

Nonmonotonic Elasticity of the Crude Oil–Brine Interface in Relation to Improved Oil Recovery

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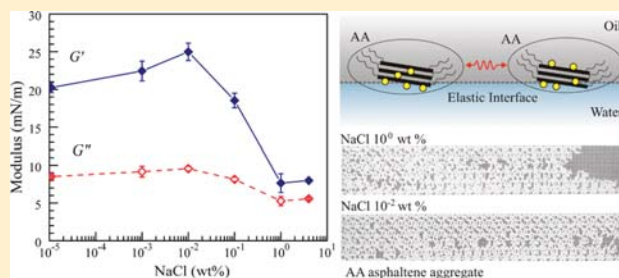
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Supporting Information

ABSTRACT: Injection of optimized chemistry water in enhanced oil recovery (EOR) has gained much interest in the past few years. Crude oil–water interfaces can have a viscoelastic character affected by the adsorption of amphiphilic molecules. The brine concentration as well as surfactants may strongly affect the fluid–fluid interfacial viscoelasticity. In this work we investigate interfacial viscoelasticity of two different oils in terms of brine concentration and a nonionic surfactant. We correlate these measurements with oil recovery in a glass-etched flow microchannel. Interfacial viscoelasticity develops relatively fast in both oils, stabilizing at about 48 h. The interfaces are found to be more elastic than viscous. The interfacial elastic (G') and viscous (G'') moduli increase as the salt concentration decreases until a maximum in viscoelasticity is observed around 0.01 wt % of salt. Monovalent (Na^+) and divalent (Mg^{2+}) cations are used to investigate the effect of ion type; no difference is observed at low salinity. The introduction of a small amount of a surfactant (100 ppm) increases the elasticity of the crude oil–water interface at high salt concentration. Aqueous solutions that give the maximum interface viscoelasticity and high salinity brines are used to displace oil in a glass-etched “porous media” micromodel. Pressure fluctuations after breakthrough are observed in systems with high salt concentration while at low salt concentration there are no appreciable pressure fluctuations. Oil recovery increases by 5–10% in low salinity brines. By using a small amount of a nonionic surfactant with high salinity brine, oil recovery is enhanced 10% with no pressure fluctuations. Interface elasticity reduces the snap-off of the oil phase, leading to reduced pressure fluctuations. This study sheds light on significance of interface viscoelasticity in oil recovery by change in salt concentration and by addition of a small amount of a nonionic surfactant.



1. INTRODUCTION

Water is often used to displace oil from the subsurface, and generally seawater is used for this purpose. Recently, water injection processes are being studied in the laboratory by modification of the chemistry of the injected water. By injecting low salinity water or by the use of low dose of surface active chemicals, the oil recovery is generally observed to improve.

Most authors speculate that low-salinity water alters the wettability to a more water-wetting state.^{1–9} The wettability alteration is advocated as the main reason for improved recovery. In addition to wettability alteration, the increase in the thickness of thin film of water on the substrates at low salt concentration has been reported.¹⁰ A recent review by Myint and Firoozabadi¹¹ in low salinity water injection includes the wettability alteration and thin water film thickness changes. In the past 15 years the research on low salinity water injection in relation to improved oil recovery has accelerated. In some petroleum fluids there is substantial increase from injection of low salinity brine, but in others there is no effect of salt content in the injected brine on improved oil recovery.¹² Some authors are of the opinion that even after some 500 published papers,

the mechanisms of low salinity water injection remain largely unknown.¹³ In all the past work, the molecular structure of the fluid–fluid interface has been neglected except in a recent paper by Alvarado et al.¹⁴

The formation of organized molecular structures at fluid–fluid interfaces increases interfacial viscoelasticity. In the lung, surfactants give the tissues adequate elasticity to expand and contract during the breathing cycle.^{15,16} In the eye, surfactants may increase the elasticity of the eyedrops forming tear films, preventing them from dewetting and maintaining the eyes humected.¹⁷ In both examples, viscoelasticity of the interface increases the thin film stability.

A number of authors have studied crude oil–water interfacial rheology in relation to stability of water-in-oil emulsions.^{18,19} These authors relate the elasticity of the fluid–fluid interface to stability of emulsion due to formation of interfacial structures from amphiphilic molecules in the crude in relation to the salt

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concentration in the aqueous phase. In the case of elasticity of the fluid–fluid interface in oil recovery, Alvarado et al.¹⁴ report an increase in elastic modulus as the salinity is reduced and observe a maximum of 38 mN/m at the Na₂SO₄ concentration of 6.724 mM (0.09 wt %). By using the low concentration brine in a water injection test in rock, Alvarado et al. report an increase in oil recovery of 20% in water injection in comparison to high salinity brine (0.6724 M, 9 wt %). The increase in oil recovery is suggested to be due to high elasticity of the brine–oil interface. The elasticity hinders the snap-off of the oil into small droplets, leading to a more continuous interface that can be swept more easily.

Surfactants may accumulate at the fluid–fluid interfaces in water injection. At the fluid–solid interface, surfactants may adsorb on the mineral surface and alter the wettability of the rock.²⁰ At the fluid–fluid interface, surfactants are known to reduce the interfacial tension; however, they may also increase or decrease the viscoelasticity of the water–oil interfaces. In other words the change from interfacial tension (thermodynamic property) alone does not describe improved oil recovery from surfactant injection. Viscoelasticity (rheological property) of the fluid–fluid interface may critically contribute to improved oil recovery.

The main goal of this work is to conduct a systematic study of viscoelasticity of the oil–water interface in two different crude oils. We use two different salts at various concentrations. One of the salts is monovalent, and the other is divalent. We will also investigate the additional effect of a surfactant in the aqueous phase in one of the two crude oils. The viscoelasticity measurements are then related to oil recovery. The investigation of the combined effect of salt concentration and surfactant on interface viscoelasticity is reported for the first time.

2. EXPERIMENTAL SECTION

2.1. Materials. Crude oils used in this work were obtained from two different reservoirs: one from the Gulf of Mexico and the other from the Middle East. Relevant data of the two oils are displayed in Table 1.

Table 1. Properties of the Oils

crude oil sample	density (g/mL)	API gravity	viscosity at 25 °C (Pa·s)	asphaltene content (wt %)
X	0.87	36.5	0.016	2.1
Y	0.84	37.1	0.005	1.0

DI water, NaCl, MgCl₂, dichloromethane, chloroform, and toluene were reagent grade from chemical distributors and used without further purification.

The functional molecule used in this work is a nonionic surfactant; the main structure is an ethoxylated resin, provided by CECA, France. It is an emulsion destabilizer used in crude oils which form tight w/o emulsions with water. A detailed study of the demulsifier (DEM) is discussed in ref 21.

2.2. Interfacial Tension and Interfacial Rheology Measurements. Interfacial tensions were measured using a Kruss “Processor tensiometer K12” adapted with a duNoüy ring. Interfacial rheology measurements are performed using the “TA Instruments ARG2” rotational rheometer adapted with a double-wall Teflon vessel and a du Noüy ring. Interfacial properties are obtained by the applied stress (σ) and strain response (γ) in terms of the frequency of oscillations (ω). σ_0 and γ_0 correspond to the stress and strain at the maximum:²²

$$G^* = \frac{\sigma_0}{\gamma_0} \exp[i\delta(\omega)] \quad (1)$$

The complex modulus G^* can be split into two components:

$$G^* = G'(\omega) + iG''(\omega) \quad (2)$$

where G' is the storage or elastic modulus related to the elastic character, G'' is the loss or viscous modulus related to the viscous character of the interface, and δ is the phase angle which gives a direct measure of the viscous and elastic character of the interface ($\delta = 0^\circ$ interface is elastic while $\delta = 90^\circ$ interface is viscous).

In each experiment, the Teflon vessel is cleaned using wipes soaked in chloroform and dried with clean wipes and dry air. The DuNoüy ring is cleaned by soaking into chloroform, then fired to remove any residue, and allowed to cool down to room temperature.

Rotational and oscillatory mappings are performed before each test to ensure that the device is calibrated and that the experimental conditions are maintained the same in all tests. Constant oscillation tests are performed for 48 h at constant temperature (24 °C) with small strain amplitude (1.0%) and frequency (0.5 rad/s). Oscillations are performed each 15 min. The evolution of the storage elastic modulus (G') and loss viscous modulus (G'') is analyzed as well as the phase angle (δ). Each test is carried out two times, and average measurements are presented.

2.3. Micromodel Experiments. Water injection experiments are performed using a commercial microfluidic device from Dolomite Microfluidics. The sketch and relevant dimensions and data of the micromodel are depicted in Figure S1 of the Supporting Information.

The aqueous phase at various salt (NaCl) concentrations is used to displace the crude oils. In one of the two oils, we also investigate the effect of surfactant addition to the aqueous phase on flow performance. Prior to each test, the micromodel is cleaned with solvents (toluene and dichloromethane) in three consequent cycles and then blown with high pressure air. Drying is performed in the oven at 120 °C overnight. After the water injection experiments, the device is only flooded with dichloromethane in forward and reverse directions until no oil residue is observed and then blown with high pressure air and dried overnight in the oven at 120 °C.

Oil is injected into the device by a 3 cm³ plastic syringe and pressurized by a “Genie Touch” syringe pump. The device is left pressurized overnight. Before the run, 1 cm³ of oil is flowed through the device.

Water injection in the microfluidic device is performed using a “Hamilton” 500 μ L glass syringe and a “Genie Touch” syringe pump. Flow rate is maintained constant at 0.1 μ L/min. After water breakthrough the injection is continued for 1 h or until only water is observed in the outlet. A transducer is used to measure the pressure at the inlet of the system. The outlet is open to the atmosphere.

3. RESULTS AND DISCUSSION

3.1. Interfacial Tension and Interfacial Rheology.

Interfacial tension of crude oil X shows that equilibrium is established in about 6 h. The equilibrium interfacial tension of the same crude oil decreases monotonically with increase in salt (NaCl) concentration. In crude Y, the interfacial tension is nearly constant with salt concentration (Figure S2). The increase of interfacial tension with increase in salt concentration is often observed in simple oils. However, crude oil are very complex fluids. There could be an increase or decrease with salt concentration. But the trend in both are monotonic. There is significant reduction of interfacial tension by addition of DEM at 100 ppm in water (1 order of magnitude). As we will see shortly, the evolution of viscoelasticity and behavior with salt concentration is very different than interfacial tension.

Interfacial storage and loss moduli evolution for oils X and Y are shown in Figure 1. Both oils form viscoelastic interfaces with DI water; however, the evolution of the viscoelasticity is

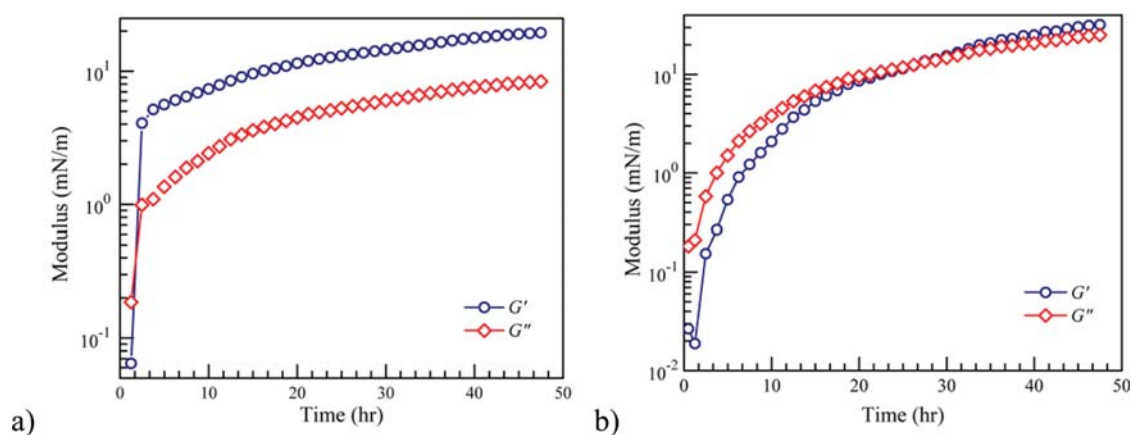


Figure 1. Storage (G') and loss (G'') moduli evolution for crude oil–DI water interfaces: (a) oil X and (b) oil Y.

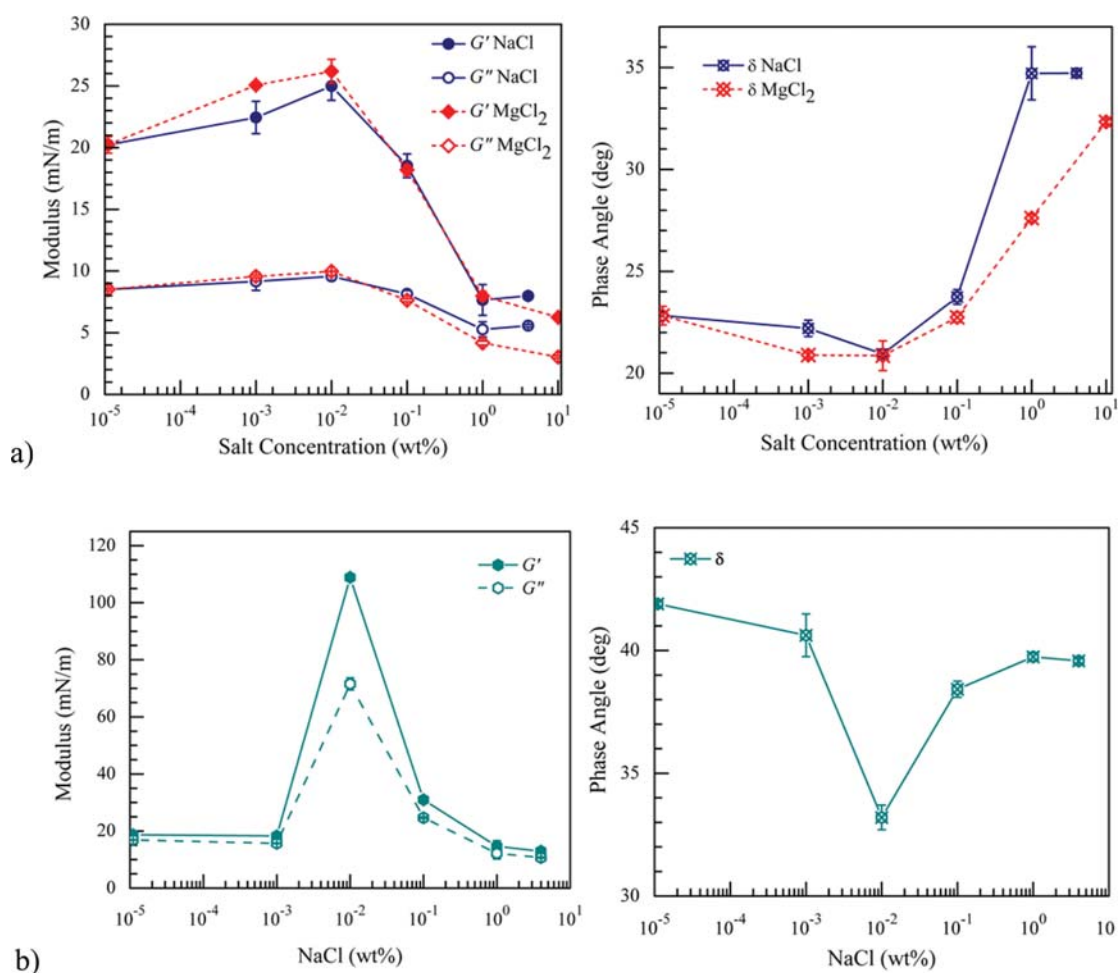


Figure 2. Storage moduli (G'), loss moduli (G''), and phase angle (δ) vs salt concentration (a) for oil X at time = 48 h and (b) for oil Y at time = 48 h.

different in the two oils. Oil X (Figure 1a) develops viscoelasticity faster than oil Y but slower than the evolution of the interfacial tension. In oil Y the interface remains elastic at all times. Oil Y (Figure 1b) develops viscoelasticity slower than oil X, and it turns from viscous to elastic. The viscoelastic behavior of the interfaces is different but both reach stabilization at about 48 h.

Figure 2 shows the stabilized viscoelasticity of the water–oil interface vs the salt concentration in oil X and oil Y. The measurements are carried out with NaCl and MgCl_2 brines in oil X and with NaCl brine in oil Y. As the salt concentration increases, the elasticity of the interface first increases, and with further increase in salt concentration there is a decrease. The effect of salt concentration on interface viscoelasticity is not

monotonic. We plot the DI water as 10^{-5} wt % salt on the logarithmic axis. In both oils, the interface seems to reach the maximum elasticity at around 0.01 wt %, regardless of the type of salt.

The change to maximum in viscoelasticity is not pronounced in oil X (Figure 2a). The elasticities are close at the low salinity and without salt. There is also no appreciable difference from NaCl and MgCl₂ at low concentrations; however, the difference becomes pronounced at high salinities. In oil Y (Figure 2b), the viscoelasticity increases sharply at 0.01 wt % NaCl. As both moduli increase steeply, the elastic character (δ) is lower than in oil X.

The viscoelasticity of the interface is a result of molecular structure formed at the interface. As Figure 1 and Figure S2a show, equilibrium interfacial tension which is related to accumulation of species at the interface evolves faster than interface viscoelasticity which is a measure species structure. Amphiphilic molecules affect the interface structure; these structures may lead to a highly viscous or highly elastic interface.²² In the oil–water interface, compounds that may form organized structures are the asphaltenes, resins, and surfactants added externally. The asphaltenes are perhaps the most complex molecules in a petroleum fluid.²³ Spiecker and Kilpatrick report the formation of elastic films of asphaltenes in water–oil interfaces.¹⁷ The elasticity of these films may be related to the molecular structures formed by the asphaltene aggregates. Asphaltenes can organize forming networks; however, the steric hindrance between aggregates prevents packed and tight structures and allows the final structure to depend as depicted in Figure 3.

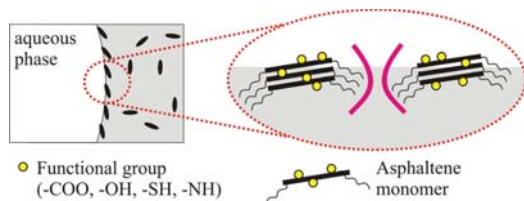


Figure 3. Asphaltenes adsorb at the crude oil–water interface. They are not tightly packed due to steric hindrance.

The effect of low salinity on the viscoelasticity of the interface can be explained in terms of the electrostatic interactions at the interface. The electrical double-layer expansion,²⁴ which has been used to explain the effect of the low salinity on the rock–fluid interface,²⁵ may be the reason for high amount of oil surface active components at the fluid–fluid interface.

Ions close to the interface adsorb to the electrically negatively charged water–oil interface forming a diffuse ionic layer. This diffuse layer screens all the interactions with the bulk solution. The effective layer thickness is related to the Debye length κ^{-1} , expressed as

$$\kappa^{-1} = \left(\frac{\epsilon_r \epsilon_0 k_B T}{2 N_A e^2 I} \right)^{1/2} \quad (3)$$

where ϵ_r is the dielectric constant of brine, ϵ_0 the permittivity of free space, k_B the Boltzmann constant, N_A the Avogadro number, e the electron charge, T is the temperature, and I the ionic strength, defined as

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (4)$$

In eq 4, c_i and z_i are the molar concentration and the valence of species i , respectively, and n is the number of different species.

The Debye length is inversely proportional to the ion concentration in brine. In Figure 4 we display a sketch of the

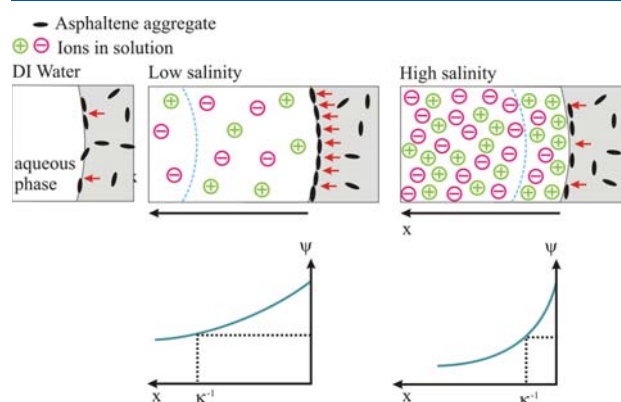


Figure 4. Ions affect the electrostatic potential (ψ) and the Debye length (κ^{-1} , dashed line) at the water–oil interface.

phenomenon. Without salts, the polar components in the oil such as asphaltenes and resins may adsorb onto the interface due to their polarity. At low concentration, the diffuse layer is very broad, so the screening is stronger and the polar components of the oil (asphaltenes and resins) are adsorbed and organized at the interface by electrostatic attractions. At high salinity, the Debye length is thin; the counterions reduce the screening of the charge reducing the attraction of the polar components to the interface.

By adding a small amount of a surfactant, the interface viscoelasticity may be tuned. In Figure 5, the viscoelastic parameters measured in the brine–oil X interface with and without surfactant are displayed. At relatively high salt concentrations the elasticity of the fluid–fluid interface decreases significantly as evidenced by the phase angle.

DEM is a nonionic surfactant known to adsorb preferentially to the water–oil interface.²⁰ The surfactant adsorbs onto the fluid–fluid interface and prevents the interaction between the polar components in the oil and the ions in the water phase as shown schematically in Figure 6. At the same time, surfactant may also stabilize asphaltenes in the oil bulk phase preventing them from stacking and forming other types of structures at the interface.

3.2. Micromodel Experiments. Low salinity brines (salt 0.01 wt %), where the maximum elasticity is observed, and high salinity brines (salt 1.0 wt %) were used to displace the two oils X and Y in the micromodel. Figure 7 shows the pressure profile at the inlet of the micromodel and images of the micromodel after displacement with aqueous solutions that form elastic and nonelastic interfaces.

In both oils, fluctuations in the pressure profiles are more pronounced in high salinity brine injection. In low salinity brine injection the pressure profile appears to be smooth (Figure S3). Pressure fluctuations can be related to oil snap-off during the course of water injection. The images at the end of the flooding are depicted in Figure S4. The measured oil recoveries are listed in Table 2.

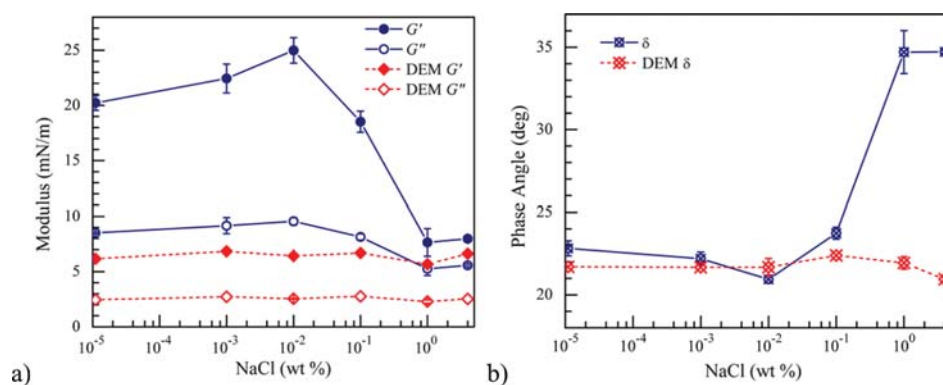


Figure 5. (a) Storage (G') and loss (G'') moduli and (b) phase angle (δ) vs NaCl concentration for oil X without and with 100 ppm of DEM.

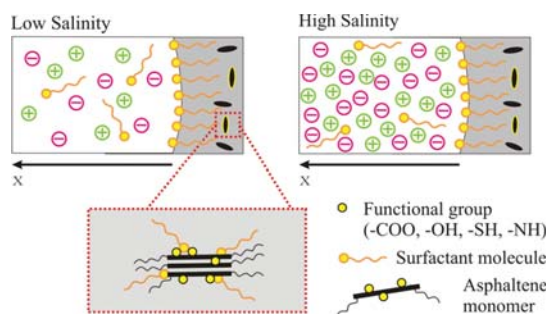


Figure 6. Sketch on the effect of surfactant at the water–oil interface.

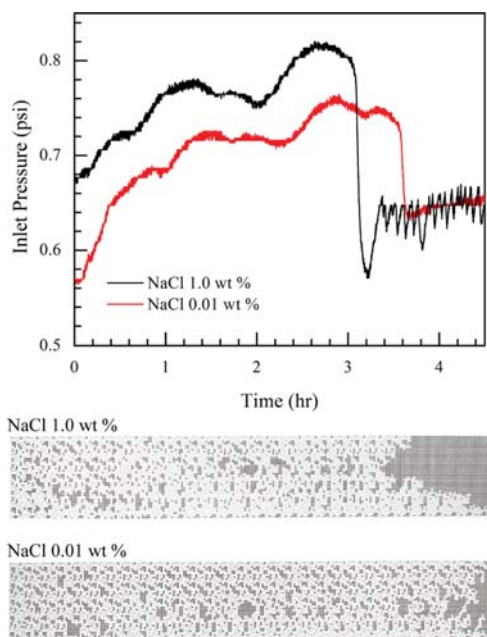


Figure 7. Pressure profile and images at the end (time = 5 h) of water injection in oil X.

The recovery efficiency increases $\sim 10\%$ in oil X from the low salinity brine in comparison with the high salinity brine while in oil Y the oil recovery increases $\sim 5\%$. At high salinity there is a distinct end effect toward the end of the micromodel at the upper right corner in Figure S4a–c. Examination of inlet pressure profiles in Figure S3 shows delayed breakthrough in two of the three tests. The increase in recovery efficiency can be

Table 2. Measured Recovery in Microfluidic Device (Time = 5 h)

oil	aqueous solution	recovery (%OOIP)
X	NaCl 1.0 wt %	50.8 ± 0.5
	NaCl 0.01 wt %	60.7 ± 1.0
	100 ppm DEM in NaCl 4.0 wt %	60.5 ± 0.4
Y	NaCl 1.0 wt %	53.6 ± 0.7
	NaCl 0.01 wt %	57.9 ± 0.4

attributed to either interfacial elastic character and or the wettability change. At the start of the tests, the wettability of the micromodel is the same in all tests; it is assumed to be mainly oil-wet. In an elastic interface, the interface becomes more deformable and delays the breakthrough and prevents snap-off of the oil phase. The pressure fluctuations in the high salinity brine injection and their absence in low salinity are likely related to the effect of viscoelasticity. However, the end effect seen in the upright corner of the glass etched micromodel may be related to wettability change. According to Freer, Svitova, and Radke,²⁶ the elastic interface may be a consequence of accumulation of higher amount of oil surface active components at the water–oil interface, as we already discussed. The surface-active components at water–oil interface may also alter wettability.

The difference in recovery efficiencies between the two oils can be explained in terms of the kinetics of the formation of the elastic interface. In oil X, the interface is elastic at all times, which corresponds to the time scale of the micromodel waterflooding, while in oil Y, the interface elasticity may takes longer to develop. Therefore, a strong elastic effect may not show up in the time scale of the experiments.

The interface viscoelasticity may also develop when a small amount of the nonionic surfactant is added to the injected water. In a number of water injection tests in rocks we have observed pronounced pressure fluctuations from displacement of oil by water.²¹ The addition of DEM reduces pressure fluctuations. It also reduces pressure drop. In this work we conduct microfluidic tests. Because of the addition of surfactant, the interface develops an elastic character as in the low salinity, although the modulus values are lower. The pressure profile in the micromodel shows much less fluctuations with added DEM. Surfactant effect on viscoelasticity becomes predominant at high salinity (Figure 5).

4. CONCLUSIONS

In this work we have investigated interface viscoelasticity of the petroleum fluid–water interface over a wide range of salt concentrations. We have also studied the combined effect of surfactant and salt concentration on the interface viscoelasticity. The surfactant is known to accumulate at the fluid–fluid interface of petroleum fluid–water systems. In parallel with viscoelasticity data, we have also investigated the effect of salt concentration on flow and oil recovery efficiency in a microfluidic device. Two different salts and two different petroleum fluids are used in our investigation. The essences of the findings from this work are:

1. Oil–water interface viscoelasticity may have a non-monotonic behavior as a function of salt concentration. A maximum is observed at low salt concentration. The trend is observed with two different salts (NaCl and MgCl₂) and in two petroleum fluids. The effect of salt concentration on viscoelasticity of one the two crudes is stronger.

2. The introduction of a small amount of a nonionic surfactant, 100 ppm, makes interface viscoelastic over the whole range of salt concentration. There is no appreciable effect of salt concentration on interface viscoelasticity with the added surfactant.

3. Results from oil displacement by water in a microfluidic device show that, in low salinity water injection, higher oil recovery is observed. At high salinity water injection there is significant pressure fluctuations after water breakthrough. We interpret pressure fluctuations to be from interface breakup.

This investigation has set the stage for molecular simulations to improve the understanding of the basic mechanisms of molecular structure formation at the fluid–fluid and fluid–rock interfaces and practical determinations in relation to brine chemistry for improved oil recovery. The results from molecular modeling will be submitted for publication separately.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.5b04354.

Figures S1–S4 (PDF)

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Notes

The authors declare no competing financial interest.

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