ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD)
in the educational program 8D05301 - Chemistry

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Synthesis and properties of preformed particle gel (PPG) for optimizing oil well performance

General overview of the work

The dissertation research is devoted to the synthesis and investigation of new composite polyelectrolyte, polyampholyte, and hydrophobically modified preformed particle gels (PPG) based on acrylamide (AAm) with the addition of bentonite, capable of swelling in low-, medium-, and high- salinity formation waters. The obtained samples were studied using various physicochemical methods and tested as flow-diverting agents for profile control of reservoir injectivity during oil production under model conditions.

Relevance of the research topic

Currently, domestic oilfield service companies involved in enhanced oil recovery (EOR) operations widely employ water-soluble and/or water-swelling polymeric systems as agents for conformance control, i.e., for the regulation and redistribution of filtration flows within heterogeneous reservoir formations. These polymers include various chemically modified forms of polyacrylamide that differ in molecular weight, degree of hydrolysis, thermal stability, salinity tolerance, and other performance characteristics under reservoir conditions. Water-soluble natural polysaccharides, such as xanthan, welan, gellan, and other biopolymers, are also used for similar purposes due to their favorable rheological behavior and relative environmental compatibility.

However, these polymeric materials are not produced within the territory of Kazakhstan, which results in a strong technological and economic dependence of oilfield service companies on imported supplies and limits the possibility of adapting formulations to specific local reservoir conditions. In this context, the development of domestic polymeric materials aimed at improving the efficiency of oilfield development and reservoir management represents a highly relevant scientific and practical task. PPGs are considered one of the most promising classes of EOR materials, as they are capable of selectively blocking high-permeability watered-out channels and fractures, thereby redirecting the injected fluid into previously unswept oil-saturated zones and increasing sweep efficiency. The topic of this dissertation corresponds to the priority research areas in the field of high-molecular-weight polymer chemistry and functional polymer materials.

The aim and Objectives of the Study

The aim of the dissertation is to synthesis PPGs based on various polymer systems aimed at reducing the water cut of oil wells.

In accordance with this purpose, the following objectives are addressed:

1. To synthesize polyelectrolyte, polyampholyte, and hydrophobically modified hydrogels based on a nonionic monomer-acrylamide-possessing high swelling capacity, mechanical strength, and thermal stability.
2. To investigate the structure of the synthesized hydrogel particles using IR spectroscopy and scanning electron microscopy, as well as to study the thermal, mechanical, and swelling properties of the PPGs.
3. To investigate the plugging properties of the polymeric materials using core samples of a physical model of a highly permeable oil reservoir.

Object of the Study

The objects of the dissertation research are polyampholytic hydrogels based on sodium 2-acrylamido-2-methyl-1-propanesulfonate (AMPS) and (3-acrylamidopropyl)trimethylammonium chloride (APTAC) in combination with AAm; polyelectrolyte hydrogels based on sodium acrylate (ANa) and AAm; as well as hydrophobically modified hydrogels that combine the hydrophilic properties of AAm (water solubility) with the hydrophobic properties of octadecyl acrylate (lauryl acrylate).

Subject of the Study

The subject of the dissertation research is the synthesis of hydrogels, their swelling capacities, mechanical strength, thermal stability, and the evaluation of the effectiveness of the hydrogels in an oil-core model for enhancing oil recovery.

The author's personal contribution consists of the independent formulation and definition of the dissertation research objectives, conducting an analytical review of the current state of the problem, synthesizing gel materials, performing a set of physicochemical studies, and analyzing the obtained experimental data.

The author took an active part in carrying out the main experimental stage, including work with the oil core model. The analysis and systematization of the experimental results, as well as the formulation of the main conclusions and generalizations reflecting the outcomes of the research, were performed by the author in collaboration with the scientific supervisors.

Theoretical and Methodological Framework of the Study

The dissertation research was carried out on the basis of physicochemical methods of analysis. The synthesis was performed by free-radical copolymerization. The investigation of the hydrogels was conducted using gravimetry, FTIR spectroscopy, thermogravimetry, and scanning electron microscopy. The Young's modulus of the hydrogels was determined by mechanical analysis. The PPG samples were tested using an oil-core model.

The ChemDraw software was used for graphical representation of structural formulas of chemical elements and compounds. The following programs were used for statistical processing of the research results and their graphical representation: Origin and Microsoft Office.

Scientific Novelty

The scientific novelty of this work lies in the first-time synthesis of composite polyelectrolyte, polyampholyte, and hydrophobically modified hydrogel particles capable of controlled swelling in various types of formation waters over a wide temperature range and specifically intended for injection profile modification and conformance control in heterogeneous oil reservoirs. The proposed approach is based on a one-stage synthesis of swellable hydrogel materials that does not require the use of additional crosslinking agents (such as chromium acetate or aluminum citrate) during field application, thereby simplifying the technological scheme and reducing operational complexity.

Moreover, subsequent mechanical grinding of the bulk hydrogel material allows precise and reproducible control of the final particle size and particle size distribution, which represents a significant technological advantage for adapting the material to different reservoir permeability ranges and injection conditions. Considering the pronounced geological diversity of oil fields in Kazakhstan, including the presence of technogenic fractures, naturally fractured reservoirs, and highly heterogeneous permeability profiles, the developed PPGs with tunable and predictable swelling behavior are capable of effectively blocking large fractures (≥1 mm) and high-permeability flow channels.

In addition, the absence of syneresis, which is a critical drawback commonly observed in crosslinked polymer systems based on partially hydrolyzed polyacrylamide and chromium acetate, makes the application of pre-crosslinked composite hydrogels particularly promising for enhanced oil recovery operations, ensuring higher long-term stability and reliability under reservoir conditions.

Key provisions for defense

Provision №1

The use of initial monomer mixtures based on [AAm:NaA = 95:5], [AAm:APTAC:AMPS = 95:2,5:2,5], $[AAm:LA]_{15\%}$, and $[AAm:ODA]_{15\%}$ makes it possible to obtain composite polyelectrolyte, polyampholyte, and hydrophobically modified hydrogels that remain stable in highly saline solutions (150 g/L), exhibit high mechanical strength (up to 500 Pa), and possess thermal stability (up to 200°C).

Provision №2

The chemical nature of the monomers determines the set of functional properties of polymer hydrogels: the swelling degree is maximal for polyelectrolyte hydrogels (29 g/g), whereas it is significantly lower for polyampholyte and hydrophobically modified systems (13-15 g/g); at the same time, polyampholyte hydrogels, in contrast to polyelectrolyte and hydrophobically modified systems, exhibit enhanced stability to changes in temperature (20 - 80 °C), salinity (10 - 150g/L), and pH (2 - 12).

Provision №3

The use of hydrogels based on [AAm_{95}-NaA_5], [AAm_{95}-$APTAC_{2,5}$-$AMPS_{2,5}$], $[AAm\text{-}LA]_{15\%}$ and $[AAm\text{-}ODA]_{15\%}$ as PPG agents reduces water permeability under filtration experiments on sandy packed-bed models by 8000, 5700, 3400, and 1700 times, respectively, confirming their high potential for optimizing oil well performance.

Theoretical Significance of the Research Results

The results obtained in the course of the dissertation research are significant for the development of theoretical and methodological foundations related to the synthesis and investigation of the physicochemical properties of hydrogels. The findings of this research may serve as a basis for formulating new scientific problems and research directions.

Practical Value of the Research Results

As a result of the work, experimental samples of composite-based PPGs incorporating mineral fillers into their structure were obtained. These samples exhibit mechanical and thermal stability and are capable of swelling in highly mineralized formation waters at various temperatures. The hydrogel particles produced can be used to establish industrial-scale production processes and applied in oil fields in Kazakhstan to enhance oil recovery.

Relation of work with research programs

The dissertation was carried out within the framework of the grant funding project of the Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan on the topic “Development of preformed hydrogel particles (PPGs) for enhanced oil recovery”, for 2022 - 2024 (AP13068286). The project supervisor is PhD A. V. Shakhvorostov.

Approbation of the results of the dissertation work

The main statements and results of the dissertation were presented at 6 international and national scientific conferences: International Scientific Conference of Students and Young Scientists “FARABI ÁLEMI,” (Almaty, Kazakhstan, 2023, 2024), Polish-Kazakh Meeting: Relationship Between Chemistry and Biology (Poland, 2023, 2024), 11th Conference Times of Polymers and

Composites (Italy, 2023), XV National Scientific - Practical Conference (with international participation) “Environmental Readings - 2024” (Russia, 2024)

Publication of Research Results

The results of the dissertation research were published in 3 articles in journals with a non-zero impact factor and included in the international information resources Scopus and Web of Science and in 1 article published in scientific journals recommended by the Science and Higher Education Quality Assurance Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan.

Description of the doctoral student's contribution to each publication

Gizatullina N., Yelemessova G., Klivenko A., Shakhvorostov A. Synthesis of Composite Hydrogels for Enhanced Oil Recovery // Macromol. Symp. - 2024 - Vol. 413. - P. 2300258 (3). https://doi.org/10.1002/masy.202300258 - research, methodology;

Yelemessova G., Gussenov I., Ayazbayeva A., Shakhvorostov A., Orazzhanova L., Klivenko A., Kudaibergenov S. Preparation and Characterization of Preformed Polyelectrolyte and Polyampholyte Gel Particles for Plugging of High-Permeability Porous Media // Gels. - 2024. - Vol. 10. https://doi.org/10.3390/gels10090562 research, methodology, validation, visualization, writing – original draft, editing;

Yelemessova G., Gussenov I., Klivenko A., Orazzhanova L., Sabitova A., Shakhvorostov A., Bardadym Y., Aseyev V. Hydrophobically Modified Acrylamide Hydrogel Particles for Conformance Control: Synthesis, Characterization and Enhanced Oil Recovery Performance // Journal of Applied Polymer Science. - 2025. - Vol.0:e57900. - P. 1-16. https://doi.org/10.1002/app.57900 - research, methodology, validation, visualization, writing – original draft, editing;

Yelemessova G., Orazzhanova L., Klivenko A., Nurgaliyev N., Ayazbayeva A., Shakhvorostov V. Synthesis and characterization of preformed particle Gels (PPG) to increase oil recovery // NEWS OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN. - 2023. - V.4. - 457. - P.79–91 https://doi.org/10.32014/2023.2518-1491.194 - research, methodology, validation, visualization, writing - original draft, editing.

Structure and Volume of the Dissertation

The dissertation consists of a table of contents, a list of definitions, symbols and abbreviations, an introduction, three chapters, a conclusion, and a list of references. The total volume of the dissertation is 103 pages of typeset text and includes 17 tables, 51 figures, and 4 formulas. The list of references contains 125 sources.