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Thesis Changes Log

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PhD Program: Petroleum Engineering

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

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The thesis document includes the following changes in answer to the external review process.

I have modified my PhD thesis accordingly to the comments given by Ajay Mandal as follows:

1) **The research goal part in introduction chapter has been modified by adding the summary of the lack of studies in the relevant field and innovation ideas. The following text has been included (P.38):**

   "As shown in Chapter 1, it is important to study the rock/brine/oil chemical interactions as it gives insight into how to optimally modify wettability towards mixed or water – wet using surfactant-based solutions, which in turn would increase the oil recovery factor from carbonate reservoirs. However, due to complexities associated with existing laboratory methods, which are typically based on macroscale (mm) observations, there is a serious lack of information about microscale wettability characterization of pores that describes the fluid-rock interactions.
   Furthermore, although many studies have been published regarding the nanoparticles' influence on surfactant properties, there is still a lack of understanding of their interactions' mechanisms. A systematic and comparative study of interactions between nanoparticles and surfactant molecules under different temperatures and various salinity conditions is also missing in this field.
   Moreover, due to complexities associated with the experimental procedures and limitations of experimental equipment, it is challenging to investigate the effect of ions at the atomic scale in surfactant systems and to capture their precise molecular arrangements at the interface.
   Importantly, there are no MD simulation studies developing nanoparticles and surfactant molecules interaction models at the interfaces so far. The lack of this information can stem from the absence of well-tested hydrocarbon–water force fields and complexities associated with nanoparticles parametrization."

2) **As it was suggested by the reviewer, the discussion part about zeta potential of carbonates and the reasons of oil wetness of carbonates has been added in P.14-15:**

   "It should be pointed out that the wetting properties of carbonates can be described by means of the zeta potential of the mineral surface. The zeta potential influences the electrostatic forces, which act between the polar organic groups in the oil and the surface, in accordance with the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. Indeed, the zeta potential of carbonate surface depends on the adsorption of ions, such as Ca2+, CO32- and Mg2+ in the Stern layer. In typical formation brines, the concentration of Ca2+ and Mg2+ is high, resulting in the positive zeta potential of the carbonate surface. Reduction of Ca2+ and Mg2+ concentration, for instance, by bulk dilution, leads to negative zeta potential. Therefore, in the initial state, the zeta potential of carbonate surface is positive, resulting in the facilitation of adsorption of carboxylic acids or polar organic components from oil. As a result, the initial wettability of carbonate reservoir rocks is generally oil-wet or mixed-wet..”

Additional information regarding why carbonate reservoir rocks are mostly oil wet can be found in P.13-14.

As it was suggested, the information regarding previous studies has been also added in the P.17:

“For instance, the authors[150] carried out the micro-wettability (µm) measurements using ESEM with the middle Bakken samples and inferred that these results could be used for more accurate estimation of multi-phase flow parameters (e.g. relative permeability, capillary pressure), which in turn would improve primary and secondary oil recovery processes.”

Additional information regarding using SEM and EDX techniques can be found in P.17.

3) **As it is shown in Chapter 1, anionic surfactants have been widely studied in carbonate reservoirs as wettability modifiers towards more water-wet condition (P.25, T.1). Therefore, in this work the anionic surfactant was also tested in order to compare the data with the data for cationic surfactant. Moreover, the adsorption of anionic surfactant onto carbonate rocks could be decreased by addition of nanoparticles, which serve as sacrificial agents. However, the adsorption was not an objective of this study, we plan to do in the future work. However, to meet the reviewer concern, the information regarding HLB values is added in P.62:**

“The hydrophilic-lipophilic balance (HLB) of SOS surfactant is 40, which corresponds to a solubilizing agent for oil-in-water emulsions. Owing to the lack of information available for cationic hydrophilic groups, it is challenging to calculate the HLB value for EHAC surfactant. However, for typical cationic surfactant CTAB, the HLB value is 21.8, which also represents the solubilizing agent for oil-in-water emulsions.”

Figure 23 illustrates the IFT data for two surfactants – EHAC (top) and SOS (bottom). Figure 24 represents the data for SOS surfactant with nanoparticles inclusion. As it can be seen from Figures 23 and 24, the IFT values with nanoparticles are less than for only SOS solutions at particular nanoparticles and SOS concentrations. The explanation of this phenomenon is given in P.68-70. However to meet the reviewer concern and avoid misunderstanding the description of Figure 23 has been modified as follows:

“Figure 23. Interfacial tension of n-decane against aqueous surfactant solutions – EHAC (top) and SOS (bottom) as a function of surfactant concentration (at 25 (black squares) and 65 (black circles) °C).”

As it was suggested by the reviewer the explanation has been added in P.74:

“This phenomenon can be explained by taking into account the same negative charge of nanoparticles and surfactant molecules that prevent their interactions.”

4) **As it was suggested by the reviewer, the following information has been added (P.124):**

“It should be pointed out that this study aids in the prediction of interfacial properties of the mixture of surfactants and nanoparticles using the MD tool, which in turn can help in predicting the overall performance of nanoparticles augmented surfactant solutions’ performance as an injected fluid.”

In this work, the main objective was to study the nanoparticles influence at the surfactant/oil interface. The results represent the innovative data obtained by MD approach. However, the settling issue of nanoparticles has not been studied with MD, however it was discussed in chapter 3 P.68 and 75 by means of experimental results.

Heterogeneity in the reservoir system is very challenging to be handled with MD. So far, in the existed literature relatively simple models of reservoirs, e.g. either calcite or silica, have been studied. The one of the main reason is the lack of computational resources. However, our future research include studying the more advanced systems, including adsorption of nanoparticles on calcite via MD.

5) **The text has also been revised carefully to check for all misprints, grammar and punctuation mistakes.**