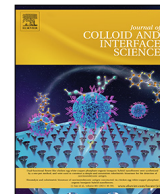




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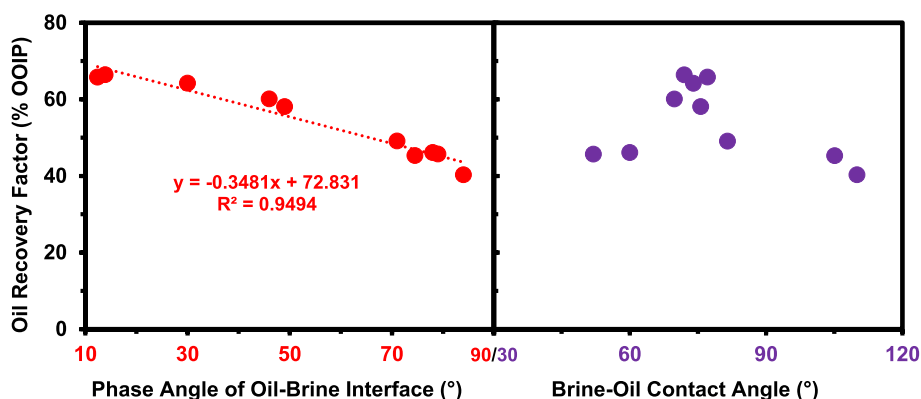
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Assessment of low salinity waterflooding in carbonate cores: Interfacial viscoelasticity and tuning process efficiency by use of non-ionic surfactant

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Hypothesis. A large number of papers discuss merits and mechanisms of low salinity waterflooding. For each mechanism proposed, there are counter examples to invalidate the stated mechanism. The effect of wettability from low salinity water, which is predominantly stated in literature as the dominant mechanism, may not be valid. We introduce a direct correlation between oil-brine interfacial viscoelasticity and oil recovery from waterflooding.

Experiments. The oil recovery is investigated in carbonate rocks for three light crude oils; by injection of a wide range of aqueous phases, ranging from deionized water to very high salinity brine of 28 wt%, and low concentration of a non-ionic surfactant at 100 ppm. The oil-brine interfacial viscoelasticity is quantified and supplementary measurements of interfacial tension and wettability are performed.

Findings. In our experiments, oil recovery is higher from high salinity water injection than from low salinity water injection. A strong relationship is observed between interface elasticity and oil recovery for different concentrations of salt in the injected brine as well as for ultra-low concentration surfactant. An elastic oil-brine interface results in high oil recovery. The surfactant molecule we have selected prefers the oil–water interface despite high solubility in the oil phase and makes ultra-low concentration of 100 ppm in injection water very effective. Contrary to widespread assertions in the literature, we find no definitive correlation between oil recovery and wettability.

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1. Introduction

Enhancement of oil recovery by modification of the injection brine composition or supplementation with surfactants and polymers has been widely researched. Low salinity waterflooding (LSW) was first investigated in sandstones [1] and has been extensively studied in carbonates in recent years [2,3]. Improved oil recovery (IOR) in carbonates by LSW has primarily been thought to be due to wettability alteration from mixed-wet to water-wet [4–7]. This mechanism is argued to be different in sandstones and carbonates due to different surface charges. There may also be a significant effect of injection rate on oil recovery at less water-wetting conditions. Tang and Firoozabadi [8] have performed detailed investigations on the effect of water saturation and wettability state on water flooding as well as imbibition for carbonate rock. They conclude that the wettability state does not necessarily determine waterflooding efficiency. Additionally, spontaneous imbibition may not relate to field performance. Some surfactants in the injected brine alter wetting from less water-wetting to more water-wetting conditions. There have been reports of IOR in LSW without change of wettability in carbonates. Zahid et al. [9] found a 10% improvement in oil recovery by waterflooding in chalk samples despite the fact that the rock was water-wet in both low and high salt water injection. The authors attribute the extra oil recovery to chemical reactions on the surface of chalk due to sulfate in brine and the composition of crude oil, rather than to wettability alteration. Some prominent studies have proposed mechanisms including fines migration and consequent permeability reduction for sandstones [10], increase in pH and reduction in interfacial tension [11], multicomponent ion exchange [12], and double layer expansion [13]. Most of these mechanisms are, in turn, related to wettability and are proposed as causes of wettability alteration. LSW has more commonly been investigated for tertiary recovery compared to secondary recovery, but not always with success [14–17]. Results from Zhang and Morrow [18] show lower recovery from LSW compared to high salinity injection. There have been attempts to further improve LSW efficiency by modifying injection brine composition. Uetani et al. [19] reported a 23% increase in recovery from tertiary LSW by adding 1.1 wt% naphthenic acid to the crude oil (compared to a 2–4% increase using original crude oil). Chávez-Miyauchi et al. [20] studied LSW in both secondary and tertiary modes in Berea sandstone with three crude oils. They observed a synergy between secondary oil recovery and oil-brine interface elasticity. LSW in tertiary mode is not found to significantly increase oil recovery after secondary-mode high salinity waterflooding. Even in secondary recovery mode, LSW is found to be more efficient than high salinity water injection for only one oil. In the case of the other two crude oils, heating the crude resulted in improved recovery from LSW. The finding of no substantial efficiency of LSW in similar studies motivates our investigation to expand the range of injection brine salinity and to observe the effect on IOR in relation to oil-brine interfacial viscoelasticity.

The above studies indicate that LSW is not universally effective and may even be ineffective compared to seawater injection, depending on the oil, brine, and rock. An important issue is the uncertainty as to the primary mechanism. Despite numerous studies and vast literature on the subject, there is no universal consensus on the primary mechanism of LSW [13,21–30].

In a departure from the mechanism of wettability alteration, Emadi and Sohrabi [31] proposed two hypotheses for the efficiency of LSW: wettability alteration and swelling of formation brine due to movement of water-in-oil micro-emulsions through the bulk oil phase to the connate brine film. The swelling of formation brine is hypothesized to release trapped oil droplets, leading to a decrease in residual oil saturation. Ayirala et al. [32] find an increase in vis-

cus modulus of oil-brine interface with decrease in brine salinity. The authors attribute the increase in interface viscous modulus to increased interfacial film stability and increased coalescence time of oil droplets. They conclude that an increased film stability reduces affinity of water ions towards the rock surface and releases the trapped oil by wettability alteration, which reduces residual oil. In a recent study, Song et al. [33] have performed spontaneous imbibition on seven oils (six crude oils and one model oil) using Indiana limestone carbonate rock and found a strong correlation between IFT of oil-brine system and increase in recovery. Low salinity brine induces favorable wettability alteration, and the authors state the formation of micro dispersions is not a prerequisite for efficiency of low salinity brine injection.

While IFT is a thermodynamic property, interfacial viscoelasticity is a mechanical property and relates to molecular structure. Interfacial viscoelasticity is represented in terms of two parameters: storage modulus, quantifying the elastic nature of the interface; and loss modulus, which characterizes the viscous nature of the interface [34]. These moduli can be obtained in rheometers by performing either [35] controlled shear deformation on a constant interfacial area [36–38] or dilatational rheological measurements on a changing interfacial area [39–42]. The setups used for the interfacial measurements are extremely sensitive [43,44].

The alteration of dilatational rheological properties by movement of surfactant molecules towards the oil–water interface has been studied for desorption of asphaltenes using demulsifiers to break water-in-oil emulsions by asphaltene stabilization during crude oil production [45]. Freer et al. [46] have measured the oil–water interfacial viscoelasticity for two crude oils of varying asphaltene content. They have found the crude oil with higher asphaltene content to have slower growth in elasticity, while the other quickly stabilizes but forms a weak elastic interface due to the development of a weaker asphaltene network. They emphasize the significance of sufficient aging time of the oil–water interface during rheology and wettability measurements due to the movement and arrangement of surface-active molecules. The oil-brine interfacial rheology can be studied to shed light on oil recovery [47,48]. The oil-brine interfacial elasticity may depend on brine concentration, oil type, and salt composition. In oil recovery during waterflooding, an elastic interface implies uniform progression of the oil front. The snap-off of oil phase is reduced, resulting in alleviated pressure fluctuations after breakthrough, which gives higher oil recovery [49]. Addition of a surfactant at a low concentration can significantly affect the interface elasticity.

The effect of oil-brine interfacial viscoelasticity in waterflooding has been explored recently [20,49–51]. In a study on the effect of asphaltenes and organic acids on oil-water interfacial viscoelasticity and oil recovery in sandstones, Garcia-Olvera et al. [52] conclude that higher asphaltene content in crude oil may lead to higher interfacial viscoelasticity, while organic acids may lower the viscoelasticity. However, in the coreflood experiments, addition of naphthenic acid to the injected brine led to significantly higher oil recovery, as compared to naphthenic acid added to crude oil or no acid addition. The authors suggest an optimum interfacial viscoelasticity wherein the snap-off reduction and increase in coalescence speed of oil droplets during waterflooding are combined to provide desirable recovery. Cho et al. [53] have found significant increase in interfacial elasticity when a very small amount of a non-ionic surfactant is added to injected high salinity brine. Higher interface elasticity gives higher oil recovery in carbonate waterflooding in two different carbonate rocks. LSW does not give significant increase in the interface elasticity and oil recovery. In a recent work [54], we have expanded the salinity range of injection brine and investigated the effect of ultra-low concentration of non-ionic surfactant on oil-brine interface viscoelasticity and its influence on oil recovery from waterflooding. A non-monotonic trend

of oil-brine interface elasticity is established with respect to brine salinity and addition of the surfactant in high salinity brine gives similar elasticity results as low salinity brine, leading to an increase in oil recovery compared to high salinity brine injection alone. Very recently, Wu and Firoozabadi [55] have conducted microscopic imaging analyses using the same non-ionic surfactant as in our previous work [54] and found evidence of demulsification in the bulk oil phase and spontaneous emulsification near the oil-brine interface. The spontaneous emulsification near the interface is surmised to be related to the IOR efficiency when surfactant is added to the injection brine.

In this study, we investigate oil recovery for three crude oils extracted from different regions in the Middle East. Expanding on our previous works [53,54], we use seawater rather than brine with sodium chloride alone in order to simulate a more realistic approach to process efficiency. The focus of this work is the effect of oil type on oil-brine interface elasticity and implications for IOR. With one of the crude oils, the interfacial elasticity between the oil and injected brine is high, and the functional molecule does not appreciably change the interfacial viscoelasticity. In the other two crude oils, addition of the functional molecule (non-ionic surfactant) to the injection brine increases the interface elasticity, resulting in increased oil recovery. We perform wettability and IFT measurements, with and without the functional molecule, along with viscoelasticity measurements to improve our understanding of the waterflooding process and to determine the primary mechanism. Interfacial viscoelasticity measurements are performed by adding 100 ppm surfactant in brine and in the oil in different experiments to examine the transfer to the interface. These new experiments establish the process which makes the surfactant so effective at ultra-low concentration of 100 ppm in the aqueous phase despite high solubility in the oil phase. The effect of brine salinity on oil-brine interface elasticity is investigated using injection water with a wide range of salt concentrations. The efficiency of seawater is compared to that of low salinity water. Ultimately, the recovery performances for all three crude oils are correlated to a single parameter: phase angle representing the interface elasticity. A strong linear relation between recovery and interface phase angle reaffirms the primary parameter affecting waterflooding performance.

2. Experimental procedure

The experimental procedures for characterizing the oil samples, wettability, interfacial tension, interfacial viscoelasticity measurements, and core preparation have been presented in [53,54]. The Supporting Information includes a brief description for the sake of completeness. Experimental details of interfacial viscoelasticity measurements from surfactant dissolution in both oil and aqueous phases and coreflood tests are presented in the main manuscript. As mentioned above, the interfacial viscoelasticity change is from the dissolution of 100 ppm surfactant in the aqueous phase in most measurements and also from dissolution in the oil phase in a number of measurements.

Table 1
Brine composition (weight percent).

Salt	Salt Concentration (wt%)						
	Very High Salinity (VHS)	Formation water (FW1)	Formation water (FW2)	Seawater (SW1)	Seawater (SW2)	High Salinity (HS)	Low Salinity (LS)
NaCl	20.49	6.03	6.03	3.16	3.16	4.00	0.10
KCl	0.64	0.30	0.30	0.09	0.09	–	–
CaCl ₂	5.60	1.44	1.90	0.13	0.18	–	–
MgCl ₂	1.30	0.74	1.59	0.54	1.15	–	–
SrCl ₂	–	–	0.06	–	0.002	–	–
Na ₂ SO ₄	0.05	–	–	–	–	–	–

Fluids. Properties of the three oils (A, B, and C) used in this study are listed in the Supporting Information (Table S1). Brines are prepared by mixing salts in deionized (DI) water. Two different formation water (FW) and seawater (SW) compositions are used. Very high salinity (VHS), high salinity (HS) and low salinity (LS) water are from NaCl solutions. The brine compositions are detailed in Table 1. Toluene, dichloromethane (DCM), and methanol are from Fisher Chemical and have a purity of more than 99.5%. These three chemicals are used to clean the core before each coreflood experiment. The proprietary chemical used in this work is a non-ionic surfactant; the main structure is an ethoxylated resin from Nalco Champion, Ecolab, USA. It is an emulsion destabilizer for crude oils which form tight water-in-oil emulsions. This type of chemical has been investigated extensively in our previous works [53–56]. It is a demulsifier in the bulk oil phase but promotes spontaneous emulsification near the oil-brine interface [55]. Due to bulk oil demulsification from the surfactant, the abbreviation—“DEM” is used throughout the work to denote the surfactant. Since the critical micelle concentration (CMC) and cloud point of DEM are 30 ppm and around 200 ppm, respectively, a concentration of 100 ppm has been found to be effective in our past works. Increasing the chemical concentration to 200 ppm gives similar results [53], hence, we use a concentration of 100 ppm in the injected water.

Interfacial Viscoelasticity. An Anton Paar MCR 302 rheometer with a du Noüy ring and double wall geometry [57,58] is used for controlled shear deformation oscillatory runs. The angular frequency of oscillation and maximum amplitude strain are accordingly adjusted at 0.5 rad/sec and 1%, respectively, for Oils A and B, and at 3.14 rad/sec and 0.3% for measurements with Oil C. In the rheometer, the encoder on the head of the measuring system is divided into small angles, corresponding to the amplitude of strain required. This leads to an angular deflection. The sensors attached to the motor read the angular deflection and we apply torque to make the deformation. Depending on the viscoelasticity of the interface, there may be a response lag to deformation, indicating that strain will lag stress. At steady state conditions, the resulting stress has a sinusoidal behavior, similar to strain; however, there will be a gap of phase between the two forces, depending on the viscoelastic property of the liquid–liquid interface. This gap is referred to as phase angle. The peaks in the sinusoidal plots of shear stress and strain are read at 1-minute time intervals, and the difference between the two plot readings is the phase angle. In completely elastic interfaces, there will be no lag in response, and phase angle is 0. For highly viscous interfaces, the lag between stress and strain can be as high as 90°. Two important parameters are provided from the measurements: storage and loss moduli. Storage modulus (G') represents the elastic nature of the interface and loss modulus (G'') relates to the viscous nature of interface. Combination of these two parameters provides the phase angle (δ), which we use as a measure of oil-brine interface elasticity. The runs are continued, ranging from 18 to 48 h, until both moduli become stable. Some runs are continued up to 60 h to verify the stability of the interface.

We have found an effect of ion dissolution from the rock surface into the aqueous phase on interfacial viscoelasticity measurements, especially for DI water in our previous study [54]. To take this effect into consideration, the DI water is equilibrated with the carbonate rock for a period of 24 h. The rock-equilibrated water is then used to repeat the viscoelasticity measurement for Oil C and DI water interface.

Additional interfacial viscoelasticity measurements are conducted using a model oil; by dissolving asphaltenes separated from oil C in toluene. The purpose is to analyze the direct effect of surface-active crude oil components (asphaltenes) and the added surfactants (DEM) on the interface behavior. Experimental details and results are presented in the Supporting Information.

Coreflood. Edwards Yellow outcrop carbonate rock of 1.5" in diameter and 6.0" in length is used in waterflooding experiments. Fresh core is used for each experiment. The confining pressure is applied at 400 psi during the coreflood and the pressure at the inlet of the core is recorded. The coreflood temperature is 60C in Tests 1 to 4 and 25 °C in Tests 5 to 11. In Tests 1 and 2, back pressure is applied with nitrogen gas at 100 psi. For all other tests, the pressure at the outlet is atmospheric. At the end of the test, flow rate is increased five times (Tests 1 to 4) and three times (Tests 5 to 11) to examine the end effect and wettability state.

3. Experimental results and discussion

Interfacial Viscoelasticity. Stabilized values of the elastic moduli (G'), viscous moduli (G''), and phase angle (δ) of various interfaces of aqueous phases and oils A,B, and C, along with standard deviations from repeat tests, are reported in the Supporting Information (Tables S3-S5). The moduli for oils A and B are relatively lower compared to oil C, which may be due to higher asphaltene content in Oil C (Table S1). The effect of the difference will be discussed in an examination of the brine injection performance in the next section.

Phase angle parameter is obtained from the inverse tangent of the ratio of G'' and G' . A lower value of phase angle corresponds to more elastic interface. For Oil A, G'' is slightly lowered by addition of the non-ionic surfactant, indicating lowered viscosity of interface, but this change is not substantial. The G' values are comparable for both cases. The interface is elastic and addition of surfactant does not significantly change the interface viscoelasticity. The results for Oil B show a pronounced effect of non-ionic surfactant on G' . It increases significantly with the addition of DEM, especially at higher salt concentrations. This indicates increase in oil-brine interface elasticity. In oils B and C, the interface is more viscous than Oil A, and the highest interface viscosity is obtained for

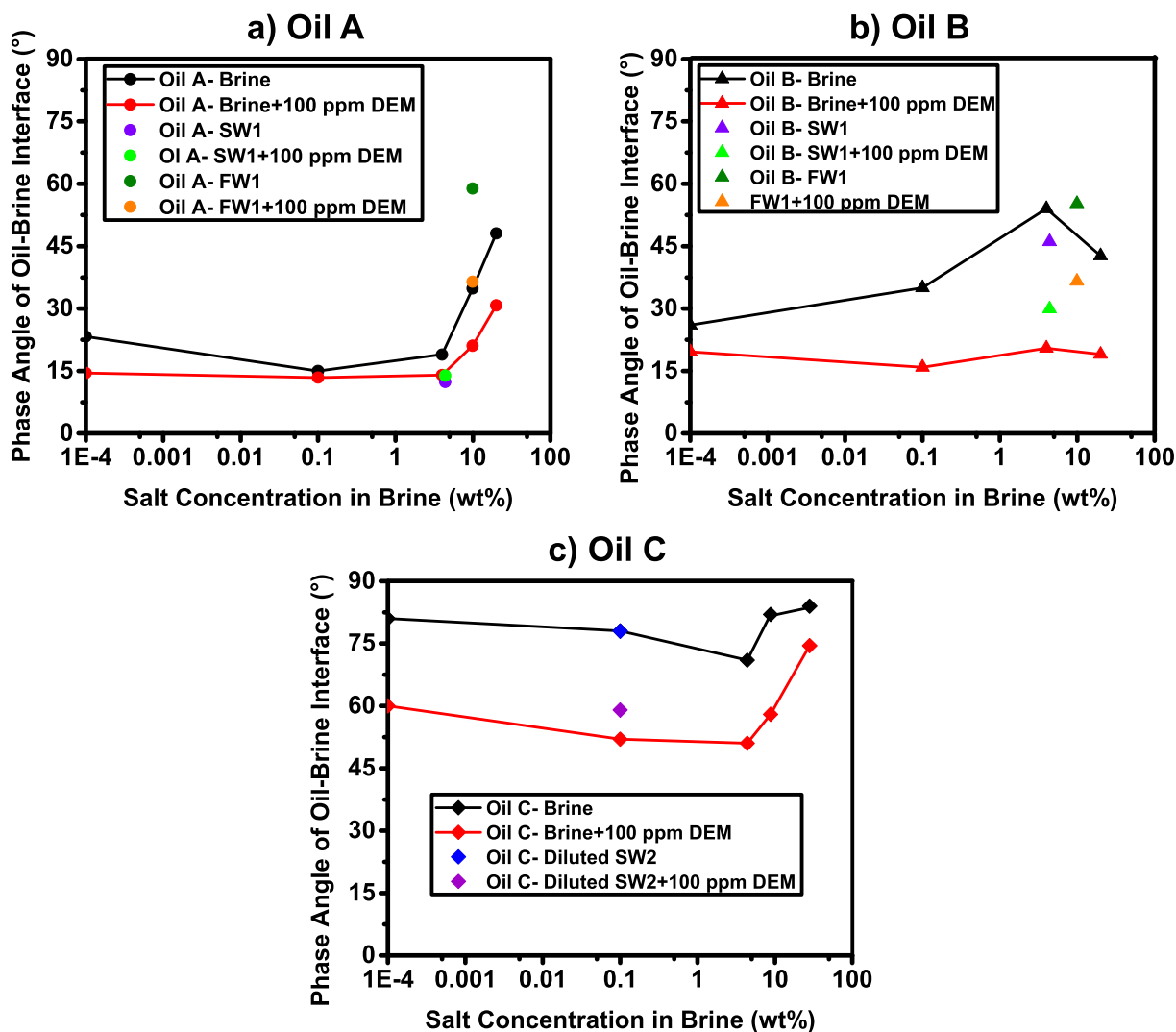


Fig. 1. Phase angle vs. salt concentration in brine, without surfactant DEM (black) and with 100 ppm surfactant DEM (red).

Oil C. The addition of 100 ppm of DEM in brines significantly improves the interface elasticity over the whole range of salinities examined. A non-monotonic trend for phase angle vs. brine salinities is observed for all three oils; see Fig. 1.

Coreflood Performance. Pore volume (PV) injection at breakthrough, recovery at breakthrough, injection rate, and cumulative oil recovery obtained from all coreflood runs are shown in Table 2. The recovery vs. PV injection is plotted in Fig. 2.

For Oil A, there is no significant difference in oil recovery or breakthrough time between the seawater (SW1) injection with and without DEM. The Coreflood breakthrough by SW1 injection is at 45% oil recovery; it is at 43% oil recovery by SW1-DEM injection. Final oil recovery from seawater injection alone is about 66 % (Oil A). The high recovery may be related to high elasticity of the oil-brine interface. Addition of surfactant does not significantly change oil recovery (about 66.5%). The oil-brine interface elasticity, represented by the phase angle parameter, is about the same with and without DEM for Oil A (Fig. 1a). There is no extra oil recovery when the flow rate is increased from 4 PV/d to 20 PV/d, implying no end effect (Fig. 2a).

For Oil B, breakthrough time in injection of SW1 with DEM is delayed, with a higher recovery (Test 4; 0.46 PV injection, oil recovery 53%) compared to that of SW1 injection (Test 3; 0.3 PV injection, oil recovery 33%). The final oil recovery at 2 PV/d of SW1-DEM is higher than that of SW1 injection (64.2% for SW1-DEM and 60.1% for SW1). This is corroborated by the interfacial elasticity of Oil B-seawater, which has substantially higher elasticity with the addition of 100 ppm of DEM, as seen in Fig. 1b. There is no significant extra oil recovery after the flow rate increases to 10 PV/d. The final oil recovery is about 66% from SW1-DEM and 62% from SW1 injection.

The recovery of Oil C is comparatively lower than those from oils A and B. This is in line with the more viscous oil-brine interface of Oil C, corresponding to a less controlled movement of oil front in the porous media. Surprisingly, recovery from LS is lower than from SW2 injection, but the difference is not significant. DI and LS injection result in comparable recoveries (45.7, 46.1%). The addition of 100 ppm DEM to SW2 gives an increase in recovery of 18%, owing to a 31% increase in oil-brine interface elasticity (reduction

in phase angle). The addition of 100 ppm DEM to very high salinity (VHS) brine increases the recovery by 12.4%, which is less than when it is added to SW2 (Table 2). This is consistent with the lower change in interface elasticity. When 100 ppm DEM is added to VHS brine, phase angle is reduced by about 12%, which is comparatively lower than the change from DEM addition to SW2 and other brine concentrations (Table S5). Increasing the flow rate from 1 to 3 PV/day results in less than 10% increase in recovery for all six brine injections, indicating no significant end effect and limited effect from wetting, as shown in Fig. 2c.

Relation between Interfacial Viscoelasticity and Oil Recovery. For all the 11 coreflood experiments, measured phase angle of the oil-brine interface has a strong correlation with oil recovery (Fig. 3). Lower phase angle relates to higher interface elasticity and higher oil recovery. This correlation holds true regardless of the oil type, salt concentration and type, and presence of surfactant in brine. Fig. 3 displays the essence of our investigation.

No definitive trends can be observed from the plots of contact angle and IFT data, with respect to oil recovery from coreflood experiments, as shown in Figs. 4 and 5. A general trend of increase in recovery with decrease in IFT is observed from Fig. 5. The relation is not as pronounced as the strong linear relation observed for the interfacial viscoelasticity with respect to oil recovery.

To better understand the effectiveness of the DEM at 100 ppm, we measure interfacial elasticity from dissolution of DEM in the oil phase (Oil C). The concentration is 100 ppm. The development of phase angle from viscoelasticity measurements, is compared with that of the base case (Oil C-seawater SW2 interface with no surfactant) and the case of 100 ppm DEM added to SW2. The results are presented in Fig. 6. As stated earlier, the decrease in phase angle represents an increase in interfacial elasticity. For the base case, interface viscoelasticity is influenced by surface-active components at the oil-brine interface; these are mainly polar oil components (asphaltenes and resins). When DEM is added to seawater (Fig. 6), there is an instantaneous effect on increase in interface elasticity compared to the base case. This indicates the affinity of the surfactant towards the interface, where it undergoes interaction and rearrangement with other polar species. The DEM near the interface may also attract more surface active species from

Table 2
Breakthrough performance and final recovery from coreflood experiments.

Test No.	Oil	Injection Brine	PV required for BT (PV)	Oil Recovery Factor at BT (% OOIP)	PV Injected (PV)	Injection Rate (PV/day)	Oil Recovery Factor (% OOIP)
1	A	SW1	0.37	45	0–1.8	4	65.8
2	A	SW1 + 100 ppm DEM	0.37	43	1.8–5	20	65.8
					0–2	4	66.4
3	B	SW1	0.30	33	2–5	20	66.4
					0–2	2	60.1
4	B	SW1 + 100 ppm DEM	0.46	53	2–5	10	62.0
					0–1.9	2	64.2
5	C	SW2	0.28	37.2	1.9–4.9	10	66.0
					0–1.8	1	49.1
6	C	SW2 + 100 ppm DEM	0.33	44.1	1.8–5	3	52.2
					0–2	1	58.1
7	C	LS	0.32	41.8	0–2	1	46.1
					2–5	3	50.3
8	C	DI	0.26	35.3	0–2	1	45.7
					2–5	3	49.3
9*	C	SW2 + 100 ppm DEM	0.31	43.5	0–1.9	1	58.0
					1.9–4.9	3	61.9
10	C	VHS	0.24	32.4	0–1.9	1	40.3
					1.9–4.9	3	43.5
11	C	VHS + 100 ppm DEM	0.26	34.9	0–1.9	1	45.3
					1.9–4.8	3	48.3

BT- breakthrough; OOIP- Original oil in place;
* Test 9 is a repeat of Test 6; different brine compositions are listed in Table 1.

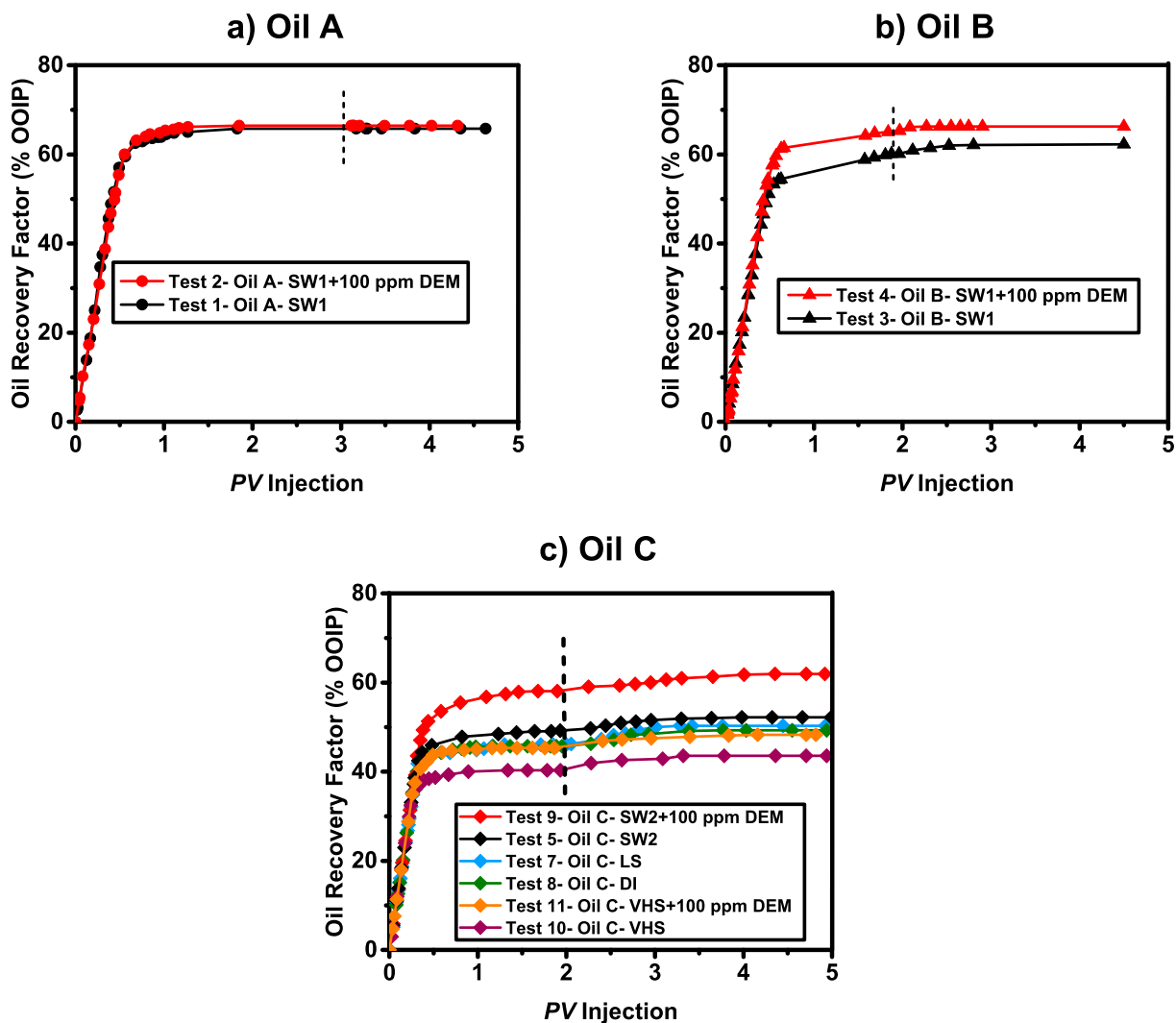


Fig. 2. Oil Recovery vs PV injection from coreflood experiments with three different oils; black dashed line represents increase in flow rate (a) from 4 to 20 PV/day; (b) 2 to 10 PV/day; (c) 1 to 3 PV/day. [(Test 9 is a repeat of Test 6)]

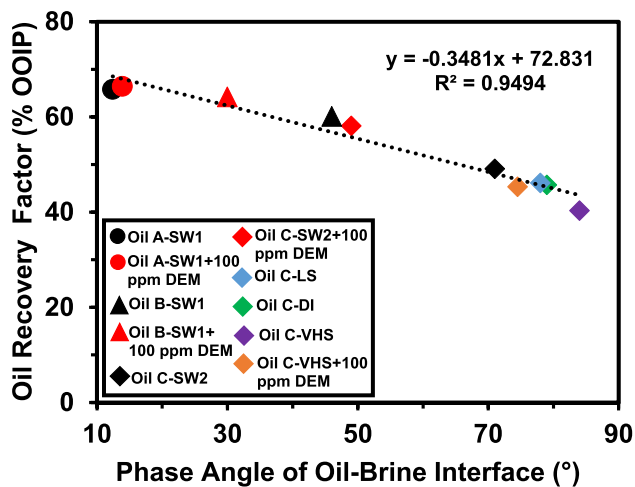


Fig. 3. Oil Recovery vs. phase angle of oil-brine interface in three different oils and injection of various brines.

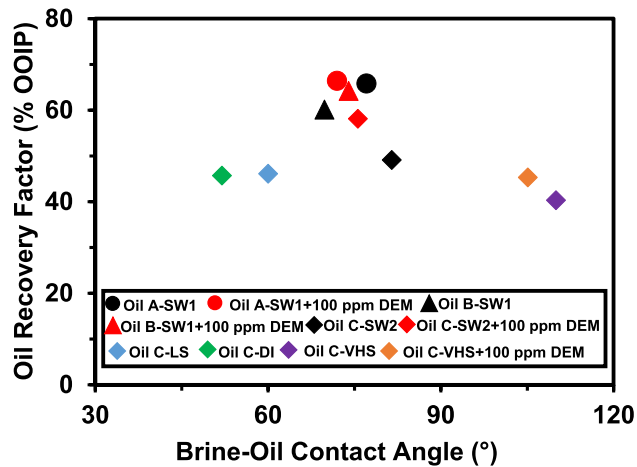


Fig. 4. Oil recovery vs. contact angle in three different oils and injection of various brines.

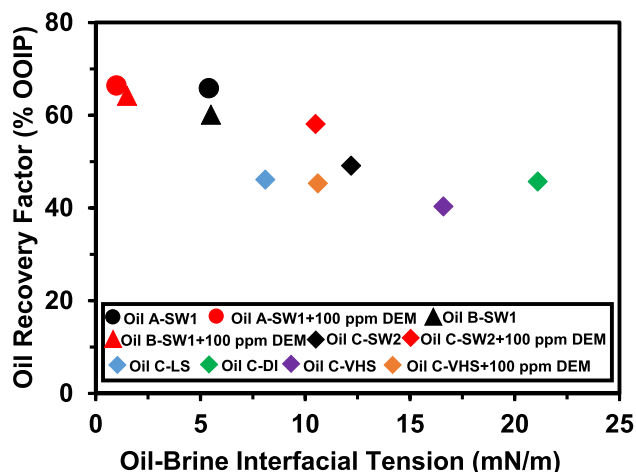


Fig. 5. Oil recovery vs. oil-brine interfacial tension in three different oils and injection of various brines.

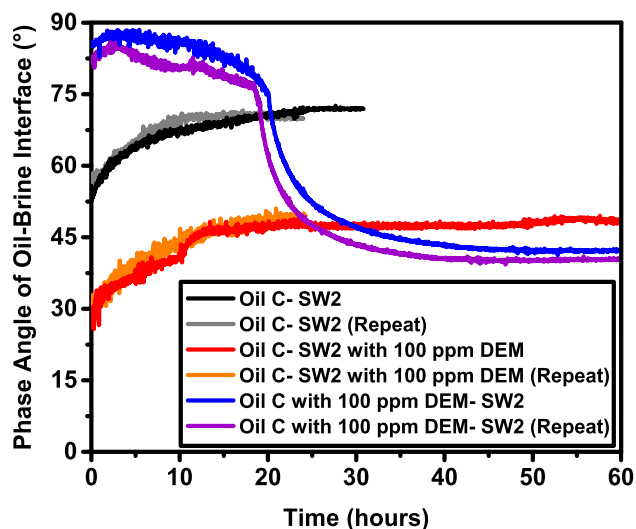


Fig. 6. Phase angle of oil-brine interface vs. time for Oil C-seawater SW2, Oil C-SW2, with 100 ppm DEM added to brine phase, and Oil C-SW2, with 100 ppm DEM added to oil phase.

the bulk oil phase towards the interface. When the structural arrangement reaches equilibrium, a stable phase angle is established. The interface development moves from elastic towards viscous. This is interpreted to be the transition of a portion of the surfactants towards the bulk oil phase from the interface region. The surfactant demulsifies the brine-oil emulsions in the bulk phase and can create spontaneous emulsification near the interface. The primary component of DEM is an ethoxylated resin, which may have an affinity towards the polar species in oil phase (asphaltenes and resins). A significantly lower initial interfacial elasticity when DEM is added to bulk oil phase (Fig. 6) may be due to considerable DEM interaction with polar oil species in the bulk oil phase. With time, the surfactant and surface-active oil components transit towards the oil-brine interface. The alignment of surfactant molecules at the interface results in increased elasticity. Equilibration takes longer when the DEM surfactant is added to the oil phase, but the stable phase angle is comparable to the equilibrium phase angle when the DEM is added to the brine phase. Fig. 6 provides a strong indication of the affinity of DEM towards interface compared to the bulk phases.

Recently it has been suggested that DEM is an effective demulsifier for water-in-oil emulsions in the bulk phase and that it promotes spontaneous emulsification at the oil-brine interface [55]. The results support our findings that the DEM accumulates near the oil-brine interface (Fig. 6). Further results from model oil (asphaltenes dissolved in toluene)-seawater system corroborate the more elastic interface behavior upon adding DEM to the aqueous phase (Fig. S2). The implication is that the adsorption onto the rock surface may be much less than reported in [54] where measurements are conducted on the brine-rock system without the presence of oil-brine interface. This leads to the conclusion that the DEM surfactant prefers oil-brine interface over the oil phase, brine phase or fluid-rock interface for accumulation. For applications in IOR the objective is a more elastic interface to propagate a smooth movement of the oil front during waterflooding. An elastic interfacial film is more stable compared to a viscous film [59]. This would mitigate breaking off of the oil phase, leading to fewer residual oil droplets. The interfacial rheology (structural arrangement of molecules), not the interfacial tension, is the determining parameter. Spontaneous emulsification near the oil-brine interface from [55] and coreflood results all point to super-efficiency of brine injection through the increase of oil-brine interface elasticity.

4. Conclusions

Based on the coreflood test results and the interfacial viscoelasticity, wettability, and interfacial tension measurements, we draw the following four conclusions:

1. When a crude oil-injection brine forms a highly elastic interface, the recovery is high whether the injection brine salt concentration is high or very low. On this basis, decrease in salinity may decrease oil recovery. Our observation of lower recovery from low salinity water compared to seawater injection, despite being different from the vast literature on the subject in carbonate rocks, is in agreement with the interface elasticity mechanism.
2. When the addition of surfactant to the injection brine results in the increase of the oil-brine interfacial elasticity, there is an increase in oil recovery. In one of the crudes used in this study, there is an 18% increase in oil recovery with surfactant addition to seawater, corresponding to a 31% increase in oil-brine interfacial elasticity represented by the phase angle.
3. Wettability may not correlate with residual oil saturation from brine injection. To a lesser degree, the same may be true for interfacial tension in the range of about 1 to 20 mN/m. Our observation from the effect of wettability on oil recovery is different from the established literature and in agreement with the results in [8].
4. When it is dissolved in either bulk water or oil phase, the non-ionic surfactant used in our work has a strong affinity for the oil-brine interface leading to an elastic fluid–fluid interface. As a result, the surfactant becomes effective at ultra-low concentration of 100 ppm.

We characterize oil-brine interfacial elasticity by the phase angle, which incorporates both the storage and loss moduli. Because the surfactant has low adsorption onto the rock [54] and has high affinity for oil-brine interface, it is very effective at ultra-low concentration. When the oil-brine interfacial elasticity is high, addition of the surfactant does not increase elasticity further. The oil-brine interfacial viscoelasticity is directly related to oil recovery over a wide range of brine salinities, brine ionic composition, and oil type for the same carbonate rock. An important conclusion to be drawn from this work is that high salt concentra-

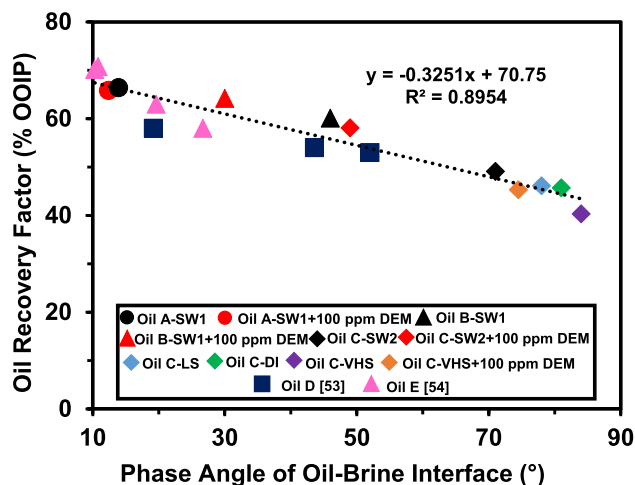


Fig. 7. Oil Recovery vs. phase angle of oil-brine interface in three different oils and injection of various brines (Fig. 6), along with data of 2 oils from previous publications [52,53].

tion brine coproduced with oil may be injected back into the carbonate formations with addition of 100 ppm surfactant, increasing recovery and helping with environmental stewardship in oil production.

In recent years the effect of oil-brine interfacial viscoelasticity on oil recovery has gained attention. The increase and decrease in interfacial viscoelasticity have been linked to brine salinity and composition [53], asphaltene content [52], and oil droplet coalescence time [32]. No relation has been put forward to the best of our knowledge. In this work, we demonstrate a clear direct relation between the interfacial viscoelasticity parameter (phase angle) and oil recovery from waterflooding by incorporating an inclusive range of brine salinities, compositions, and oils. To corroborate our findings, we have extracted data of two oils from recent publications [53,54] and found a reasonable fit (Fig. 7). The average porosity and permeability of the carbonate rocks incorporated are about 24%/40 mD [53] and 25%/12 mD [54], compared to 23%/11.5 mD in our experiments. When we include the data from two previous studies in Berea sandstone [20] and microfluidic device [49] for water injection, respectively, a deviation from trend is observed. This is also true for the carbonate rock with vugs (about 17% porosity, and 430 mD permeability) [53]. For different rocks it seems the slope of the plot varies but the trend is the same in all the reported data in the literature.

In ongoing studies, we are investigating the synergy of polymers and surfactants in oil recovery when added to injection brine, and the effect of these chemicals on interface rheology and mobility. New surfactants may also be engineered that have more drastic effect on interfacial viscoelasticity.

CRedit authorship contribution statement

Taniya Kar: Conceptualization, Experimental Work, Writing – review & editing. **Hyeyoung Cho:** Four Coreflood Experiments. **Abbas Firoozabadi:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2021.08.028>.

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