Effect of pH-values on the contact angle and interfacial tension

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As the reservoir production continues, the reservoir pressure is reduced with time and some of the reservoir oil remains as a residue that cannot be produced by classic means. Enhancing oil recovery (EOR) techniques; in this period of reservoir life; become more and more important due to the increase in demand of the world for energy.

Numerous EOR techniques are used in order to increase the oil recovery. One of the effective EOR techniques is the surfactant flooding. Surfactant is used to reduce the interfacial tension (IFT) between oil/water allowing them to mix and being displaced as one phase. But it is known that the surfactant is very expensive. However, using surfactant is not the only way to reduce the IFT. Generally, the reservoir oil is acidic by nature, and it contains a nature surface active agents. So, mixing the oil which is acidic by an alkaline will form in-situ surfactant that will reduce the IFT between oil/water. This process is called as "Alkaline Flooding" which is one of the useful EOR techniques and economically efficient than using the expensive surfactant.

Reducing the IFT is our objective to enhance the oil recovery. Therefore, a literature review of surface tension and IFT, factors affecting the IFT, alkaline flooding technique, and effect of pH on the IFT are included.

Furthermore, experimental work is done for viscosity using the Brookfield viscometer, IFT by Digital densitometer K-10 to show the effect of pH on the IFT, and density is measured also.

Three samples are used for experimental work. Arabian light sample, Udheiliyah sample, and finally Asphaltenic oil sample.

Key words: enhancing oil recovery, surfactant flooding, alkaline flooding, viscosity, density

Introduction

The oil recovery methods are divided in three stages. In the first stage, which is the primary recovery method, the reserves are produced using the natural energy inherent in the reservoir. This includes gas cap drive (expansion of gas), solution gas drive (expansion of gas coming out of solution in the oil), water drive (flow of water from an aquifer), gravity drainage (dipping in the layer of oil-bearing) or combination of these effects.

In the second stage and in order to recover the oil a fluid is injected under pressure in the oil well, replacing the oil in the pore and pushing out the oil. In secondary oil recovery water is injected to induce a driving force to move out the oil (water flooding). These involve pumping a fluid into the reservoir through one or more additional wells either to maintain reservoir pressure or to displace the oil directly.

The third stage of recovery methods is dealing mainly with the reasons behind the residual oil saturation after the application of secondary methods. To increase the recovery rates, enhanced oil recovery methods (EOR) can be applied. The mechanisms of EOR are:

- Improve sweep efficiency by reducing the mobility ratio between injected and in-place fluids,
- Eliminate or reduce the capillary and interfacial forces and thus improve displacement efficiency, and
- Act on both phenomena simultaneously

EOR-methods fall into three main categories[5]:

- Thermal methods,
- Chemical flooding (polymer and surfactant) and
- Miscible displacement

Surfactant flooding is usually used to lower the interfacial tension between oil and water and therefore to reduce the capillary pressure.

In this project, the interfacial tension (IFT) as well as the affecting factors will be discussed. Moreover, Experimental work will be performed to study the effect of pH on the IFT.

The reduction of IFT between oil and water is very important, thus allowing the recovery of oil trapped in smaller pores and part of the residual oil remained in the pores after secondary flooding (surfactant flooding) and it will lead to a reduction of the capillary pressure within the pores. By adding surface-active agents (surfactant), the IFT between water and oil can be reduced.

The molecules at the surface of a liquid are subjected to an unbalanced force of molecular attraction, as the molecules of the liquid tend to pull those at the surface inward while the vapor does not have as strong an attraction. This unbalance causes liquids to tend to maintain a minimum surface area. The magnitude of this force is called the surface tension. The symbol for surface tension is "gamma". Conventionally the tension between the liquid and the atmosphere is called surface tension while the tension between one liquid and another is called interfacial tension.

A surface-active molecule, also called a surface-active agent or surfactant, possesses approximately an equal ratio between the polar and no polar portions of the molecule. When such a molecule is placed in an oil-water system, the polar group(s) are attracted to or oriented toward the water, and the no polar group(s) are oriented toward the oil. The surfactant is adsorbed or oriented in this manner, consequently lowering interfacial tension between the oil and water phase. When a surfactant is placed in a water system it adsorbs at the surface and lowers the surface tension between the water and air.

When it is place in a mixture of solid and liquid it adsorbs on the surface of the solid and lowers the interfacial tension between the solid and the water. Since the surfactant is adsorbed at the surface it is logical that the concentration of surfactant at the surface would be greater than the concentration in the bulk solution. Surfactants have many uses. Depending on the use the surfactant can be called by many names such as - Wetting Agents, Emulsifying Agents, Solubilizing Agents, and Detergents. When two immiscible liquids are in contact, they tend to maintain as small a surface as possible. It is therefore difficult to mix these two liquids and have them stay mixed.

The interface between the two phases is a region of limited solubility, which is, at most a few molecules thick. It may be visualized as a phase boundary that occurs because the attractive forces between molecules in the same phase are much larger than those that exist between molecules in different phases. The addition of a proper surfactant will lower the interfacial tension between the two liquids and allow them to mix or to create emulsions (figures 1 and 2).

Factors Affecting the Surface Tension and Interfacial Tension

There are many factors and reservoir parameters, which can affect the IFT between oil and brine in the reservoir. Also, it is very important to reduce the IFT in the reservoir to increase the oil recovery by the reduction of capillary pressure. The capillary pressure is defined as the difference between the pressure of no wetting fluid (P_{nw}) and the pressure of wetting fluid (P_w).[1,6]

$$P_c = P_{nw} - P_w = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \quad (1)$$

r_1, r_2 = radii of curvature of interface, measured perpendicular to each other.

The capillary pressure can be also determined using capillarimetric method or capillary tube. This method is based on the hydrostatic pressure of the two phases (oil/water). The oil/water-interfaces will a rise or fall in the tube until the capillary forces balance the gravitational forces, equation 2.

$$P_c = \frac{2\sigma\cos\theta}{r} = g\left(\rho_o h_o - \rho_w h_w\right) \quad (2)$$

When a drop of liquid is placed on the surface of a solid or a liquid with which it is immiscible, it may spread to a film or remain as a drop. The surface tension of the two liquids and the interfacial tension between them determines whether or not the liquid will spread. The spreading of a liquid on a solid is controlled by the same factors. The work of cohesion is the work required to separate the molecules of the spreading liquid so it can flow over the sublayer. Spreading occurs if the attraction between two immiscible liquids or the work of adhesion is greater than the work of cohesion. The difference between the work of adhesion and the work of cohesion is known as the spreading coefficient.

Several different parameters are used to characterize the wetting of a liquid on a solid surface. The most commonly used parameter is the contact angle Young developed the following equation, which relates the contact angle to the interfacial tensions (figures 3).

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (3)$$

Fig. 1. The mechanism of surface-active agent to create oil in water emulsion
Sl. 1. Način stvaranja nafte u vodenoj emulziji pomoću površinski aktivnog agensa

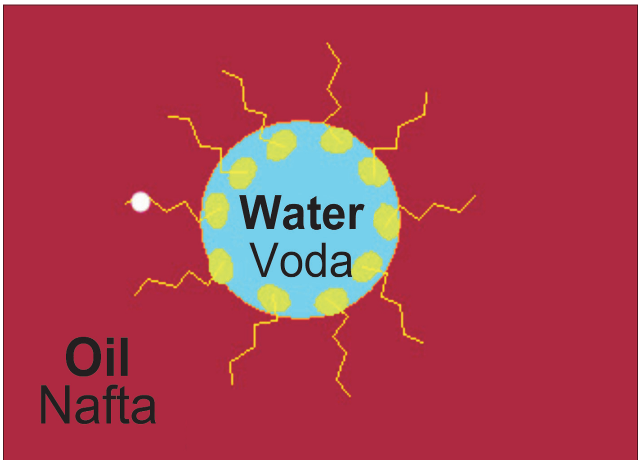

Fig. 2. The mechanism of surface-active agent to create water in oil emulsion
Sl. 2. Mehanizam stvaranja vode u naftnoj emulziji pomoću površinski aktivnog agensa

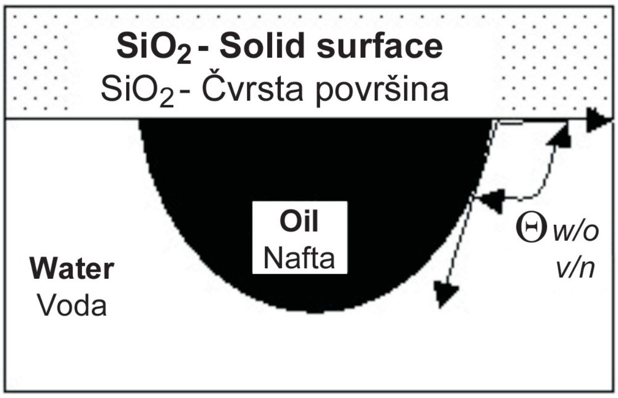

Fig. 3. Equilibrium forces at solid/oil/water (three phases) for the contact angle.
Sl. 3. Sile ravnoteže na granici krutina/nafta/voda (tri faze) za kontaktni kut

Alkaline Flooding

Alkaline flooding is one of EOR methods. Therefore, it is important for more understanding of alkaline flooding to know the importance of EOR and to explain some terminologies in the Enhanced oil recovery (EOR).

In the past, natural gas in the reservoir was depleted very rapidly, and the wells went dry in some fields after less than 15% of the available crude oil. When gas was depleted in the formation, pressure was gone, and the oil stopped flowing to the wellbore.

As a better understanding of what was happening downhole became known, better production methods come to be practiced, and percentage of available crude oil steadily increased to more than 60% of oil available in the reservoir.

Results and Discussion

The density and viscosity of the collected oil samples were measured to find their flow behaviour. The oil sample "Arabian light" has the lowest density as well as viscosity, while the Asphaltenic oil is the heaviest with the highest viscosity, which has to measure at high temperature because at temperature of 22 °C the reading was out of the range of the viscometer. However, the density and viscosity as physical properties of the oil samples are given in tables 1,2,3 and 4.

Figures 4, 6 and 8 shows the viscosity course of the different oil samples versus shear rate, while figures 5, 7 and 9 present the shear stress versus shear rate. The oil samples show clearly linear relationship between shear stress and shear rate, which indicates a Newtonian fluid behavior.

Table 1. Density for the three samples under different temperatures

Density, g/cm³	22 °C	40 °C
Arabian light	0.8332	0.8224
Asphaltenic	0.9120	0.8496
Udheiliyah	0.8416	0.8328

Table 2. Viscosity for Arabian light sample at different temperatures

Arabian light at 40 °C

RPM	Factor	Shear rate	Reading	Viscosity, mPa·s
0.3	20	0.36	0	0
0.6	10	0.73	0	0
1.5	4	1.83	0.8	3.2
3	2	3.67	2.1	4.2
6	1	7.34	4.6	4.6
12	0.5	14.68	9.5	4.75
30	0.2	36.71	25	5
60	0.1	73.42	51.5	5.15

Arabian light at 22°C

RPM	Factor	Shear rate	Reading	Viscosity, mPa·s
0.3	20	0.36	0	0
0.6	10	0.73	0	0
1.5	4	1.83	1.5	6
3	2	3.67	3.8	7.6
6	1	7.34	8.5	8.5
12	0.5	14.68	17.5	8.75
30	0.2	36.71	44.5	8.9
60	0.1	73.42	90	9

Table 3. Viscosity for Asphaltenic oil sample at different temperatures

Asphaltenic oil at 22 °C		Asphaltenic oil at 50 °C		Asphaltenic oil at 70 °C	
Reading	Viscosity, mPa·s	Reading	Viscosity, mPa·s	Reading	Viscosity, mPa·s
11.5	230	5.5	110	2.6	52
24	240	12	120	5.2	52
53.5	214	31	124	13.5	54
0	0	63	126	27.5	55
0	0	0	0	56	56
0	0	0	0	0	0
0	0	0	0	0	0

Tablica 4. Viscosity of Udheiliyah sample at different temperatures

Udheiliyah at 22 °C		Udheiliyah at 40 °C	
Reading	Viscosity, mPa·s	Reading	Viscosity, mPa·s
0	0	0	0
0.5	5	0	0
2.2	8.8	1.1	4.4
5	10	2.6	5.2
10.5	10.5	5.7	5.7
22	11	11.7	5.85
55.5	11.1	30.5	6.1
0	0	62.5	6.25

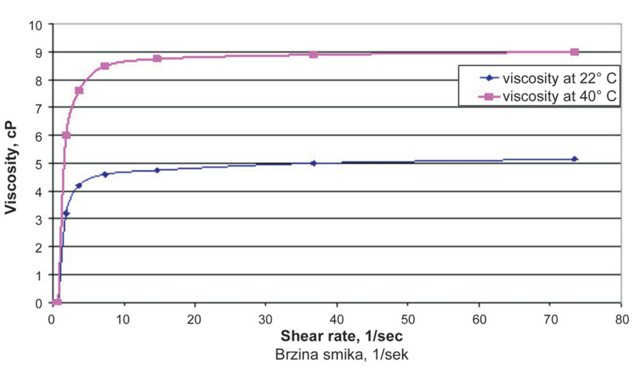

Fig. 4. Viscosity vs. shear rate for Arabian light sample
Sl. 4. Viskoznost u odnosu na brzinu smika za uzorak arapske lagane nafte

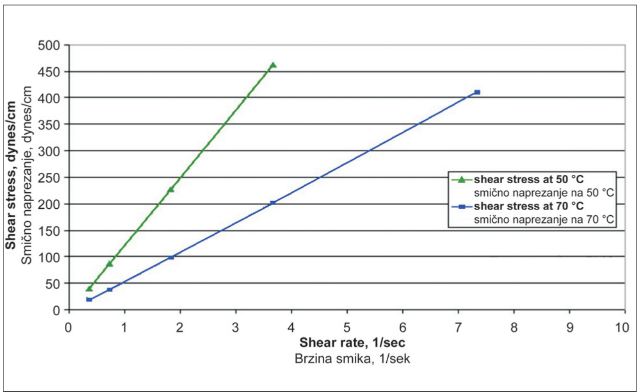

Fig. 7. Shear stress vs. shear rate of Asphaltenic oil sample
Sl. 7. Smično naprezanje u odnosu na brzinu smika za uzorak asfaltatske lagane nafte

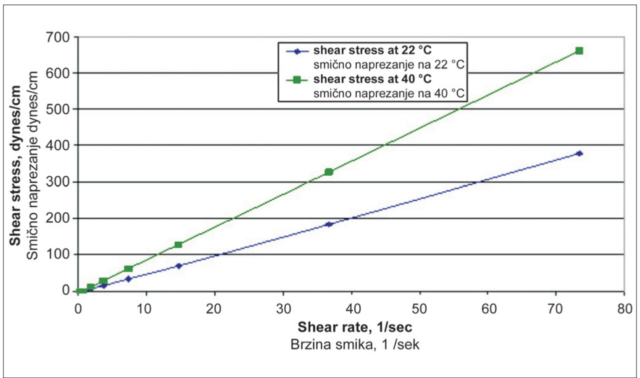

Fig. 5. Shear stress vs. shear rate of the oil sample Arabian light
Sl. 5. Smično naprezanje u odnosu na brzinu smika za uzorak arapske lagane nafte

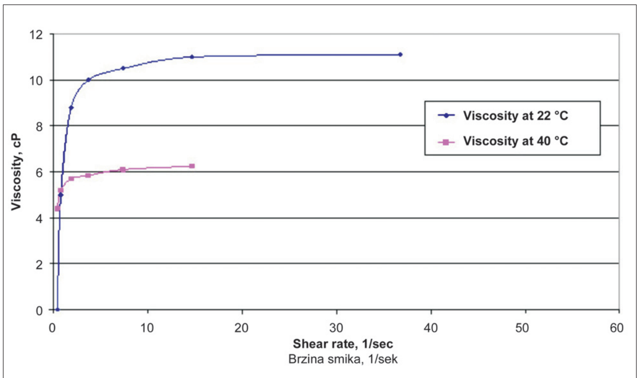

Fig. 8. Viscosity vs. shear rate for Udheiliyah oil sample
Sl. 8. Viskoznost u odnosu na brzinu smika za uzorak Udheiliyah nafte

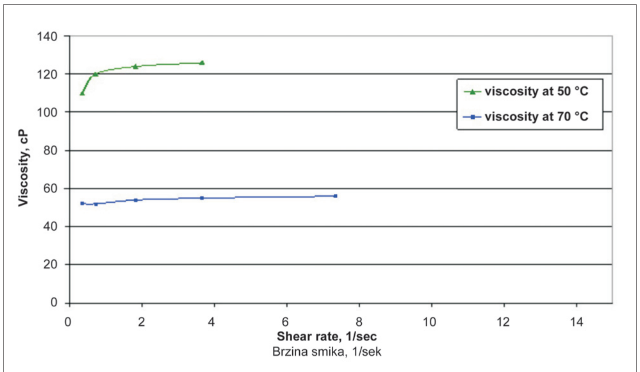

Fig. 6. Viscosity vs. shear rate for Asphaltenic oil sample
Sl. 6. Viskoznost u odnosu na brzinu smika za uzorak asfaltetske nafte

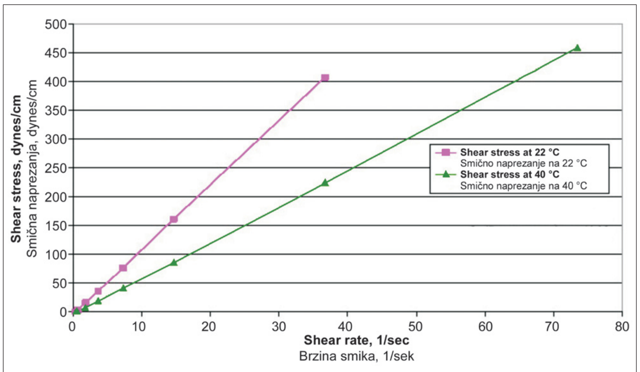

Fig. 9. Shear stress vs. shear rate of Udheiliyah oil sample
Sl. 9. Smično naprezanje u odnosu na brzinu smika za uzorak Udheiliyah nafte

Crude oils contain surface active agents, which are very important for the enhanced oil recovery methods. In this study surface and interfacial tensions of three different crude oil samples were measured using ring method at ambient temperature (Table 5) and show (Figures 10 , 11 and 12) moreover; contact angle was measured for one crude oil sample to indicate the influence of pH on the contact angle (Figures 13).

The interfacial tension, between oil samples and puffer solution show a maximum value at pH between 4.5 and

Table 5. IFT and surface tension of the three samples with different pH - values

pH	Surface	IFT/Arabian light	IFT for Asphaltenic oil (Kuwait)	IFT for Udheiliyah
2	58.8	15.8	15.5	15.5
3	61.2	17	15.2	18.3
4	62	20.2	19.4	20.1
4.5	69.1	17.8		
5.1	58.2	20		
7	54	13.9	21.2	31.5
9.21	52.8	5.4	11.4	24.5
10	61.7	5.2	12.2	28.2
13	52	0.1	0.6	11.8

Surface tension of Arabian light = 26.9 mN/m
Surface tension of Asphaltenic oil = 29.8 mN/m
Surface tension of Udheiliyah = 27.9 mN/m
Interfacial tension of Arabian Light with dest. water= 17.3 mN/m
Interfacial tension of Asphaltenic with dest. water= 21.3 mN/m
Interfacial tension of Udheiliyah with dest. water= 27.6 mN/m

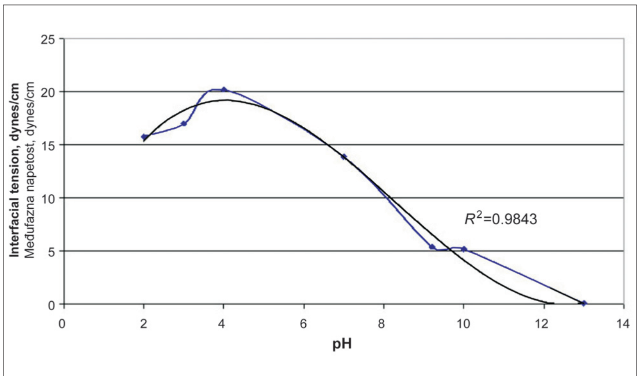

Fig. 10. IFT vs. pH of the oil sample Arabian light, (A)
Sl. 10. IFT u odnosu na pH za uzorak arapske lagane nafte, (A)

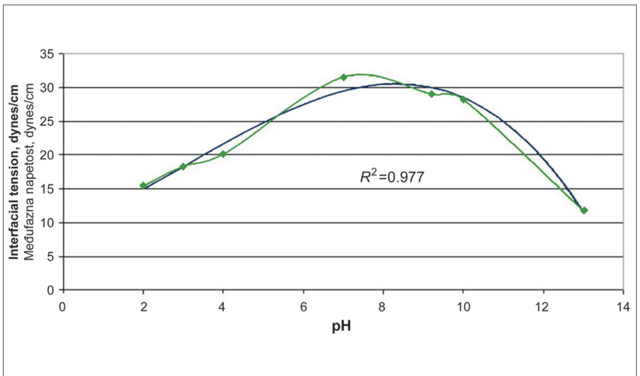

Fig. 12. IFT vs. pH of the Udheiliyah oil sample, (C)
Sl. 12. IFT u odnosu na pH za uzorak Udheiliyah nafte, (C)

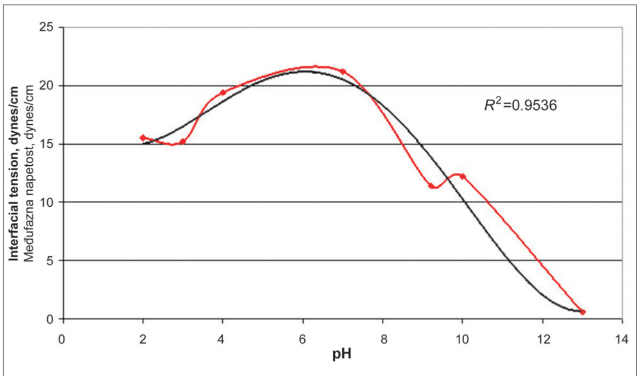

Fig. 11. IFT vs. pH of the oil sample "Asphaltenic oil", (B)
Sl. 11. IFT u odnosu na pH za uzorak asfaltenske nafte, (B)

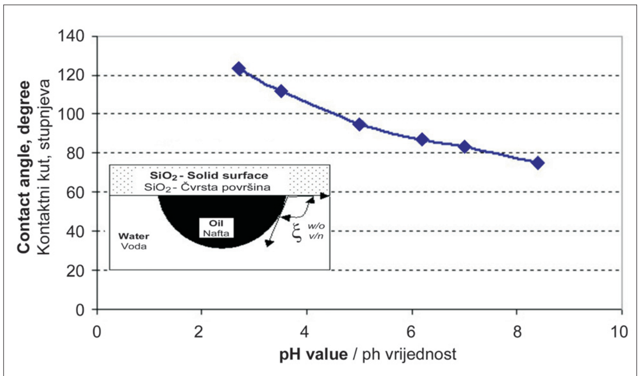

Fig. 13. Contact angle behaviour versus PH.
Sl. 13. Kontaktni kut u odnosu na pH

7.0. This indicates that the micelle agents in crude oil are not active in the mentioned pH-range.

However, some assortments of oil samples (Arabian light and Asphalting oil) show clearly that the IFT decreased significantly with increasing pH.

This trend could not be observed in the oil sample (Udheiliyah).

However, a high reduction of IFT at higher range of pH, indicates that the oil is more acidic.

The surface and interfacial tension of the oil samples varies between 20.6 to 29.8 mN/m. However, the surface tension of pure hydrocarbon components varies between 18.4 mN/m of n-Hexane and 34.2 mN/m of Tetra line. Therefore, the crude oil which may contain a significant amount of surface active agents, are not active in case of surface tension, because the values of the determined surface tensions of crude oil samples are close to that of pure hydrocarbon components.

However, the interfacial tension of oil to distilled water varies between 17.3 and 27.6 mN/m and it is lower than that of pure hydrocarbon to water, which is between 34.9 mN/m of Benzol and 51.1 mN/m of Hexane. Therefore, crude oils contain interfacial tension active substances or surface active agents which are active at the interface between crude oil and water.

Moreover, the interfacial tension of the tested oil samples is lower than their surface tensions, which confirm again that the crude oils contain interfacial active agents.

The result indicate that the sand grains become strongly oil-wet in pressure of brine at pH lower than 4.4 and remain water at pH higher than 6.5. This behaviour depends also on the composition of crude oil, and pH values for other oil samples may shift beyond these ranges. Figure 13. Shows the measured contact angle on SiO_2 – surface in presence of oil sample Arabian Light and brine with different pH. The contact angle data indicate that the pH value has a great in flounce on contact angle.

A contact angle of 90 degree could be observed of a pH of 5.5,wich indicates a neutral wet ability with increasing the pH, the contact angle of water decreased. The similar effect of pH was also observed by the measurement of IFT.

Conclusions

Based on this study following conclusions can be drawn:

(1) The interfacial tension between oil water is very important factor for the enhanced oil recovery.

(2) Decreasing the IFT would lead to reduce the capillary pressure in reservoir, resulted in more oil recovery.

(3) Crude oils content certain values of colloidal as fine suspension. These parts consist of water soluble and oil soluble.

(4) The investigation showed that the colloidal parts in crude oil sample are not surface active agents, because the measured surface tension of oil sample was higher than that of pore hydrocarbon components.

(5) Interfacial tension measurements showed that the crude oil samples content interfacial active agents, because the measured IFT with water was lower than the pure component with water.

(6) The higher is the crude oil density, the higher is the surface tension and the lower is the interfacial tension between oil and water.

(7) It was found that the oil sample (A) and (B) are suitable for alkaline flooding due to vary low IFT at a pH of between (10-13). However, oil sample (C) is not suitable for alkaline flooding.

(8) Density and viscosity of crude oil samples was measured of different temperature. The results showed that oil sample (B) and (C) might good candidate for steam flooding.

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