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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Anastasia Ivanova

PhD Program: Petroleum Engineering

Title of Thesis: Dynamic modelling and experimental evaluation of nanoparticles application in surfactant enhanced oil recovery

Supervisor: Associate Professor Alexey Cheremisin

Name of the Reviewer: A.M. Vishnyakov

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:**  **Date: 09 Nov 2020**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

OFIICIAL REVIEW on dissertation of ANASTASIA IVANOVA

"DYNAMIC MODELING AND EXPERIMENTAL EVALUATION OF NANOPARTICLES APPLICATION IN SURFACTANT ENHANCED OIL RECOVERY"

submitted in pursuit of PhD degree in Petroleum Engineering

Scientific soundness of the topic: I consider the research devoted to improving the oil recovery from carbonate reservoirs using surface active compounds (surfactants) and nanoparticles to be highly relevant. It is in the general direction of the research endeavors in enhanced oil recovery with chemical additives, but at the same time it poses new challenges.

Thesis content: After a general review, the author describes his research on the sorption of oil components on calcite and the microscopic wettability of the surface. The next chapter describes methods and results of surface tension measurements in the oil surrogate system-an aqueous salt solution in the presence of surfactants and silica nanoparticles. The final sections are devoted to molecular modeling of the interface in the presence of cationic and anionic surfactants by molecular dynamics using atomistic models.

The validity of scientific statements, conclusions and recommendations formulated in the dissertation: All statements in the dissertation are based on high-quality measurements, they are justified using correct modeling methods.

Reliability and novelty of the research, the results obtained, conclusions and recommendations formulated in the dissertation: The results obtained in the dissertation are new and reliable, and are of undoubted scientific interest. They do not contradict the considered reliable literature results on the adsorption of surfactants on mineral surfaces and the mechanical properties of surfactant and nanoparticle composites and are reasonably consistent with existing thermodynamic and kinetic theoretical concepts.

Significance of the results obtained by the author for science and practice: The results of the dissertation work make a significant contribution to the fundamental understanding of the relationship between the intermolecular structures of phase sections between oil, salt solution and carbonate minerals

Specific recommendations for using the results and conclusions of the dissertation: The research is methodically important and can be used to develop theoretical approaches to predicting the behavior of surfactants in oil production, and to characterize macroporous heterogeneous samples by sorption of surfactants. The fundamental thermodynamic conclusions of the second part should be applied in the synthesis of new composite materials.

Content of the dissertation, its completion: The dissertation is a complete, consistent research on a given topic. The strengths of the work include a large amount of interesting experimental data, most of which are not intuitively obvious. Studies of the micro-wettability of carbonates after washing out with kerosene and toluene are very sound and useful. Instead of the integral characteristics used by practitioners (such as the wettability indices of the rock as a whole), the author gets a microscopic

picture of areas that are completely cleaned out (after washing become hydrophilic) and hydrophobic areas covered with an organic film that remain hydrophobic. Film thicknesses and even their elemental composition were measured. It is not very clear why such an emphasis is placed on chemisorption of the organic matter (and how much it is chemisorption is also not very clear). The thickness of the films remaining after treatment with not only kerosene, but also toluene, is quite macroscopic, the elemental composition is homogeneous (according to the author). In this case, should chemisorption (if any) of the surface layer of molecules have such a large influence? The composition is constant with a significant proportion of heteroelements (O, S). Should we assume that all this film consists of asphaltin? Although asphaltenes are "soluble in toluene, but insoluble in heptane", in reality even the solution of asphaltenes in toluene is colloidal, not molecular (although there is evidence of a linear dependence of the surface tension at the toluene-water interface on the concentration of asphaltenes, which suggests a molecular solution). Therefore, it is not possible to dissolve a well-adsorbed, dense film of asphaltin with toluene. Partial coating of the carbonate surface after washing with toluene can be explained by the colloidal nature of the solution from which the film was obtained.

On the adsorption of surfactants and the effect on surface tension and interesting dependence of surface tension against concentrations of surfactant, salt and nanoparticles, including an increase in tension with increasing temperature and non-monotonic. A detailed study of the mutual effect on surface tension is new and looks good.

The literature review is detailed, and what is very good, has summary tables. On the other hand, from a dissertation (not a journal paper) one would expect a more critical analysis. Even Table 1 does not contain information the concentrations considered and the modes (in terms of sorption phenomena) they correspond to, at least qualitatively. It was worth starting with the sorption isotherms of typical surfactants on the materials of interest to the author and explain in what concentration modes the author intends to work, which is and is not of practical value. Many arguments imply rather low concentrations (much lower than the CMC in an equilibrium solution), and the drawings imply a large (comparable to a monolayer) sorption. The thesis itself lacks equilibrium sorption isotherms on silica and calcite. Plus, often the results are concerned with the net surfactant concentration rather than with the concentrations in equilibrium aqueous solutions.

Molecular dynamics modeling has proved to be quite useful in explaining experimental phenomena, despite the limitations of the methods (the limited size of the system and the modeling time do not allow us to achieve much using atomistic models and straightforward MD calculation techniques). The structure of the surface layer depending on the charge sign and the effect of hydroxyls in hydrophilic surfactant heads are well illustrated by the experimental data. The shortcomings in this parts of the thesis are technical for the most part: for example, the radial distribution functions seem to be three-dimensional. They mainly reflect the difference between the two – dimensional character of the surface and the three-dimensional character of the entire system (they do not decay to 1). Two-dimensional functions (in the lateral direction) are usually applied to illustrate the surface structure. The author also claims to have determined the Gibbs separating surface, although this is possible either from the mechanical characteristics (the pressure tensor) or by knowing the chemical potentials of the components, and these considerations do not always give the same answer, and the author does not perform these calculations.

In GENERAL, A. Ivanova's dissertation for the PhD degree in petroleum engineering is a qualification work, which contains a solution to the problem of linking molecular interactions with macroscopic thermodynamics and deformation-strength properties on practically important systems, which is of undoubted scientific significance for Petroleum Engineering. I believe that the thesis "DYNAMIC MODELING AND EXPERIMENTAL EVALUATION OF NANOPARTICLES APPLICATION IN SURFACTANT ENHANCED OIL RECOVERY" meets all the requirements of the Regulations on awarding academic degrees, and its author A. Ivanova deserves to be awarded PhD Engr. Degree.

A.M. Vishnyakov

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Provisional Recommendation

X *I recommend that the candidate should defend the thesis by means of a formal thesis defense*

☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*

☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*