Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Alexandra Scerbacova

PhD Program: Petroleum Engineering

Title of Thesis: Investigation of Alkyl Ether Carboxylate Surfactants Performance in Carbonate Reservoirs

Supervisors:
Professor Alexey Cheremisin, Skoltech
Associate Professor Ahmed Barifcani, Curtin University
Co-supervisor:
Associate Professor Chi Phan, Curtin University

Name of the Reviewer: Dr. Mikhail Varfolomeev, Kazan Federal University

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 17-11-2023**

Reviewer's Report
About 60% of oil world reserves belong to the carbonate layers. However, production of hydrocarbons from this kind of resources has some difficulties. First, carbonate reservoirs are characterized with multi-scale heterogeneity that results in a complex porosity-permeability relationship and poor pore connectivity. Second is rock surface hydrophobicity. Consequently, spontaneous water imbibition is restricted and gives a low recovery rate. As a result, residual oil saturation is very high after water flooding. Therefore, the average oil recovery factor value does not exceed 35% for carbonate reservoirs after primary and secondary recovery methods. All these difficulties fully confirm the relevance of the choice of carbonate deposits as an object of research in Scerbacova's dissertation. Application of EOR methods can help to overcome mentioned above problems and improve production. According to the review of Alexandra Scerbacova, among them surfactant flooding can be one of the most perspective, because surfactants are able to decrease the residual oil saturation on the pore level. However, surfactant flooding has significant challenges in implementation in case of carbonate reservoirs due to high temperature, high brine salinity and adsorption of anionic surfactants onto the rock. Therefore, the main goal of Scerbacova's dissertation was the study of surfactants based on alkyl ether carboxylates, including their interaction at the oil-water and water-rock interfaces, their adsorption, displacement ability and assessment of the effectiveness of use for EOR. This goal has theoretical and practical significance and corresponds to world-class tasks in this field of research.

Thesis contains seven chapters. Chapter 1 presents a detailed literature review about chemical flooding in carbonate reservoirs with a focus on the adsorption of surfactants and their phase behavior. It was concluded that anionic-nonionic surfactants based on alkyl ether carboxylates could be the most appropriate reagents for these conditions. However, specific components should be added in the surfactant composition to make it more stable and to decrease adsorption. In Chapter 2 author studied stability and interfacial behavior of AEC and correlated obtained results with their structure. It was found that AEC with higher amount of EO groups are more stable at high temperature and salinity. Also, interesting dependence was observed for IFT values. In contrast to the non-ionic species like ethoxylated alcohols Scerbakova found that the IFT of studied AEC in aqueous solutions at 25 and 70 °C decreased with the increase of EO groups in molecule for deionized water. However, addition of sodium chloride and Mg2+ and Ca2+ significantly reduced IFT, especially in case of C12E7A. In some cases it is achieved ultra-low values (10-2 mN/m).

In Chapter 3 Scerbacova has presented results of molecular dynamics simulations of AECs on the boundary water-decane at 25°C. It was found from calculations, that EO segment length strongly influences the adsorbed monolayer properties, but only for molecules with less than 8 EO groups. For AEC with 8-16 EO groups this effect disappeared. At the same time, alkyl chain length has almost no influence on the monolayer properties. Chapter 4 contains results of rock-fluid interactions study of AEC surfactants, including wettability, zeta potential and static adsorption measurements. It was found that the degree of ethoxylation has a strong effect on the wetting properties of AECs. Surfactant with a shorter EO chain has a better ability to wet the carbonate rock. At the same time the adsorption of AEC with a longer EO fragment was higher due to hydrogen bond formation between the ethoxy chain and OH- or COO- ions of the rock surface. It should be mentioned that author used interesting approach for the valuation of the mechanism of wettability alteration using Rock-Eval analysis and zeta potential measurements. It is a strong and innovative side of the presented thesis. Chapter 5 presented results of a coreflooding test with the most perspective AEC surfactant using X-ray device for saturation control. It was shown that application of surfactant flooding gives additional recovery of 22 wt.%, which confirms perspectives of this technology. However, there is one question to this part of the work. Why after imbibition of core in surfactant solution on displacement stage (4) author continues to inject surfactant solution on stages (5) and (6) and did not shift on water flooding again. In Chapter 6 author implemented several additives to decrease the adsorption of surfactants in harsh reservoir conditions. Good results were achieved in case of application of polyacrylate modified with protein for the first time. It is important result for the further industrial application of AEC. Chapter 7 summarizes the results obtained in the present work.

In general Alexandra Scerbacova carried our excellent and comprehensive study of surfactant flooding for carbonate reservoirs. Obtained results will be useful for different research groups working in this area. Also, this thesis is an important contribution for further successful industrial application of surfactant flooding in harsh conditions.

Some of the experimental procedures proposed by the author will help to get deeper insight in the mechanism of surfactant behavior at fluid-fluid and fluid-rock interface.

Main results of the thesis were published in 4 papers in highly ranked journals and several conference papers. This fact confirms that obtained data and “structure-property” relationships are in demand and correspond to the world level of research in this field.

Author showed strong competencies and knowledge in petroleum engineering, phase behavior, colloid

and computational chemistry.

There are some small mistakes in the text of the thesis. For example in the abstract author wrote that "The common abbreviation for AEC surfactants is CxEyA (alternatively, CnEmA, CxEyC, CxEOyC, or AxECy-Na), where x denotes the number of ethylene oxide units, and y is the number of carbon atoms in the alkyl chain.", but the notes for x and y should be opposite. However, they are not significant.

Summarizing, I consider this PhD thesis worth the degree. The author has proved herself to be a highly qualified specialist who can conduct excellent and valuable research work independently with the possibility of obtaining important scientific results. She deserves to get PhD degree in Petroleum Engineering.

Provisional Recommendation

☒ *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*