Adsorption of Anionic, Cationic and Nonionic Surfactants on Carbonate Rock in Presence of ZrO₂ Nanoparticles

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Abstract

The adsorption of surfactants at the solid–water interface is important for the control of wetting, lubrication, detergency and in mineral flotation. We have studied the adsorptions of different types of surfactants, cationic (Dodecyl trimethylammonium bromide, DTAB), anionic (sodium dodecyl sulfate, SDS) and non-anionic (lauryl alcohol-7 mole ethoxylate, LA7) on carbonate rock in presence of zirconium oxide spherical nanoparticles (17-19nm). ZrO₂ nanoparticles with tetrahedral structure have significant effect on adsorption of surfactants on the carbonate rock. We have used the measured conductivities to determine the rate of adsorption of surfactants at rock-water interfaces. The conductivity of DTAB in aqueous solutions containing calcite powder decreases more than the other surfactants in contact with ZrO₂ nanoparticles. We have also investigated the adsorption of surfactants at the air-water interface. The presence of nanoparticles, as demonstrated by our experiments, enhances the surface activity and surface adsorption of the surfactants through electrostatic forces or formation of nanostructures. Dynamic light structuring data shows similar aggregation number of nanoparticles in presence of nanoparticles.

Keywords: carbonate rock; conductivity; surfactant adsorption; zirconium oxide nanoparticles; interfacial tension; nanofluids; surface tension; homogeneous nanosphere ZrO₂

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1. Introduction

Adsorption of surfactants from aqueous solutions in porous media is very important in enhanced oil recovery (EOR) from oil reservoirs. Surfactant loss due to adsorption on the reservoir rocks impairs the effectiveness of the chemical solution injected to reduce the oil–water interfacial tension (IFT) and makes the process economically unfeasible [1]. Surfactant adsorption to solid-liquid interfaces occurs by transferring surfactant molecules from bulk solution phase to the solid-liquid interface. This phenomenon happens if the interface is energetically favored by the surfactant in comparison to the bulk solution [2]. Adsorbed surfactant monomers begin to aggregate and form micelle-like structures at higher surfactant concentration. These structures are called hemimicelles and have one or two surfactant layers. Once these structures form on a solid surface, adsorption of additional surfactant may rapidly increase until a complete bilayers of surfactant covers the solid surface. So following the trend of variations in some terms like surfactant adsorption on carbonate rock or interfacial tension can result important understanding about the surfactant-solid interactions.

The adsorption of surfactant at the solid–liquid interface plays an important role in many technological and industrial applications. The behavior of surfactants at the interface is determined by number of forces, including electrostatic attraction, covalent bonding, hydrogen bonding, hydrophobic bonding and solvation of various species [3]. For ionic surfactants, electrostatic interactions are almost the governing factors. If the surfactant and the adsorbent are oppositely charged, the adsorption process is fast. For the case of similarly charged surfactant and adsorbent the process is slow or even may be prohibited.

Nanoparticles are employed like surfactants, and often in association with them, as stabilizing additives of such disperse systems, in different fields of practical interest [4, 5]. Nanoparticles affect the interfacial behavior and the adsorption processes. The interaction between nanoparticles and surfactants plays a major role in the extensive use of nanofluids in industrial and technical applications like colloidal stability and detergency. Ma et al. [6] reported the influences of SiO$_2$ nanoparticles on the effective interfacial tensions of surfactant solutions. They found that presence of negatively charged nanoparticles enhances the adsorption of anionic surfactant at air-water interface and they related the enhanced adsorption to repulsive Coulomb interactions. Sharma et al. [7] studied the adsorption of nonionic surfactant on silica nanoparticles and discussed about the mechanism of adsorption considering the formation of bilayers.

In this study, we report the behavior of surfactants into liquid-liquid, liquid-air and also over carbonate substrate in presence of ZrO$_2$-nanoparticles. The air-water surface tension and conductivity experimental were carried out. Conductivity measurement of nanofluids is used as a method for measuring the adsorption of nanofluids on carbonate rock. In this study, homogeneous spherical nanoZrO$_2$ was fabricated and applied along with the various surfactant solutions as friendly nanofluids in water, then adsorption of these surfactants and nanofluids onto calcite were studied.

2. Methodology

2.1 Materials: C12TAB (dodecyltrimethylammonium bromide), SDS (sodium dodecyl sulfate), LA7 (Lauryl alcohol- 7 mole ethoxylated), ZrO2 nanoparticles (prepared in our Lab), n-heptane and calcite, CaCO$_3$ were used along with the distilled water in all experiments.

2.2 Samples preparation: For each surfactant we have made various solutions, called basic solutions, with 5 different concentrations that are related to the critical micelle concentration. These concentrations are 0.001, 0.01, 0.1, 1 and 5 cmc of the surfactants. Nanofluids were prepared by adding ZrO$_2$ nanoparticles to these basic solutions. We have used 3 different concentrations for ZrO$_2$ nanoparticles in nanofluids. These concentrations are 0.001, 0.01 and 0.05 gr/100ml. Also we have prepared reference
nanofluids that contains only nanoparticle (with the three mentioned concentrations) and no surfactant used in the systems.

3. Results and Discussion

3.1 Surfactant adsorption on CaCO3 rock; conductivity measurement

Effect of ZrO2 nanoparticles on adsorption of surfactants over the CaCO3 rock was determined by conductivity measurement. Carbonate rock that added to basic solutions and nanofluids was in the form of powder with a specific amount. By dynamic conductivity measurement, we could determine the variations of conductivity for each solution and plot them versus time. Figure. 1 demonstrates that conductivity decreases more when there are nanoparticles in the system and the reduction depends on the concentration of nanoparticles directly. Such effect can be due to the electrostatic repulsion between nanoparticle and surfactant.

![Figure 1](image)

Figure. 1 Comparison of conductivity versus time for aqueous solutions containing 0.01 cmc of SDS (in presence of calcite powder). (a) Only surfactant solutions, (b), (c) and (d) specify 0.001, 0.01 and 0.05 gr of ZrO2 nanoparticles aqueous dispersion respectively.

Considering the adsorption kinetics of DTAB at the substrate–aqueous interface, it is deduced that the adsorption of DTAB on carbonate rock in presence of ZrO2 nanoparticles can be in form of nanostructures and the rate is more than adsorption of SDS. The nonionic LA7, although forms nanostructures, the surfactant loss is much lower than the other cases. It is also observed that rate of adsorption in all cases is more in cmc and higher concentrations.
3.2 Surface tension measurements

We have studied the adsorption of surfactants on air-water by measuring surface tension with the Noüy ring method. The measurements were done for nanofluids, basic solution and reference nano and then data were compared together. All experiments took place under ambient pressure condition at a typical temperature of 23°C. It is found that presence of ZrO$_2$ nanoparticle has almost no effect on surface tension of DTAB and LA7 solutions, while it reduces the surface tension in SDS systems (Figure 2). As it is mentioned earlier such decrease in surface tension is due to electrostatic repulsion and consequent adsorption of SDS molecules into the surface.

![Surface tension as a function of SDS concentration](image1)

Figure 2: Surface tension as a function of SDS concentration: (▲) SDS solutions/air interface; (□), (◊) and (○) refer to the systems of SDS solutions with 0.001, 0.01 and 0.05 gr of ZrO$_2$ nanoparticles aqueous dispersion respectively.

3.3 Dynamic light scattering (DLS) test and SEM image of nanoparticles

With the aid of DLS test we could determine the average size distribution of the nanoaggregates in nanofluids. We did the tests for nanofluids (0.001 gr. ZrO$_2$ nanoparticles) containing SDS and DTAB surfactants. At cmc concentration of the surfactants, the average size for cationic surfactant determined 126 nm, but for the SDS surfactant was shown 130 nm (Figure 3-a). According to images, figure 3-b, the nanoparticles are of 17-19 nm sizes. Thus, we have aggregation of about 200 nm nanoparticles in presence of surfactant in aqueous solutions.

![Average size Distribution of SDS surfactant](image2)

Figure 3: The average size Distribution of SDS surfactant (3-a) and SEM image of nanoparticles (3-b)
4. Conclusion

We have reported the adsorption of surfactants on solid-liquid and air-liquid interfaces with an emphasis on the systems containing both surfactants and nanoparticles. The results show that interfacial tension decrease with the surfactants concentrations. Adding ZrO\textsubscript{2} nanoparticles enhances the surface activity of SDS, hence its more adsorption onto fluid/fluid interfaces. The adsorption of cationic and nonionic surfactants in presence of nanoparticle is deduced to be due to formation of nanostructures on the calcite surface.

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References