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Applications of Aluminium Oxide and Zirconium Oxide Nanoparticles in Altering Dolomite Rock Wettability using Different Dispersing Medium

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Application of nanotechnology in oil and gas industry has received great attention from many researchers. This is due to two features of nanoparticles that make them unique which are their size and the ability to adjust their behaviour. Nanoparticles are very active and energetic materials with a high tendency to form nano textured surfaces in combination with surfactants, and causing a major change in the system's interfacial properties. Surface energy of surfactants can be significantly increased by the interaction of nanoparticle and surfactant and more adsorption on the rock surface occurs with higher surface energy. The objective of this study is to investigate the effectiveness of Al_2O_3 and ZrO_2 nanoparticles to alter oil-wet dolomite rock to more water wet condition. In this study, nanoparticle was dispersed in three different surfactants namely cetyltrimethylammonium bromide, CTAB (cationic), sodium dodecyl sulphate, SDS (anionic) and TX-100 (non-ionic). Critical micelle concentration of the surfactant was determined by measuring its surface tension (SF). The CMC value of the surfactant was established at the inflection point of the curve. The IFT was determined after the addition of nanoparticles. The results revealed that there is significant reduction of IFT after addition of nanoparticles. Reduction of IFT indicates the ability of the solution to decrease capillary forces and increase mobility of the oil in pore throat. Initial wettability of the dolomite substrate was determined and then was submerged in different nanofluids at different concentration. Contact angle of the rock surface was measured as quantitative method to determine the wettability of the system. The experiment was further investigated by evaluating adsorption of the surfactant on the rock surface. Isotherm adsorption of the surfactant was studied and the result revealed that ionic surfactant has higher adsorption capacity. This is mainly because the charged group on solid surface strongly influences the adsorption of surfactant at solid-liquid interface.

1. Introduction

Nanoparticles have been widely used in many industries such as medicine, fuel cells, food, and cosmetics. In oil and gas industry, nanotechnology has received a great attention from many researchers. In reservoir management, it is used as enhanced oil recovery agent to produce the remaining oil trapped in the reservoir. One of nanotechnology application in enhanced oil recovery is wettability alteration modifier. Unfavourable wettability has been one of the obstacles in oil production especially in carbonate reservoir. It is reported that above 60 % oil reserves in the world are from carbonate reservoir (Sheng et al., 2010). Carbonate reservoirs tend to have mixed-wet to oil-wet condition and the production from these reservoirs is quite challenging because of the complex pore structures.

Mohammadi et al. (2014) conducted a research on gamma aluminium oxide (γ-Al_2O_3) dispersed in distilled water to alter wettability of carbonate rock from oil wet to more water wet condition. The maximum reduction of contact angle occurred at concentration of 0.5 wt%. The contact angle decreased with the increase of nanoparticles concentration but at above 0.5 wt% the contact angle increased and changed to neutral wet conditions. In addition to that, 0.5 wt% nanofluids was injected into the core and oil recovery increased by

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11.25 % as tertiary recovery. Giraldo et al. (2013) studied the alumina-based nanofluids towards wettability alteration of sandstone. They dispersed the aluminium oxide in anionic surfactant and the results revealed that the contact angle for water/air/rock system changed from oil-wet to strong water-wet condition. Besides that, relative permeability curve also shifted to the right after treatment with nanofluids which indicated the sand pack turned into water wet after treatment with alumina nano fluids.

A study was conducted by Karimi et al. (2012) by using zirconium oxide (ZrO_2) nanoparticles dispersed in mixture of surfactants. The results revealed that the surfactants changed the wetting property of carbonate rock from oil-wet to intermediate-wet. The introduction of ZrO_2 into the surfactants changed the wettability of carbonate rock from strong oil-wet to strong water-wet. The change of wettability by ZrO_2 is a slow process and it requires at least two days.

In spite of all reported study, there is no comparative study to investigate the performance of Al_2O_3 and ZrO_2 nanoparticles dispersed in surfactant to alter wettability of oil-wet carbonate rock system to water-wet. Therefore, the aim of this paper is to investigate and provide comparison wettability alteration of dolomite rock by Al_2O_3 and ZrO_2 in different dispersing medium through laboratory means. Cationic surfactant CTAB, nanionic surfactant TX-100 and anionic surfactant SDS were used in this study. The wettability evaluation is performed by contact angle measurement as quantitative method.

2. Material

2.1 Characterisation of crude oil

The crude oil from a reservoir located in Sarawak, Malaysia was used. The characterisation of the crude oil was conducted to determine its density, viscosity, API gravity, and total acid number. Physical properties of the crude were listed in Table 1. FTIR analysis was also conducted to determine the functional groups that are present in the crude.

Table 1: Physical properties of the crude oil

Properties	Value
Asphaltene content (wt%)	0.01
Resins content (wt%)	6.26
Kinematic viscosity at 25 °C (mm^2/s)	2.016
Density at 25 °C (g/mL)	0.8283
° API gravity	37.7

2.2 Nanoparticle, NPs

Two commercial type of nanoparticles, namely Al_2O_3 (20 nm, purity 99+ %, and specific surface area > 138 m^2/g) and ZrO_2 (40 nm, purity 99+ %, and specific surface area 20 - 40 m^2/g) were purchased from US Research Nanomaterials, Inc (Houston, TX).

2.3 Fluids

Sodium Chloride (NaCl), from Qrëc (Asia) Sdn Bhd was used as salts to make synthetic brine (20 g/L), Cetyltrimethylammonium Bromide (CTAB) was used as cationic surfactant, sodium dodecyl sulphate (SDS) as anionic surfactant and Triton X-100 (TX-100) as non-ionic surfactant. Nanofluid with weight concentration 0.05 wt% was dispersed in surfactant using high speed stirrer for 10 min at 500 rpm. A homogenous suspension was later obtained by treating the mixture in ultrasonic apparatus for 1 h prior the test was conducted.

2.4 Preparation of Porous media

Carbonate dolomite were obtained from Kocurek Industries INC, (Caldwell, TX). The core was first cut into small plate (3 mm thickness and 38.1 mm diameter) using trimming machine and is polished to obtain a flat and smooth surface.

3. Experimental

3.1 Surface Tension and Interfacial Tension

Surface tension measurement was used to determine critical micelle concentration (CMC) of the surfactants. Interfacial tension (IFT) of nanofluids/oil system was determined. In this measurement, Kruss EasyDyne tensiometer was used under ambient pressure and temperature with Du Noüy method by Harkins & Jordan correction. The ring was cleaned thoroughly with toluene and dried using the Bunsen burner before each measurement.

3.2 Contact angle

Contact angle is one of the easiest ways to measure the wettability of a rock surface. It is a quantitative method and the contact angle was measured through a denser fluid. In oil/water/rock system, contact angle was measured through water. For contact angle measurement, oil-wet dolomite substrate was submerged in different test solutions. The substrates were placed vertically in the test solution in room temperature for 48 h. Then, oil was injected onto the rock surface and side image of oil drops were taken using a camera and the contact angle was determined.

3.3 Adsorption of Surfactant

Ultraviolet visible (UV-Vis) spectrophotometer (105, BUCK SCIENTIFIC, Inc) was used to determine the concentration of surfactant at equilibrium point. For isotherm adsorption, 0.2 g adsorbent was put into 100 mL surfactants at various concentrations. The adsorption testing was conducted by constant shaking at room temperature for 24 h. After adsorption, the solution and adsorbent was separated using filter paper. After that, the residual concentration of CTAB, SDS and TX-100 were determined. The amount of adsorption capacity at equilibrium, qe (mg/g) was calculated by using Eq(1).

$$qe = (Co - Ce)\frac{v}{m} \quad (1)$$

where c_0 and c_e are the initial and equilibrium concentration of surfactant (mg/L), *v* is the volume of solution (L) and *m* is the weight of the adsorbent used (g).

4. Results and Discussion

Fourier transform infrared spectroscopy (FTIR) was used to determine the chemical groups that are present in the crude oil. FTIR spectrum for the crude oil employed in this research is shown in Figure 1. The spectra were recorded at wavelength between 500 cm^{-1} and 4,000 cm^{-1}. From Figure 3, it can be seen that adsorption at 1,820 - 1,670 cm^{-1} is due to C=O stretching meanwhile at 3,000 - 3,600 cm^{-1} is due to O-H functional group. Hence, the presence of carboxylic acid in the crude is confirmed by FTIR analysis and the total acid number of the crude oil is 0.06 mg KOH/g which supported the FTIR analysis. Other major functional groups that exist in the crude oil are alkanes groups i.e. CH_3 and CH_2 at wave number of 2,920 cm^{-1}. The peak at 1,373 cm^{-1} and 1,454 cm^{-1} indicate deformation of CH_3 and deformation of CH_2. The adsorption at peak 745 cm^{-1} is due to vibration of alkyl halide stretching.

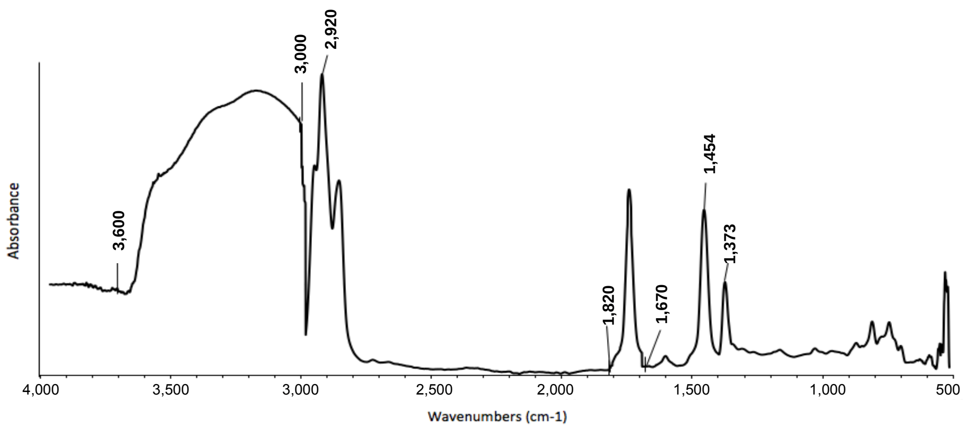

Figure 1: FTIR spectra for the crude oil

Water surface tension can be reduced by introduction of surfactant into the solution. The surface tension value was used to establish the critical micelle concentration (CMC) of a surfactant. CMC is the concentration of surfactant at which the surfactant solution starts to form micelles in bulky quantities. The surface tension of the surfactants in brine was deliberated at distinctive concentrations. A graph of surface tension versus surfactant concentration was plotted in Figure 2. The lowest surface tension value for CTAB, SDS and TX-100 is 31.75 mN/m, 26.10 mN/m, and 26.83 mN/m. CMC is measured at the inflection point of the curve and based on

Figure 2, the CMC value for CTAB, SDS and TX-100 is 1,200 ppm, 1,400 ppm and 1,200 ppm. Meanwhile, interfacial tension (IFT) was measured between two immiscible fluids and in this system; IFT was measured between crude oil/nanofluids solution and the results as shown in Figure 3. The IFT value before the introduction of nanoparticles was given at 8.46 mN/m, 9.88 mN/m and 9.13 mN/m for CTAB, SDS and TX-100. However, the IFT value reduced largely after the introduction of nanoparticles into the surfactant. The reduction of IFT value shows the efficiency of the surfactant to reduce capillary pressure in the pore throat to increase oil mobilisation.

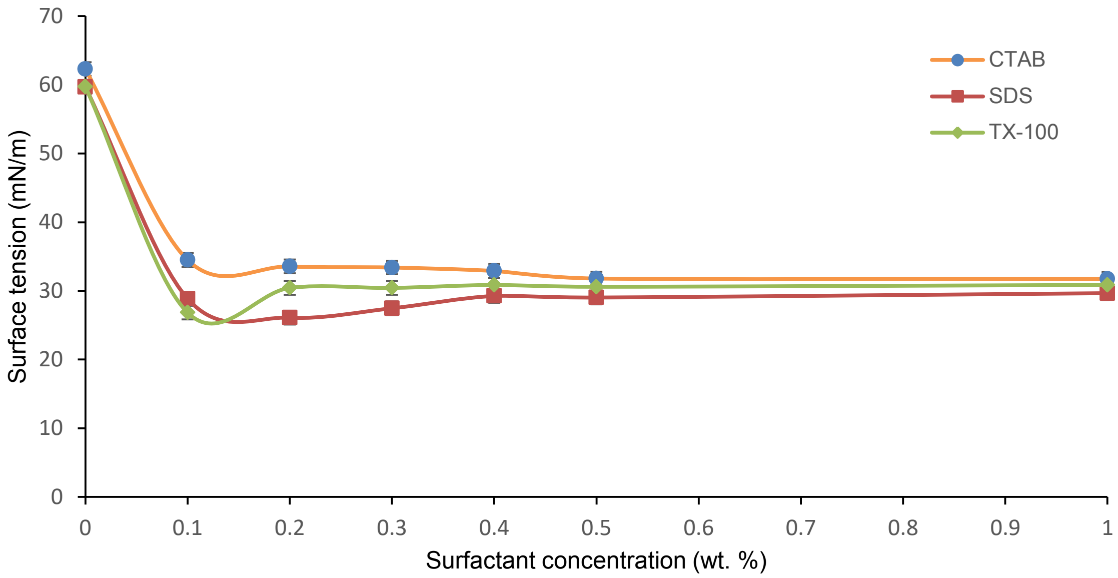

Figure 2: Surface tension versus surfactant concentration

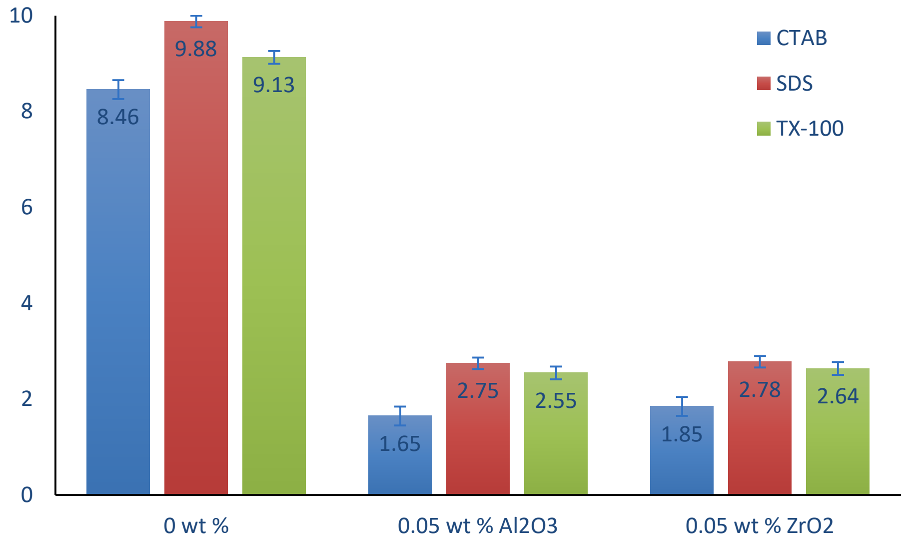

Figure 3: Oil/Nanofluids interfacial tension

Contact angle measurement was conducted at atmospheric pressure between oil drop and dolomite substrate in presence of synthetic brine. In order to minimise error during measurement, each reading was repeated three times to get the most accurate value. Initial contact angle of dolomite substrate was determined and the measurement indicates that all substrate was oil-wet condition. In order to observe wettability alteration by nanoparticles, the substrate was submerged in nine different solutions. After 48 h, the substrates were dried in

oven at 40 °C and contact angle measurement was conducted. Contact angle measurement result was shown in Figure 4. According to Figure 4, at zero nanoparticles concentration, wettability of dolomite substrate changed from oil-wet to water-wet in the event of CTAB, meanwhile in case of SDS and TX-100, the wettability of dolomite substrate changed from oil-wet to intermediate-wet.
Standnes and Austad (2003) explained that carboxylic group in crude oil when in contact with brine will become negatively charged and will absorb strongly onto the carbonate rock surface hence it changed the wettability of rock surface to strong oil-wet. The key mechanism for wettability alteration by cationic surfactant is due to electrostatic attraction between positive charged component of surfactant head molecules and adsorbed acid group on dolomite rock and this interaction is much stronger than hydrophobic interaction (Salehi et al., 2008). Thus, this explained why wettability alteration of dolomite by cationic surfactant was much greater than anionic and non-ionic surfactant. The cationic surfactant is able to desorb and strip the absorbed layer of crude oil component, exposing its original wettability properties.
The experiment was further carried out by adding 0.05 wt% Al_2O_3 and ZrO_2 nanoparticles into the surfactant. The results revealed that, after the substrate was submerged in Al_2O_3 and ZrO_2 dispersed in CTAB, the contact angle reduced to 52° and 60° which indicate strong water-wet condition. Meanwhile, in the event of Al_2O_3 dispersed in SDS and TX-100, the contact angle reduced to 75° and 62°. On the other hand, the contact angle reduced to 84 ° and 71 ° when it was treated with ZrO_2 dispersed in SDS and TX-100. Generally, the nanoparticles can cause more reduction of contact angle. However, in comparison, Al_2O_3 have performed better than ZrO_2 in all dispersion medium. During the treatment, all substrate was submerged vertically in the solution; therefore, the reduction of contact angle is the result of nanoparticles and surfactant adsorption on the rock surface. Wettability alteration by nanoparticles is caused by the wedge film formation at the contact line of oil/water/rock system.

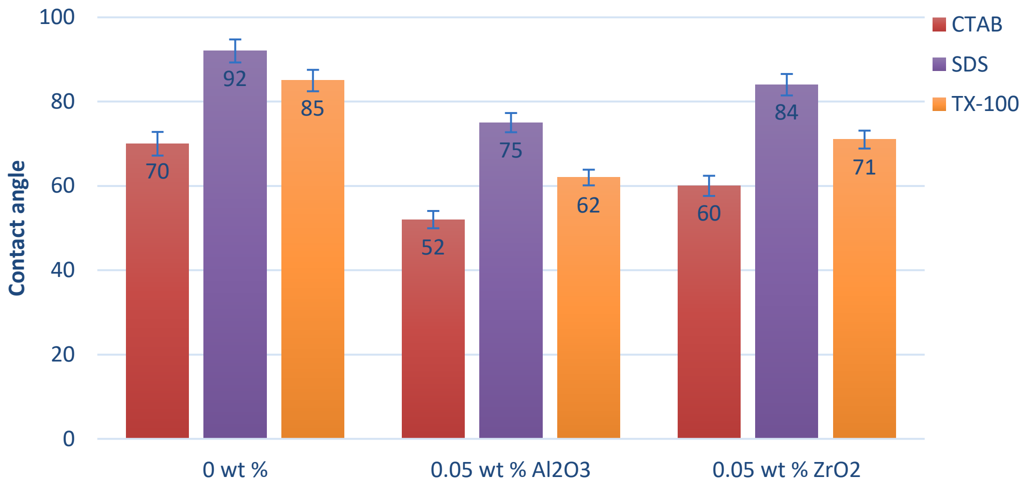

Figure 4: Contact angle measurement

Isotherm adsorption of the surfactant were conducted based on maximum wavelength which is at 202 nm for CTAB, 224 nm for SDS and 219 nm for TX-100. The results adsorption capacities versus concentration for surfactants are shown in Figure 5. Based on the graph, it can be seen that adsorption of CTAB is typical L shape type. The adsorption capacity of CTAB on the adsorbent is the highest among three surfactant followed by SDS. Meanwhile, a very little amount of TX-100 surfactant was adsorbed by the dolomite rock. The adsorption of ionic surfactant on rock surface is strongly influenced by charged group of the adsorbent (Salari and Ahmadi, 2016). The surface active group of the dolomite rock is mainly carboxyl group which has negative charge. Therefore, it has potential to associate with cationic surfactant through electrostatic force. Hence, this explained why adsorption capacity of CTAB is the highest among three surfactants. Meanwhile, as for anionic surfactant, the adsorption capacity is lower may be due to electrostatic repulsion between negatively charged surfactant molecules and the carboxyl group adsorbed on the rock surface. In the event of TX-100, adsorption is mainly caused by hydrophobic and hydrogen bond interaction, and this interaction is weak between surfactant and the adsorbent (Zhang and Somasundaran, 2006).

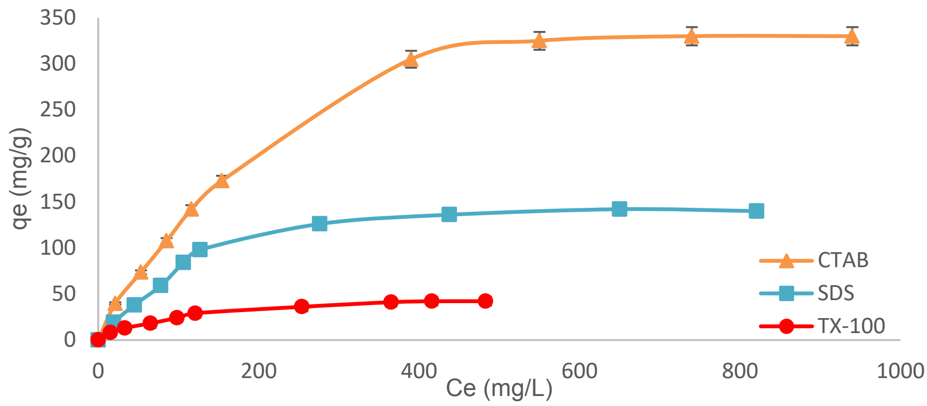

Figure 5: Isotherm adsorption of surfactants

5. Conclusion

The experimental results from this study are consistent with the hypotheses that wettability alteration by electrostatic interaction is greater than wettability alteration by hydrophobic interaction. The results also confirmed that cationic surfactant is more effective in altering wettability of oil-wet dolomite rock to more water-wet condition through ion-pair formation. After the introduction of Al_2O_3 and ZrO_2 nanoparticles, it can be seen that nanoparticles can enhance the wettability alteration of oil-wet dolomite rock and can be considered as an effective wettability alteration agent. In comparative study, Al_2O_3 performed better than ZrO_2. The average size for Al_2O_3 nanoparticle used in the experiment is smaller than ZrO_2. The smaller particle size means it has higher surface energy and thus, bigger repulsion force. This can be one of the reasons that explained the superior performance of Al_2O_3 ZrO_2 in term of wettability alteration.

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