**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 | Eligible (check one answer option) | Justification of the official reviewer's position. |
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| 1. | The topic of the dissertation (as of the date of its approval) corresponds to the directions of scientific development and/or government programs | 1.1 Compliance with priority areas of scientific development or government programs: | |
| | | 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)<br>2) The dissertation was completed within the framework of another state program (indicate the name of the program)<br>3) 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) | A thesis was carried out within the framework of state grant funding and was financed by the Ministry of Education and Science of the Republic of Kazakhstan for the following projects:<br>1) AP08855552 «Synthesis and Study of Thermo- and Salt-Sensitive Polyampholyte Nano- and Microgels», 2020-2022;<br>2) AP09260574 «Development of New Thermal and Salt-Resistant Amphoteric Terpolymers for Enhanced Oil Recovery», 2021-2023;<br>3) AP14972771 «Synthesis and Study of New Modified Complexes Based on Synthetic and Natural Polyampholytes for Water-Based Drilling Fluids», 2022-2024, « ZhasGalym» project. |
| 2. | Importance for science | The work does/does not make a significant contribution to science and its importance is/is not well disclosed | The work makes a significant contribution to science, and its importance is well disclosed. Acrylamide-based polyampholytes were synthesized in this work. Subsequently, they were characterized by a set of methods and tested as additives to oil production fluids to enhance oil recovery, to drilling fluids and also to indicator fluids, which makes a significant contribution to science and is |

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| | | | important for practical application. |
| 3. | The principle of independence | Level of independence:<br>1) **High**;<br>2) Average;<br>3) Low;<br>4) No independence | The level of independence of the author of the thesis is high. It consists of analyzing literary studies, performing the experimental part of the work, performing physicochemical methods of analysis, summarizing and interpreting the obtained experimental data and conclusions. |
| 4. | The principle of internal unity | 4.1 Justification of the relevance of the dissertation:<br>1) **Justified**;<br>2) Partially justified;<br>3) Not justified. | Research to enhance oil recovery (EOR) is a relevant modern direction, which is fully justified in the work, since the property of amphoteric polyelectrolytes to swell and be an effective viscosity enhancer in reservoir with high salinity and high temperatures plays a critical role. Kazakhstan needs salt-resistant polymers capable of thickening brines. The results of the work have both fundamental and applied significance. |
| | | 4.2 The content of the dissertation reflects the topic of the dissertation:<br>1) **Reflects**;<br>2) Partially reflects;<br>3) Does not reflect | The thesis is devoted to the development of polyampholytes based on acrylamides and the study of their properties in oil production, namely in enhancing oil recovery, as additives to fluids used in drilling, as well as to indicator solutions, which fully reflects the topic of the dissertation gives a complete understanding of the meaning of thesis. |
| | | 4.3. The purpose and objectives correspond to the topic of the dissertation:<br>1) **correspond**;<br>2) partially correspond;<br>3) do not correspond | A thesis is distinguished by the integrity and logic of setting goals and objectives, as well as ways of their implementation. The purpose and objectives are closely related to the research topic, and the author effectively shows the achievement of these goals by diligently performing all related tasks. The set goals were achieved and all objectives were completed in full. The results of fundamental |

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| | | | research on the use of polyampholytes were applied to solve current applied problems. |
| | | 4.4 All sections and provisions of the dissertation are logically interconnected:<br>1) **completely interconnected**;<br>2) the relationship is partial;<br>3) there is no relationship | The sections and provisions of the dissertation work are logically interconnected. The dissertation exhibits a highly organized and well-structured format, wherein all chapters are interrelated and systematically present an elaborate account of the research results. The results are characterized by the internal unity of purpose, results and conclusions obtained in the process of performing the work. |
| | | 4.5 New solutions (principles, methods) proposed by the author are reasoned and evaluated in comparison with known solutions:<br>1) **there is a critical analysis**;<br>2) partial analysis;<br>3) the analysis does not represent one's own opinions, but quotes from other authors | The new solutions proposed by the author are argued and evaluated in comparison with known solutions. They are justified by the positive results of the performed research. The high scientific level of the completed research is confirmed by scientific publications both in Kazakh journals and in foreign journal, approbation of the results at international conferences and symposiums. The author presented logically verified substantiations of the main provisions of the thesis. |
| 5. | The principle of scientific novelty | 5.1 Are the scientific results and provisions new?<br>1) **completely new**;<br>2) partially new (25-75% are new);<br>3) not new (less than 25% are new) | The degree of novelty of each scientific result formulated in the thesis is that new high-molecular-weight polyampholytes were developed, which were synthesized for the first time and had excellent oil-displacing properties with increased salt resistance, viscosity and filtration properties, and also made it possible to minimize or prevent adsorption. |
| | | 5.2 Are the findings of the thesis new?<br>1) **completely new**; | The conclusions of the dissertation are completely new, which is confirmed by the |

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| | | 2) partially new (25-75% are new);<br>3) not new (less than 25% are new) | publication of the main conclusions of the work in the article "Comparative study of oil recovery using amphoteric terpolimer and hydrolyzed polyacrylamide" in the journal Polymers (Q1, percentile 77%). |
| | | 5.3 Technical, technological, economic or management solutions are new and justified:<br>1) **completely new**;<br>2) partially new (25-75% are new);<br>3) not new (less than 25% are new) | Technical, technological and economic solutions are completely new. They are based on a large amount of experimental material. The main results represent new material, which is conclusively confirmed by the results of a detailed analysis of experimental data aimed at solving current problems. |
| 6. | Validity of the main conclusions | All main conclusions are/are not based on scientifically sound evidence or are reasonably well substantiated (for qualitative research and areas of training in the arts and humanities) | All main conclusions are based on scientifically sound evidence. The degree of validity of the main conclusions of the thesis is based on a large amount of experimental material performed using modern physicochemical methods for studying synthesized polyampholytes, as well as a detailed study of their properties. The analysis of the products is beyond doubt. The results of the work were repeatedly presented at international scientific conferences of near and far abroad. Based on the results of the research, 12 scientific works were published. All this indicates the validity and reliability of the results obtained in the thesis. |
| 7. | Main provisions submitted for defense | It is necessary to answer the following questions for each provision separately:<br>*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-* | This position has been proven using physicochemical methods. The dynamic viscosity of solutions of amphoteric terpolymers steadily increases from 7.45 mPa·s to 14.25 mPa·s with increasing salinity from 200 to 300 g·l-1 (Fig. 3.17). Terpolymer |

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| | | *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.*<br>7.1 Is the position proven?<br>1) **proven**;<br>2) rather proven;<br>3) rather not proven;<br>4) notproven<br>7.2 Is it trivial?<br>1) yes;<br>2) **no**<br>7.3 Is it new?<br>1) **yes**;<br>2) no<br>7.4 Application level:<br>1) narrow;<br>2) **average**;<br>3) wide.<br>7.5 Is it proven in the article?<br>1) **yes**;<br>2) no | solutions retain relatively high viscosity in the salinity range from 200 to 300 g·l-1 (Fig. 3.18). The results are reflected in the article "Comparative study of oil recovery using amphoteric terpolimer and hydrolyzed polyacrylamide" in the journal Polymers (Q1, percentile 77%). |
| | | *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.*<br>7.1 Is the position proven?<br>1) **proven**;<br>2) rather proven;<br>3) rather not proven;<br>4) notproven<br>7.2 Is it trivial?<br>1) yes;<br>2) **no** | The results are proven and presented in sections 4.4.2 and 4.4.3. The Figure 4.18 shows the oil displacement coefficients obtained by introducing the TPA and HPAM polymers into the model. As can be seen in the figure, oil displacement coefficients obtained as a result of injection of 0.25 wt % TPA and HPAM solutions through the sand-packed models were 28% and 18%, respectively. Therefore, the TPA has a higher oil displacement capacity than HPAM in high salinity conditions. The results are reflected in foreign and Kazakh articles. |

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| | | 7.3 Is it new?<br>1) **yes**;<br>2) no<br>7.4 Application level:<br>1) narrow;<br>2) **average**;<br>3) wide<br>7.5 Is it proven in the article?<br>1) **yes**;<br>2) no<br>*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.*<br>7.1 Is the position proven?<br>1) **proven**;<br>2) rather proven;<br>3) rather not proven;<br>4) notproven<br>7.2 Is it trivial?<br>1) yes;<br>2) **no**<br>7.3 Is it new?<br>1) **yes**;<br>2) no<br>7.4 Application level:<br>1) **narrow**;<br>2) average; | The results confirming this provision were presented and discussed in detail in section 5.4.1 in Table 5.3 of the thesis and in SEM images in Figure 5.10. The results are reflected in foreign and Kazakh articles. |

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| | | 3) wide<br>7.5 Is it proven in the article?<br>1) **yes;**<br>2) no<br>*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·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.*<br>7.1 Is the position proven?<br>1) **proven**;<br>2) rather proven;<br>3) rather not proven;<br>4) not proven<br>7.2 Is it trivial?<br>1) yes;<br>2) **no**<br>7.3 Is it new?<br>1) **yes**;<br>2) no<br>7.4 Application level:<br>1) narrow;<br>2) **average**;<br>3) wide<br>7.5 Is it proven in the article?<br>1) **yes**;<br>2) no | A new ternary polyampholyte was synthesized and characterized as an oilfield tracer. Globular and nanometer-sized macromolecules in aqueous and aqueous-salt solutions have proven effective in minimizing adsorption to the rock, resulting in a recovery rate of 90% when injecting 0.1 wt% aqueous polyampholyte solution (Chapter 6). The results are reflected in foreign and Kazakh articles. |
| 8. | Principle of reliability Reliability of sources and information provided | 8.1 The choice of methodology is justified or the methodology is described in sufficient detail<br>1) **yes**;<br>2) no | The methodology of the work is described in sufficient detail in the experimental section. It includes a description of the used chemicals, sand pack models, brines, crude oils from various fields, and bentonite clay. Calculations for measuring the permeability and porosity of sand pack, an experimental |

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| | | | setup used in the sand-pack flooding and other techniques are presented. All experiments were carried out until constant values, which is necessary to ensure the validity, reliability and reproducibility of the results. |
| | | 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:<br>1) **yes**;<br>2) no | Physico-chemical analysis techniques are also described: FTIR spectroscopy, NMR spectroscopy, UV-Vis and fluorescence spectroscopy, dynamic light scattering and zeta-potential measurement, gel-permeable chromatography, differential scanning calorimetry and thermogravimetric analysis, scanning electron microscopy and transmission electron microscopy, chemical and elemental analyzes, rheological study etc. |
| | | 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):<br>1) **yes**;<br>2) no | The main results of research on the synthesis of polyampholytes and their use in oil production are a contribution to fundamental and applied developments on this topic. The high scientific level of the completed research is confirmed by scientific publications both in domestic and foreign journals, as well as by approbation of the results at international conferences and symposia. |
| | | 8.4 Important statements are confirmed/partially confirmed/unsupported by references to current and reliable scientific literature | Important statements are confirmed by references to modern and reliable domestic and foreign scientific literature. |
| | | 8.5 The literature sources used are/are not sufficient for the literature review | The list of references contains 206 sources, which is sufficient for a literature review. |
| 9 | Principle of practical value | 9.1 The dissertation has theoretical significance:<br>1) **yes**;<br>2) no | This work is a scientific research that investigates theoretical issues, the solution of which will make it possible to apply the acquired knowledge in practice. The use of modern methods of analysis makes it possible |

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| | | | to explain the identified theoretical conclusions at a higher level, to determine the patterns on the basis of which theoretical positions that contribute to fundamental science are formulated. |
| | | 9.2 The dissertation has practical significance and there is a high probability of applying the results obtained in practice:<br>1) **yes**;<br>2) no | This thesis is devoted to the synthesis and characterization of specially designed polyampholytic terpolymers with antipolyelectrolyte action, which are capable of increasing the viscosity of the formation waters. Therefore, the practical importance of the work is beyond doubt. |
| | | 9.3 Are the practice suggestions new?<br>1) **completely new**;<br>2) partially new (25-75% are new);<br>3) not new (less than 25% are new) | TPA is becoming a new alternative to HPAM for enhanced oil recovery applications in high salinity conditions. Triple polyampholytes significantly improve the rheological properties of drilling fluids, indicating their potential as a fluid loss additive for salt-tolerant water-based drilling fluids. Due to these favorable properties, they are considered a suitable choice for drilling fluid applications. The novel ternary polyampholyte may be useful as a suitable polymer tracer for oil well monitoring. |
| 10. | Quality of writing and design | Quality of academic writing:<br>1) high;<br>2) **average**;<br>3) below average;<br>4) low. | The quality of academic writing is quite satisfactory. |

**Conclusion:**

There are several comments and suggestions regarding the presented work:

1 A literature review carried out at a good scientific level presupposes the presence of conclusions and the formulation of tasks for the implementation of future research.

2 It remains unclear from the results of the experiment which part of the experiment was done in Kazakhstan and which part in Finland.

3 Why is a Finnish scientific consultant featured in only one of the twelve publications?
4 In my opinion, there is no need to write in the Annotation that the author deserves to be awarded the degree of Doctor of Philosophy (PhD). This is usually suggested by reviewers and members of the Dissertation Committee.
5 The work does not provide data on measurement accuracy.
6 In the Russian version of the Abstract there are no provisions put forward for defense.
7 There are some inaccuracies and typos in the work, for example, instead of a PhD thesis, a candidate dissertation is mentioned, etc.

However, these comments are not of a fundamental nature and do not affect the main provisions, conclusions and scientific results of the work.

Official reviewer's decision:
Award the degree of Doctor of Philosophy (PhD) in specialty 6D073900 – Petrochemistry.

**Reviewer:**
**Doctor of Chemical Sciences**
**Professor** _____ **Tungatarova S.A.**