

Written review by an official reviewer for the dissertation work of Nurbatyr Mukhametgazy on the topic "Synthesis and characterization of acrylamide-based polyampholytes for EOR, drilling of wells and tracer applications", submitted to fulfill the requirements for the Doctor of Philosophy (Ph.D.) degree in the specialty 6D073900-Petrochemistry.

| No. | Criteria | Justification of the official reviewer's position. |
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| 1. | <p>The topic of the dissertation (as of the date of its approval) corresponds to the directions of scientific development and/or government programs</p> <p>Eligible (check one answer option)</p> <p>1.1 Compliance with priority areas of scientific development or government programs:</p> <p>1) The dissertation was completed within the framework of a project or target program financed from the state budget (indicate the name and number of the project or program)</p> <p>2) The dissertation was completed within the framework of another state program (indicate the name of the program)</p> <p>3) <u>The dissertation corresponds to the priority direction of scientific development, approved by the Higher Scientific and Technical Commission under the Government of the Republic of Kazakhstan (indicate direction)</u></p> | <p>The Ph.D. thesis of Nurbatyr Mukhametgazy entitled "Synthesis and characterization of acrylamide-based polyampholytes for EOR, drilling of wells and tracer applications" complies with priority areas of scientific development or government programs.</p> <p>1) The dissertation work was performed in laboratory of engineering profile (LIP) of Kazakh National Research Technical University and Institute of Polymer Materials and Technologies (IPMT) in the framework of several grant projects financed from the budget of the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan.</p> <p>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.</p> <p>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".</p> <p>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".</p> |

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| | | <p>Therefore, the author of the dissertation deserves the degree of Doctor of Philosophy (Ph.D.) in the specialty 6D073900-Petrochemistry. 3).</p> |
| 2. | <p>Importance for science</p> <p>The work does/does not make a significant contribution to science and its importance is/is not well disclosed</p> | <p>The content and research results of the dissertation well disclosed the relevance and importance of the work. This thesis is devoted to developing synthesis optimization was achieved to obtain a novel high molecular weight ternary polyampholyte AAm-co-AMPS-co-APTAC with a composition of 80:10:10 mol.%. Which demonstrates a superior oil displacement capability compared to hydrolyzed polyacrylamide (HPAM) for enhanced oil recovery (EOR), water-based drilling fluids (WBDFs) and as tracer applications in high-saline reservoirs as well as these studies make a significant contribution to the development and practical application of science.</p> |
| 3. | <p>The principle of independence</p> | <p>Analyzing the dissertation, it can be seen that the candidate has conducted comprehensively studied of the subject area and is capable of independently addressing both theoretical and practical tasks outlined in the research work.</p> |
| 4. | <p>The principle of internal unity</p> | <p>The work is mainly aimed at solving fundamental problems. Simultaneously, considering the thorough review of recent year literature provided in the dissertation, along with the research findings achieved by the author, there appears to be great promise in testing the novel TPA as viscosifying agents in enhanced oil recovery (EOR), as theology enhancers and fluid loss additives for water-based drilling fluids (WBDFs), and also as tracer agents in applications within the oil industry.</p> |

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| | <p>4.2 The content of the dissertation reflects the topic of the dissertation:</p> <ol style="list-style-type: none"> 1) Reflects: 2) Partially reflects; 3) Does not reflect | <p>The topic of the dissertation is reflected on the content and gives a complete understanding of the meaning of the dissertation.</p> |
| | <p>4.3. The purpose and objectives correspond to the topic of the dissertation:</p> <ol style="list-style-type: none"> 1) correspond; 2) partially correspond; 3) do not correspond | <p>The goals and objectives set out in the dissertation work are closely related to the research topic and the author effectively shows the achievement of these goals by diligently performing all related tasks.</p> |
| | <p>4.4 All sections and provisions of the dissertation are logically interconnected:</p> <ol style="list-style-type: none"> 1) are fully interconnected; 2) the relationship is partial; 3) there is no relationship | <p>The dissertation demonstrates a highly organized and well-structured format, wherein all chapters are interrelated and systematically present an elaborate account of the research results.</p> |
| | <p>4.5 New solutions (principles, methods) proposed by the author are argued and evaluated in comparison with the known solutions:</p> <ol style="list-style-type: none"> 1) there is a critical analysis; 2) partial analysis; 3) the analysis does not represent one's own opinions, but quotes from other authors | <p>The author presented accurate, logically verified substantiations of the main provisions of the dissertation submitted for defense.</p> |
| <p>5. The principle of scientific novelty</p> | <p>5.1 Are the scientific results and provisions new?</p> <ol style="list-style-type: none"> 1) completely new; 2) partially new (25-75% are new); 3) not new (less than 25% are new) | <p>The results obtained in the dissertation work are completely new.</p> <p>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.</p> <p>Moreover, the salt-tolerant ternary polyampholyte AAm-co-AMPS-co-APTAC was applied for preparation of water-based drilling fluid. The novel amphiphilic terpolymer possessed not only</p> |

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| | | <p>5.2. Are the findings of the thesis new? 1) completely new; 2) partially new (25-75% are new); 3) not new (less than 25% are new)</p> <p>5.3. Technical, technological, economic or management solutions are new and justified: 1) completely new; 2) partially new (25-75% are new); 3) not new (less than 25% are new)</p> | <p>to boost its salt tolerance but also to enhance drilling mud performance (viscosity and filtration properties) under lower temperature geothermal conditions.</p> <p>For the first time, a trace amount of fluorescent monomer – Acrylamide Nile Blue (ANB) was introduced into the composition of AMPS-<i>co</i>-APTAC copolymer. As a result, a novel ternary polyampholyte [AMPS]₁:[APTAC]₁:[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.</p> <p>The conclusions presented by the author are entirely novel as they offer innovative solutions to the emerging challenges in polymer flooding technology for chemical enhanced oil recovery (EOR) and oil well drilling operations in Kazakhstan.</p> <p>The results obtained are mostly fundamental and technologically new. 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 WBDP 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.</p> |
| 6. | Validity of the main conclusions | All main conclusions are based /not based on scientifically sound evidence or are reasonably well substantiated (for qualitative research and areas of training in the arts and humanities) | The obtained data were confirmed using selective, accurate, and modern analysis methods, as well as the scientific methods. To ensure reliability and |

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| 7. | Main provisions submitted for defense | <p>It is necessary to answer the following questions for each provision separately:</p> <p>7.1 Is the position proven? 1) proven; 2) rather proven; 3) rather not proven; 4) not proven</p> <p>7.2 Is it trivial? 1) yes; 2) no</p> <p>7.3 Is it new? 1) yes; 2) no</p> <p>7.4 Application level: 1) narrow; 2) average; 3) wide</p> <p>7.5 Is it proven in the article? 1) yes; 2) no</p> |
| | | <p>reproducibility, all experiments were conducted in several parallels.</p> <p>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.</p> <p>2. The injection of 0.25 % TPA and HPAM solutions, prepared in 200 g.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.</p> <p>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</p> |

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| | | <p>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.</p> <p>4. A novel ternary polyampholyte composition (AMPS-<i>co</i>-APTAC-<i>co</i>-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·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.</p> |
| <p>8. Principle of reliability of sources and information provided</p> | <p>8.1 The choice of methodology is justified or the methodology is described in sufficient detail</p> <p>1) <u>yes</u>; 2) no</p> <p>8.2 The results of the dissertation work were obtained using modern methods of scientific research and techniques for processing and interpreting data using computer technologies:</p> <p>1) <u>yes</u>; 2) no</p> | <p>The obtained data were confirmed using good choice, accurate, and modern analysis methods, as well as scientific methodologies. To ensure reliability and reproducibility, all experiments were conducted in several parallels to provide a detailed description of the research.</p> <p>The results of the dissertation work were obtained using modern methods of scientific research and techniques for comprehensive characterization:</p> <ol style="list-style-type: none"> 1. FTIR spectroscopy 2. ¹H and ¹³C-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 |

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| 9 | Principle of practical value | <p>9.1 The dissertation has theoretical significance: 1) <u>yes</u>; 2) no</p> <p>9.2 The dissertation has practical significance and there is a high probability of applying the results obtained in practice: 1) <u>yes</u>; 2) no</p> | <p>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</p> |
| | | <p>8.3 Theoretical conclusions, models, identified relationships and patterns are proven and confirmed by experimental research (for areas of training in pedagogical sciences, the results are proven on the basis of a pedagogical experiment): 1) <u>yes</u>; 2) no</p> | <p>The principle of consistency consists of several main points, among which it is worth noting that the results achieved in the research work are undoubtedly obtained by using modern advanced computer technologies, instrumentation, various research methods, and diagrammatic processing of data. The dissertation work was carried out at the LIP of Satbayev University, the IPMT, and with technical support from Nazarbayev University (Astana), as well as within the framework of several grant projects funded by the Ministry of Science and Higher Education of the Republic of Kazakhstan. The results of the research are reflected in 12 publications.</p> |
| | | <p>8.4 Important statements <u>are supported</u>/partially confirmed/unsupported by references to current and reliable scientific literature</p> | <p>The results of the work are consistent with the published works. Exact references to related sources are provided.</p> |
| | | <p>8.5 The literature sources used are/are not sufficient for the literature review</p> | <p>The literature sources used are sufficient for the literature review.</p> |
| | | <p>9.1 The dissertation has theoretical significance: 1) <u>yes</u>; 2) no</p> | <p>The dissertation has high theoretical value.</p> |
| | | <p>9.2 The dissertation has practical significance and there is a high probability of applying the results obtained in practice: 1) <u>yes</u>; 2) no</p> | <p>The dissertation can find application for solving problems in enhanced oil recovery (EOR) 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 inter</p> |

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| | <p>9.2 The dissertation has practical significance and there is a high probability of applying the results obtained in practice:</p> <p>1) <u>yes</u>; 2) no</p> | <p>The dissertation can find application for solving problems in enhanced oil recovery (EOR) 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 inter well 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.</p> <p>Suggestions are new</p> |
| 10. | <p>9.3 Are the practice suggestions new?</p> <p>1) <u>completely new</u>; 2) partially new (25-75% are new); 3) not new (less than 25% are new)</p> <p>Quality of academic writing:</p> <p>1) <u>high</u>; 2) average; 3) below average; 4) low.</p> | <p>The quality of academic writing is high: the work is written in precise scientific and technical language, and the research process is logically presented.</p> |

Conclusion

The dissertation work demonstrates scientific novelty, with results, discussion, and conclusions that meet the criteria set by the Committee of Higher and Postgraduate Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan, showcasing its relevance and scientific merit. Mr. Nurbayr Mukhamegazy has become a specialist in his field of research, and his qualifications can be highly valuable for advancing new directions in the field of science in our country. I am very pleased with his work and truly recommend him to defend his Ph.D. thesis, meeting the requirements for the Doctor of Philosophy (Ph.D.) degree in the specialty 6D073900-Petrochemistry.

Reviewer:

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Minavar Shaimardan