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Effect of Simple Polar Compounds and Salinity on Interfacial Tension and Wettability of Rock/Oil/Brine System

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Abstract. The objective of this study was to investigate the effect of polar compounds and salinity on the interfacial tension and wettability characteristics of rock/oil/brine systems. Crude oil and core samples from Safaniya formation in Saudi Arabia were used in the study. The concentration of polar compounds in the crude oil was varied by adding different amounts of oleic acid and octadecylamine to the crude oil.

Results showed that, the interfacial tension between crude oil and brine was lowered to a minimum value when oleic acid concentration of 0.028 gm-mole/lit. and brine salinity of 40,000 ppm NaCl were used. In case of using octadecylamine, the optimum salinity for obtaining the minimum interfacial tension lies between 4,000 and 10,000 ppm NaCl. The studied rock/oil/brine system is water-wet when oleic acid concentrations of 0.007 and 0.0105 gm-mole/lit were used for brine salinities of 10,000 and 0.0 ppm NaCl, respectively. The existence of octadecylamine in oil and sodium chloride in water reverses the system wettability from oil-wet to water-wet.

Introduction

Wettability of a rock surface describes the tendency of a fluid to adsorb to the rock surface in the presence of other immiscible fluids in a rock/oil/brine system. A major role of wettability in a reservoir is that of determining the distribution of reservoir fluids that affect the relative permeabilities and consequently oil recovery efficiency [1]. The factors affecting the wettability are pore-surface roughness, mineralogic composition and polar compounds. The latter can either exist in the crude oil or be injected into the reservoir [2-3]. The presence of such polar compounds alters wettability as well as interfacial tension. The interfacial tension was related to the wettability and pore geometry by the following relation [4].

$$\sigma_{wo} = \frac{r\,P_c}{2\cos\theta} \tag{1}$$

Several investigators have reported that the capillary forces that trap residual oil in porous media can be reduced by lowering the interfacial tension between oil and water or changing the wettability conditions using surface active compounds for the purpose of improving oil displacement efficiency [5-8]. Since most of the surface-active agents are still highly expensive to be commercially used in an enhanced oil recovery process, it is prudent to look for less expensive chemicals to lower the interfacial tension and/or change reservoir wetting conditions. Fortunately, the use of simple polar compounds such as organic acids and bases in releasing the trapped residual oil is economically feasible [2].

In the present work, the effect of polar compounds (oleic acid and octadecylamine) on wettability and interfacial tension characteristics in sandstone/oil/brine systems was investigated. The effect of brine salinity on wettability and interfacial tension was also studied.

Experimental work

The experiments conducted comprise the measurements of interfacial tension between brine and crude oil and wettability of rock/oil/brine systems.

Materials

Crude oil obtained from a Saudi oil field, Safaniya reservoir was used in this study. The properties of the crude oil are given in Table 1. Oleic acid $C_{17}H_{33}COOH$ and octadecylamine [$CH_3(CH_2)_{17}NH_2$], were used as simple acidic and basic polar compound additives, respectively. The oleic acid was added to crude oil with concentrations of 4,7,11,14,18,21,28 and 42 $\times 10^{-3}$ gm-mole/lit. The amine concentrations in another oil samples were 7,15,30,45 $\times 10^{-3}$ gm-mole/lit. The brine salinity was varied in the range from 0.0 to 200,000 ppm NaCl.

Table 1. Properties of Safaniya crude oil

Property	Value
1. API gravity	33
2. Pour point, °C	−4
3. Flash point, °C	20
4. Cloud point, °C	−2
5. Surface tension, mPa/cm	28
6. Total acidity, gm KOH/gm	1.93
7. Organic acidity, gm KOH/gm	0.4

Procedure

Wettability measurements

The contact angle method was used to evaluate wettability at room temperature and in absence of air. The sandstone cores were obtained from wells in the Aramco production area, Safaniya field. Samples 1.5 inches (3.81 cm) in diameter and 1 inch (2.54 cm) long with highly smoothed surfaces were used. Toluene saturated with water and methanol plus toluene mixtures were used for cleaning the samples. Drying was conducted under controlled humidity. The samples were then evacuated and saturated with brine aqueous solution. The oil droplet was placed in contact with the downward surface of a sandstone core immersed in the brine in a glass container. The oil droplet was photographed at periodic time intervals (1 hour) to investigate the change of the contact angle with time until equilibrium was reached. Equilibrium is judged to have been attained when no changes in the shape of oil drop is observed. Equilibrium contact angles for all brine salinities and polar compounds concentrations were reached after about 10 hours. A slide projector is used to determine the droplet dimensions, and the contact angles is calculated from the following formula:

$$\tan(\theta/2) = D/(2\,H) \tag{2}$$

where, H and D are the dimensions of the droplet. The system whose contact angle ranged from 0 to 90° is strongly water-wet, and from 90 to 180° is strongly oil wet.

Interfacial tension measurements

Tensiometer (K_{10}) was used to determine the brine-oil interfacial tension. Twenty cm^3 brine was poured into the glass cup of the tensiometer and then the ring was immersed in the brine phase prior to each measurement. Crude oil was then poured into the cup to reach about one centimeter above the aqueous phase surface. Time of 30 minutes was allowed for interface aging. The platinum ring was then raised to the interface and the zero reading was adjusted. The reading which permits the ring to cross the interface is the interfacial tension of the system. The procedure was repeated for crude oil samples at different brine salinities.

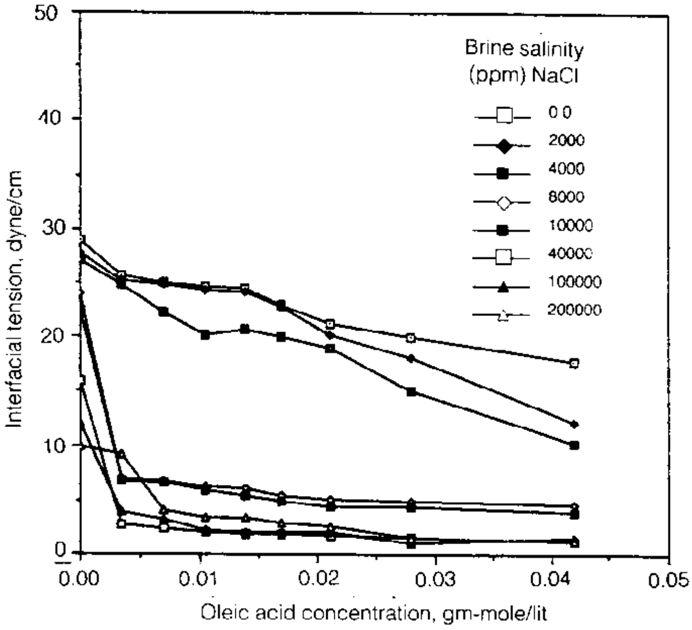

Fig. 1. Effect of oleic acid concentration on oil-water interfacial tension for different brine salinities.

Results and Discussion

Effect of acidic polar compound

Effect of oleic acid concentration and salinity on interfacial tension are given in Figs. 1 and 2 respectively. Figure 1 shows that the interfacial tension decreases with increasing oleic acid concentration for low brine salinities of 0.0, 2000, 4000 ppm NaCl. For other brine salinity curves, the interfacial tension decreases as the oleic acid concentration increases from 0.0 to 0.028 gm-mole/lit and then stabilizes with increasing oleic acid concentration. Figure 2 shows that the interfacial tension decreases as the brine salinity increases from 0.0 to 40,000 ppm NaCl, and then increases with increasing brine salinity. Lowering interfacial tension as a result of

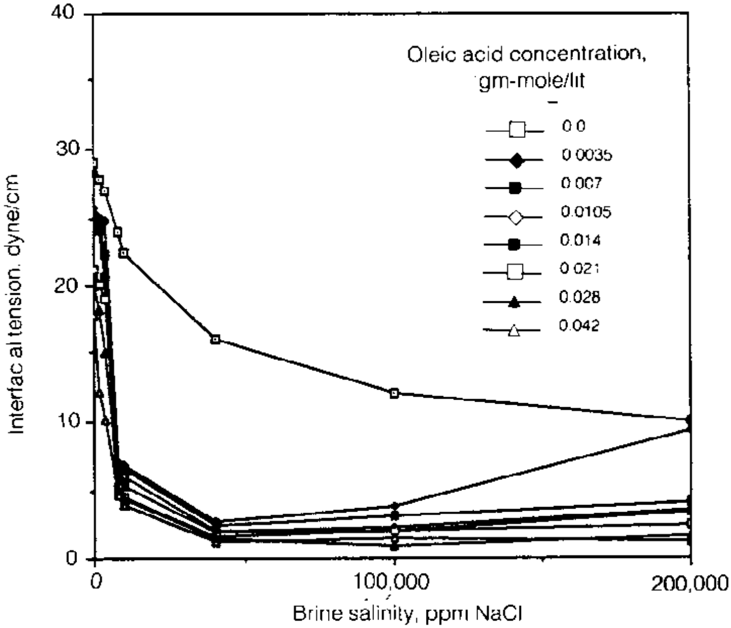

Fig. 2. Effect of salinity on oil-water interfacial tension for different oleic acid concentrations.

increasing oleic acid concentration for brine salinity less than or equal to 40,000 ppm NaCl is due to the action of the oleic acid as an anionic surfactant. The increase in interfacial tension with increasing brine salinity from 40,000 to 200,000 ppm NaCl is due to that, the positive charge of sodium (Na^+) attracts to the negative charge of the polar moiety (hydrofoil) and consequently decreases the solubility of oleic acid in water. These results indicate that the optimum concentration of oleic acid is 0.042 gm-mole/lit while the optimum brine salinity ranges from 40,000 to 80,000 ppm NaCl. Since the salinity of Safaniya formation water is equal to 42,000 ppm (total dissolved salts) [9], it can be concluded that an oleic acid slug of 0.042 gm-mole/lit may enhance the recovery of Safaniya oil in the future tertiary stage.

The effect of oleic acid concentration and brine salinity on wettability change is shown in Fig. 3. It is clear that, there is a large effect of oleic acid on wettability in the presence of salt. Although, the curves have no determined trend, it can be observed that, the system is generally oil-wet. However, a wettability reversal occurs at oleic acid concentrations of 0.007 and 0.0105 gm-mole/lit for brine salinities of 10,000 and 0.0 ppm NaCl, respectively.

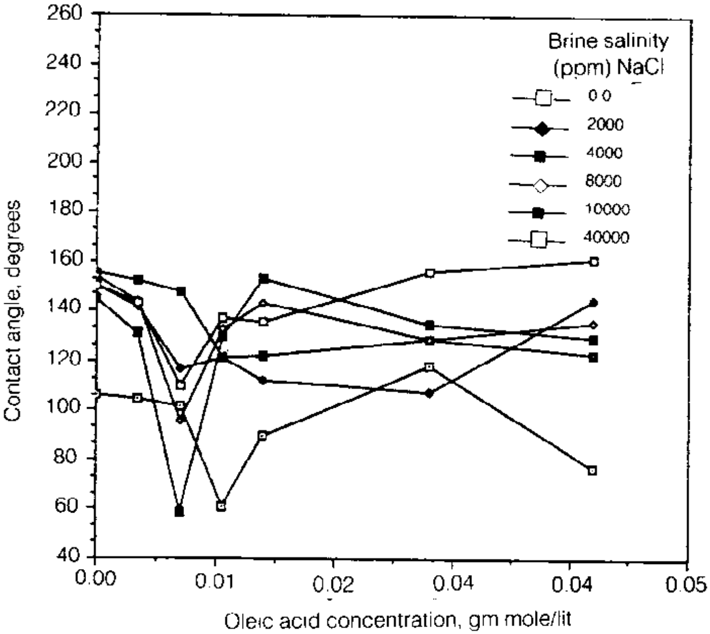

Fig. 3. Effect of oleic acid concentration on contact angle of rock/oil/brine systems for different brine salinities.

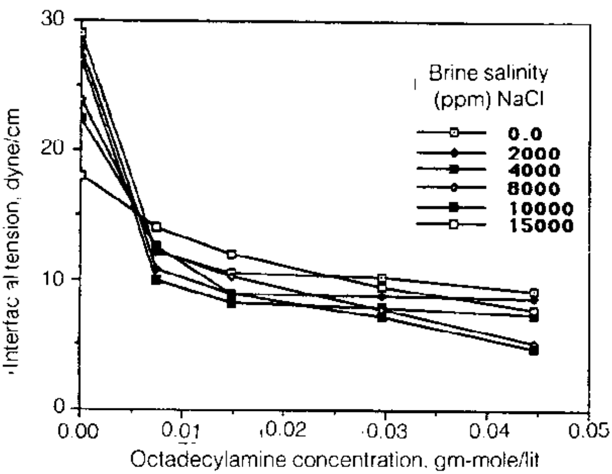

Fig. 4. Effect of octadecylamine concentration on oil-water interfacial tension for different brine salinities.

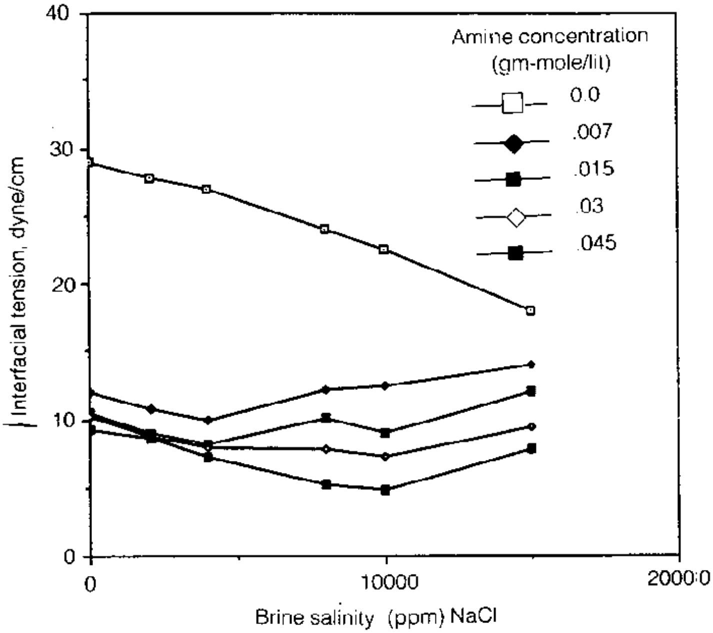

Fig. 5. **Effect of salinity on oil-water interfacial tension for different octadecylamine concentrations.**

Effect of basic polar compound

Effect of octadecylamine concentration and salinity on interfacial tension are given in Figs 4 and 5 respectively. Figure 4 shows that the interfacial tension decreases with increasing concentration of octadecylamine for all brine salinities. Figure 5 shows that the interfacial tension decreases with increasing brine salinity for zero concentration of octadecylamine. It can also be observed that the interfacial tension between basic polar compound oils and brine decreases to a minimum value as the brine salinity increases and then increases with increasing brine salinity for octadecylamine concentrations of 0.007 to 0.045 gm-mole/lit. This means that the salinities required for lowering the interfacial tension to a minimum value would range from 4,000 to 10,000 ppm NaCl.

Figure 6 shows the effects of octadecylamine and brine salinity on wettability. It is clear that, for zero water salinity, the oil wettability is slightly changed and the system is still oil-wet. For brine salinities of 4,000 and 10,000 ppm NaCl, the system reverses from strongly oil-wet to strongly water-wet as the octadecylamine concentration increases from 0.0 to 0.0075 gm-mole/lit. Increasing the amine concentration of the system to 0.015 gm-mole/lit, the system wettability reverses again to strongly

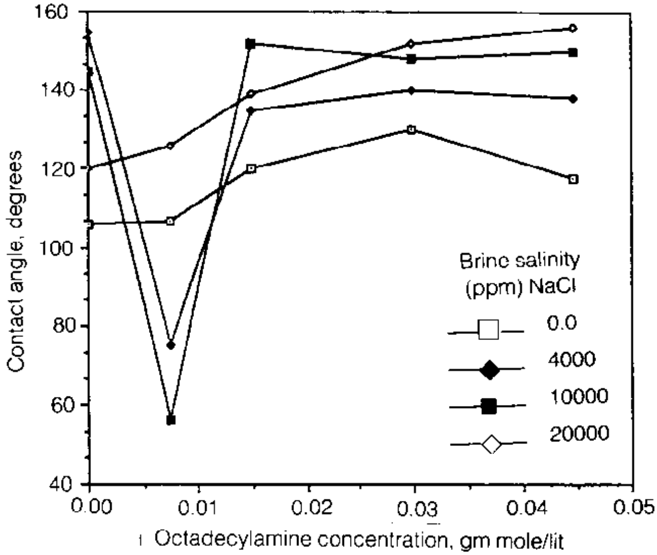

Fig. 6. Effect of octadecylamine concentration on contact angle of rock/oil/brine systems for different brine salinities.

oil-wet. As the brine salinity increases to 20,000 ppm NaCl, the effect of octadecylamine is diminished and the system wettability changes slightly towards more oil-wetness. This clarifies that the octadecylamine concentration and the brine salinity that lower the oil-water interfacial tension also reverse the system wettability from water-wet to oil-wet.

In the absence of salt, a sandstone surface tends to adsorb simple polar organic bases [1]. This occurs because silica normally has a negatively charged, weakly acidic surface in water near normal pH. This was noticed in this study in which the contact angle measurements showed that the rock/oil/brine system is mildly oil-wet when distilled water and crude oil without any additives of polar compounds were used, as shown in Figs 3 and 6. These results emphasize that the crude oil contains small fractions of the natural polar organic bases. Addition of salts to the water causes a change in the system wettability from mildly oil-wet to strongly oil-wet system. Thus, the salts strongly affect the surface charge on the rock surface and fluid interfaces which in turn can affect the adsorption of polar compounds.

Because of the complex rock/oil/brine system, the mineral surface will not necessarily have a preference for compounds of opposite acidity. Previous studies showed that the presence of salts can promote the adsorption of polar compounds with the same acidity at the sandstone surface [1,10,11]. In addition, the adsorption of any single polar compound in the crude might be enhanced or depressed by the adsorption of other compounds. The results of this study agreed well with that finding where the oleic acid, which is a negatively charged polar compound, is adsorbed on the sandstone surface of the same acidity. Also, the results showed that the wettability of sandstone rock could be altered by both the acidic and basic polar compounds in the presence of salts. Furthermore, the adsorption of polar compounds at the oil-water interface is affected by changing the salt concentration and consequently reflected the oil-water interfacial tension reduction.

Conclusion

Based on the results of the experimental work, the following conclusions are drawn:

1) The interfacial tension between Safaniya oil and brine is lowered to a minimum value of 2 dyne/cm for brine salinities of 40,000 to 80,000 ppm NaCl and oleic acid concentration of 0.042 gm-mole/lit.

2) The rock/oil/brine system is water-wet when oleic acid concentrations are equal to 0.007 and 0.015 gm-mole/lit at brine salinities of 10,000 and 0.0 ppm NaCl, respectively.

3) The optimum salinities required for lowering the interfacial tension to a minimum value between brine and Safaniya oil containing octadecylamine ranged from 4,000 to 10,000 ppm NaCl.

4) The presence of octadecylamine in oil and sodium chloride in water can reverse the system wettability from oil-wet to water-wet and again to oil-wet.

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تأثير المركّبات القطبية البسيطة ودرجة الملوحة على الشد البينسطحي للزيت والماء ودرجة تبلل الصخر النفطي

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(سُلِّم في ٢٩/١١/١٩٩٤م؛ قُبل للنشر في ١٥/٥/١٩٩٥م)

ملخص البحث. في هذه الدراسة، تمّ استخدام حمض زيتي وأوكتاديسيل أمين كُلٍ على حدة بتركيزات متعدّدة في زيت السفانية الخام المستخرج من أحد الحقول السعودية، كما تمّ استخدام عيّنات صخرية ممثلة للمكمن لقياس درجة التبلل.

وقد أظهرت النتائج أن قيم الشد البينسطحي للخام والماء المالح تنخفض إلى أقل قيمة لها عند تركيز ٠,٠٢٨ جرام جزيئي/لتر من الحمض في الخام وملوحة ٤٠٠٠ جزء في المليون في الماء. كما وجد أن الملوحة المثلى في حالة استخدام الأوكتاديسيل أمين كانت تتراوح بين ٤٠٠٠ إلى ١٠,٠٠٠ جزء في المليون للحصول على أقل قيمة للشد البينسطحي عند تركيز ٠,٠٤٥ جرام جزيئي/لتر. ومن جهة أخرى، أظهرت النتائج أن الصخر قد أبدى أفضلية للتبلل بالماء عند درجات تركيز للحمض بين ٠,٠٠٧ و٠,٠١٠٥ جرام جزيئي/لتر عند ملوحة ١٠,٠٠٠ جزء في المليون. أما مع وجود الأوكتاديسيل أمين في الخام وفي وجود ملح كلوريد الصوديوم في الماء فقد أظهرت النتائج انعكاس درجة التبلل للصخر من أفضلية التبلل بالزيت إلى التبلل بالماء.

وقد خلصت الدراسة إلى أنه يمكن تغيير الخواص البينسطحية لسوائل المكمن والصخر والتي يمكن أن تساعد في تحسين كفاءة إزاحة الزيت الخام بوساطة استخدام بعض المركبات القطبية البسيطة في عملية الإزاحة وبالتالي تحسين العائد النفطي من المكمن.