl, sulfomethyl, ether) surfactant polyelectrolytes;

- the effect of MPAA-3 concentration (formation water 100 g/l) on the kinematic viscosity of Kumkol oil is shown, which decreases to 13-14 $mm^2/s$ at a composite polymer concentration of C = 0.4%;

- on the laboratory installation UIK-S (2) it was determined that on rock samples (core) using an aqueous solution of MPAA-3 with a concentration of C=0.4%, the coefficient of displacement of Kumkol oil from the soil formation is K=7%;

- using the DTA method, it was shown that the resistance of composite surfactant polymers to high temperatures remains up to 180°C; increasing the temperature above 200°C leads to destructive decomposition of the polymer.

**Theoretical and practical significance of the work.** The development of technologies for the production of composite surfactant polymers using local raw materials and production waste is of great importance for the oil and gas industry of Kazakhstan. Surface-active wetting of polymer compositions based on fatty acids: gossypol resin, formalin, glycerin, potassium persulfate and sodium bisulfite helps increase oil production from underground formations.

The practical significance of the work lies in establishing the possibility of using composite surfactant polymers to displace residual oil in order to increase the flow rate of producing wells. The effectiveness of using composite surfactant polymers for displacing residual oil evidenced by the results of field tests, which established the possibility of using them in displacing residual oil in order to increase the volume of oil production from underground formations (Field testing report of LLP "Munayshy". №374, 18.05.2021). The results of the work also introduced into the educational process in the discipline "Technology of Organic and Petrochemical Production": №446, 10.06.2021. "Study of the possibility of using water-soluble composite polymers based on PAA in the presence of gossypol resin for oil displacement," №447, 10.06.2021. "Synthesis and study of physicochemical properties of polyelectrolyte surfactants".

Based on the research results, a patent decision for a utility model of the Republic of Kazakhstan №2023/0378.2 dated April 20, 2024 "Method for producing modified polyacrylamide" obtained.

**Compliance of the dissertation with the directions of scientific development or government programs.** The dissertation work carried out at the department of "Technology of inorganic and petrochemical production" at the NJSC "M. Auezov South Kazakhstan University", research laboratory "Petrochemistry and composite polymer materials" within the framework of the state budget research work B-22-03-05: according to topic "Development of methods and technologies for producing highly effective multifunctional gel-forming polyelectrolytes, surfactants, composite polymer materials based on industrial and household waste" and State Fund AR05135236: "Development of a comprehensive colloid-chemical technology for increasing oil production of heat-resistant and salt-resistant nanostructured polycomposites in Kazakhstan".

**The doctoral student's personal contribution to the preparation of each publication:**

19 scientific papers have been published on the topic of the dissertation, including in international scientific publications included in the Scopus database – 1; in journals recommended by the Committee for Quality Assurance in the Field of Science and Higher Education of RK– 4; in collections of international and republican conferences – 13 articles and 1 patent decision received for a utility model of the Republic of Kazakhstan.

1. Article "Polymeric compositions to increase oil recovery" in the journal "Rasayan Journal of Chemistry" http://www.rasayanjournal.com (2023, pp. 876-

883, India). The article explores the conceptualization, in particular the hypothesis, data collection, analysis and interpretation of the processes for obtaining surface-active composite polyelectrolytes, their physicochemical properties and oil displacement efficiency.

2. Article “Obtaining polyelectrolyte sorbents, studying their physical and chemical properties and using them in the process of hydrogen sulfide removal at oil refineries” in the journal “Bulletin of KazNITU” (2019, pp.185-193, Almaty, RK). The article determines the optimal conditions for obtaining polymers and planning the experiment.

3. Article "Investigation of modified polyacrylamide for the displacement of oil" in the journal "Chemical Journal of Kazakhstan" (2023, pp.141-151, Almaty, RK). Discussion and obtaining of experimental data carried out in the article.

4. Article "Polymer composition for the displacement of oil" in the journal "Neft and Gas" (2023, pp.197-206, Almaty, RK). Obtaining and discussing experimental data carried out in the article.

5. Article "Oil-displacing capabilities of colloidal solutions of nonionic surfactants". In the collection of materials of the II-Republican scientific and practical conference "Innovative development and prospects for the development of chemical technology of silicate materials" (2022, pp.289-291, Tashkent, UR). The article provides an overview of literature data.

The full contribution of the doctoral student to the preparation of each publication given in the dissertation.

Dissertation structure and volume. Dissertation work consists of introduction, literature review, main part, including 4 chapters, 41 figures, 16 tables, conclusion, list of used sources includes 200 items.