



ENHANCED RECOVERY

A correlation of interfacial charge with various interfacial properties in relation to oil recovery efficiency during waterflooding

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ABSTRACT

The objective of this study was to correlate the interfacial charge with other properties of the crude oil/brine interface in relation to oil recovery efficiency. The dispersed droplets of Seeligson crude oil in brine solution exhibited a maximum in electrophoretic mobility at 3.5% NaCl concentration. At the same NaCl concentration, the drop-volume of the crude oil in brine was minimum, which suggested that the interfacial tension was also minimum. Moreover, minimum interfacial viscosity between a thin crude oil film and brine occurred at 3.5% NaCl concentration. The surface-active components in the crude oil were eluted by chromatography in silica gel columns. The results showed that a maximum amount of surface-active material was eluted by 3.5% NaCl. We propose that the striking changes observed at 3.5% NaCl concentration are due to the maximum surface charge density at the crude oil/brine interface.

Furthermore, we observed the maximum oil recovery efficiency in sandpacks and Berea cores when the crude oil was displaced by 3.5% NaCl brine. Because contact angle measurements of crude oil droplets on quartz plates submerged in brine did not show a significant change at 3.5% NaCl, the wettability alteration as a possible mechanism for enhanced oil recovery in this system is ruled out. The capillary number at 3.5% NaCl also remained below 10^{-6} and hence cannot account for the enhanced oil recovery. A possible explanation for the maximum oil recovery efficiency at a specific brine concentration is proposed in terms of interfacial charge at the crude oil/brine interface and that at the sand/brine interface. It is further emphasized that surface charge is an important parameter which can influence interfacial tension and interfacial viscosity at the oil/brine interface.

Introduction

Since the first field application in 1865⁽¹⁾, the waterflooding process for oil recovery has evolved from plain water injection to the complicated processes involving the addition of solvents, chemicals, gas or heat. These additives

change either one or several of factors such as water mobility^(2,3), oil viscosity^(4,5), rock wettability^(6,7) and water-oil interfacial tension^(8,9,10). The incorporation of these additives increases the oil displacement efficiency, the sweep efficiency, or both. Therefore, it is evident that in order to achieve a better oil recovery, the physical and chemical properties of the injected brine are of the utmost importance. The main objective of this investigation was to elucidate the influence of salt concentration on the properties of the crude oil/brine interface and to correlate it with the oil displacement efficiency in sand packs and Berea cores.

Experimental Materials and Methods

Materials

The crude oil used in all experiments was obtained from Seeligson Oil Field, Texas. It was collected at the well-head prior to the addition of any agents and shipped directly to us from the field. The crude oil had 39.4°API and a viscosity of 2.54 cp at 25°C.

The brine solutions were prepared by adding NaCl to deionized-distilled water on the weight per cent basis. Fine silica sand of 150-200 mesh size was used as received from Agsco Corp., Paterson, N.J., in sand shaking and sand-pack experiments. Berea cores (1" x 1" x 12") were purchased from Cleveland Quarry, Cleveland, Ohio.

Methods

Interfacial Tension: Interfacial tension between brine and crude oil was measured by the drop volume method^(11,12). Crude oil was released from a microsyringe immersed in a constant-temperature glass container filled with brine. The microsyringe had a 0.008-in.-ID flat-tip steel needle. Each drop volume was derived from the average of 5 readings, each of which was derived from the average size of 10 droplets formed continuously and very slowly. About 3 minutes were spent forming a drop. Then, interfacial tension values were calculated according to Wilkinson⁽¹³⁾.

Interfacial Viscosity: Interfacial viscosity of a thin crude oil film on brine was measured by a knife-edge surface viscometer constructed according to Karam⁽¹⁴⁾. A thin layer of the crude oil was spread as follows. A known

TABLE 1. Oil displacement in sand packs

NaCl Concentration (wt. %)	Pore Volume (ml)	Porosity (%)	Permeability (darcy)	Oil-in-Place (ml)	OIP P.V. (%)	% OIP Recovered
0.0	118.5	39.3	—	106.25	89.7	65.7
2.0	118.5	39.1	2.422	98.00	82.7	68.8
3.5	116.0	38.7	—	97.25	83.8	73.2
4.5	111.3	38.7	—	105.07	94.4	68.6
6.0	115.5	38.3	2.502	96.25	83.3	71.1
7.0	113.5	37.7	2.337	96.00	84.6	70.7

TABLE 2. Oil displacement in Berea cores

NaCl Concentration (wt. %)	Permeability (millidarcy)	Porosity (%)	Pore Volume (ml)	Oil-in-Place (ml)	% OIP Recovered
1.0*	165.3	14.0	54.8	34.3	51.3
1.0*	—	15.6	61.5	29	48.4
1.5	201.3	12.1	23.7	19.5	47.4
2*	—	14	54.8	48.3	44.4
3.5	182.7	18.4	36	19	57.9
3.5	—	17.9	35.1	26.8	53.7
3.5*	—	15.6	61.5	29	57.7
4	248	18	35.3	23	43.9
4*	—	14	54.8	43.2	44.4
5	347.6	17.9	35.1	22.8	48.7
5	148.4	17.9	35.1	22.0	50.4
5*	—	15.6	61.5	43.2	44.4

*Core dimension: 1.43" × 1.42" × 11.69"

TABLE 3. The effect of NaCl concentration on drop volume and interfacial tension

NaCl Concentration (wt. %)	Drop Volume V (ml)	$\frac{r^2}{V^{1/3}}$	r/a^2	a^2	Brine Density ρ_w (gm/ml)	Density Difference* $\Delta\rho = \rho - \rho_w$	Oil/Water Interfacial Tension γ_{ow} (dynes/cm)
0 %	0.0189	0.07628	0.0354	0.3295	0.99708	0.12708	20.5386
2 %	0.0180	0.07753	0.0365	0.3099	1.01112	0.14112	21.4511
3 %	0.0171	0.07888	0.0376	0.2921	1.01821	0.14821	21.2348
3.5 %	0.0118	0.08924	0.0451	0.2030	1.02176	0.15176	15.1110
4 %	0.0166	0.07966	0.0381	0.2844	1.02530	0.15530	21.6641
5 %	0.0162	0.08032	0.0384	0.2800	1.03251	0.16251	22.3191

* $r = 0.02032$ cm; No. 26 gauge needle radius. $\rho_o = 0.87$ gm/ml; Seeligson crude oil density.* r/a , numerical solution to the differential equation tabulated by Wilkinson¹².

* Density of NaCl solutions, taken from Chemical Engineering Handbook, 5th Ed., (Perry R.H., and Chilton, C.H.) pp. 3-78.

* $\gamma_{ow} = \frac{\Delta\rho g r^2}{2}$; $g = 981$ cm/sec.²

amount of crude oil was dissolved in a spreading solution (chloroform + methanol + n-hexane, 1:1:3 v/v/v ratio) at a concentration of 1 mg/ml. The solution was spread on the brine surface by a microsyringe⁽¹⁴⁾. An interval of 15 minutes was allowed for evaporation of the volatile fraction of the crude oil and the spreading solvent. The volume of the solution spread on the surface was chosen so that the crude oil film would be 350 Å thick, assuming no evaporation of the crude oil. However, the evaporation of volatile components would decrease the film thickness significantly. Such films were used for surface viscosity measurements.

The knife-edge disk pendulum of the surface viscometer was suspended in the surface of the rotating dish containing brine. As the dish rotated at a constant speed, the oil film-brine interface produced a torque on the pendulum. This torque or deflection of the pendulum was measured accurately by using an optical micrometer.

Electrophoresis: The electrophoretic mobility of the crude oil droplets in brine of different salinities was measured by a Zeta-Meter² (Zeta-Meter, Inc., New York City) at

25°C. The procedure consisted of first sonicating 0.5 ml oil in 80 ml brine solution. Then, after 24 hours of equilibration, electrophoretic mobility was measured by taking the average of twenty readings. Repeatability was greatly improved when measurements were taken with oil droplets having the same size.

Wettability and Contact Angle: The wettability of the quartz surface used to simulate the surface of sand particles was studied by a contact-angle goniometer. A crude oil droplet was deposited on the underside of a smooth polished quartz surface submerged in brine of different salinities. Then, the angle through the oil phase was measured at 25°C.

Extraction of Surface-Active Material from Crude Oil: Natural surface-active material in the Seeligson crude oil was extracted as follows:

(1) Silica gel of Davidson grade 60 was packed into a long glass tube (0.375 in. diameter, 8.0 in. length). The pore volume of the packed tubes was determined to be about 5 ml.

(2) Brine solution (10 ml) was aspirated through the

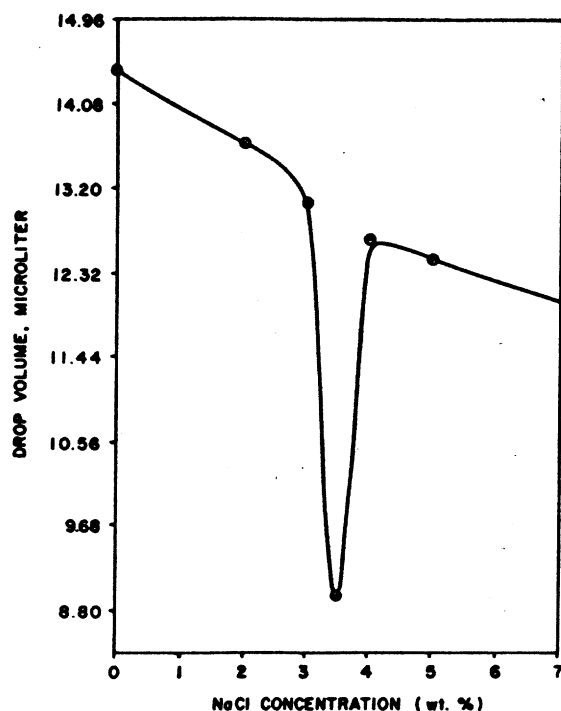


FIGURE 1. The effect of brine concentration on the drop volume of crude oil in brine.

packed tube, followed by 5 ml crude oil; and then 10 ml hexane was put through to wash away the oil-soluble fraction of the crude oil. This permitted the surface-active components of the crude oil to stay behind in the pack.

(3) Finally, 10 ml solution of 20% isopropanol in distilled water was dripped through the tube under gravity to extract the adsorbed surface-active material from the silica gel.

The elutant was analyzed for surface-active materials by the methylene blue spectrophotometric method⁽¹⁸⁾, a modified version of the method reported by Smith and Malmberg⁽¹⁹⁾.

Oil Separation by Sand Shaking: Samples of dry sand of equal weight were first saturated with the same amount of crude oil in test tubes. Then, brine of different salinity was introduced to each tube and the capped tubes were put onto a wrist-action shaker for 30 minutes. Finally, after two weeks of standing, qualitative results of oil separation were noted.

Oil Displacement in Porous Media: Horizontally mounted sand packs and Berea cores encased in an air-circulating constant-temperature box were used for oil displacement efficiency tests. The details of each displacement experiment are listed in Tables 1 and 2. The sand pack was 1.3 in. diameter by 18 in. long. It had an average porosity of 38.6% and permeability of 2.4 darcy. The Berea core was 1 in. by 1 in. by 12 in., cast in epoxy resin. It had an average porosity of 16% and permeability of 220 millidarcy.

After the porous medium was characterized by distilled water for the sand pack or 1% brine for the Berea cores, it was prewashed by 5 pore volumes (PV) brine of the same concentration as the displacing brine. Then two PVs of crude oil were pumped through the sand pack at 5 psi or through the Berea core at 30 psi and the oil-in-place (OIP) was obtained by material balance. The volumes of

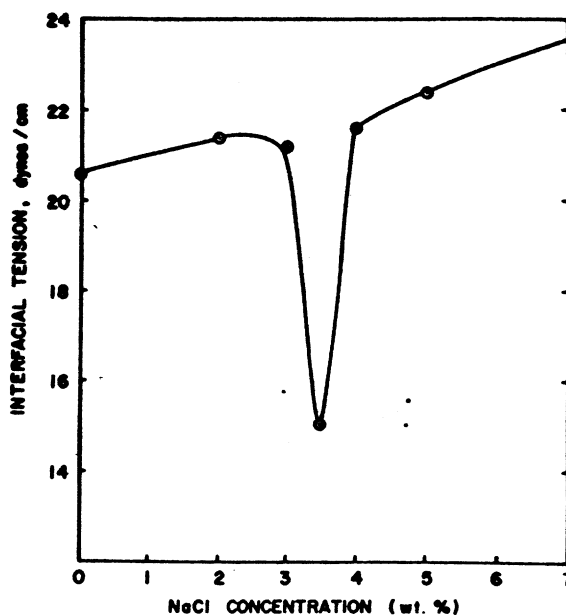


FIGURE 2. The effect of brine concentration on the interfacial tension of the crude oil/brine interface.

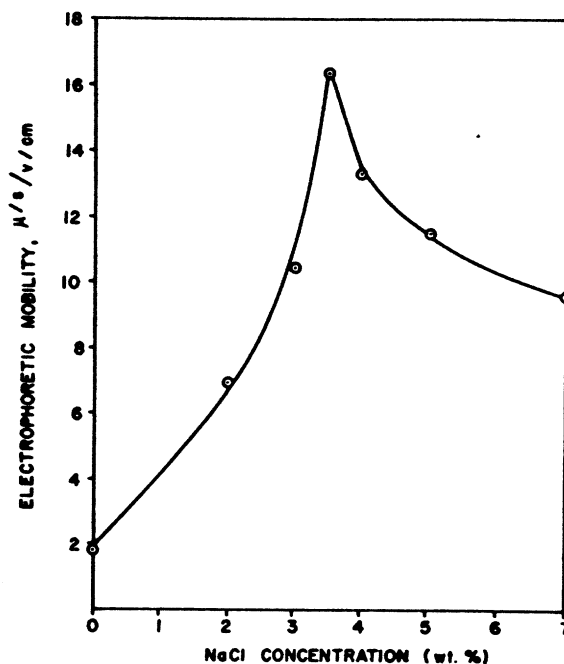


FIGURE 3. Effect of brine concentration on the electrophoretic mobility of Seeligson crude oil.

the crude oil and the displaced brine were measured to the nearest 0.1 ml. Immediately after the saturation with crude oil, the waterflooding was started at a constant frontal velocity of 3.0 ft/day or 1.9 ft/day for the sand pack or Berea core, respectively. The effluent stream was then collected in a fraction collector and volumes of oil and brine were carefully measured to the nearest 0.1 ml. The run was terminated after injecting approximately 5

PVs brine; at this stage, no measurable quantity of oil came out of the porous media. New sand packs and clean Berea cores were used for each run. Also, no attempt was made to match the mobility of displacing and displaced fluids.

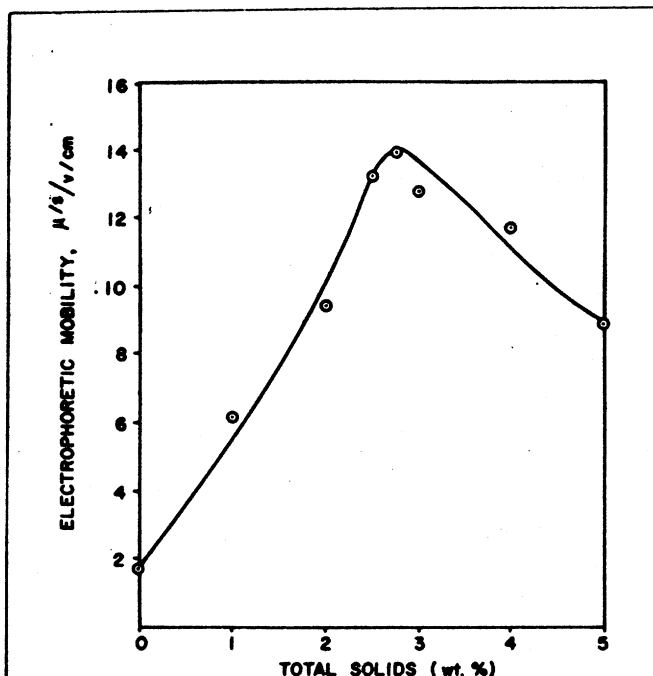


FIGURE 4. Effect of multicomponent brine concentration on the electrophoretic mobility of Seeligson Crude oil. NaCl: CaCl₂: MgCl₂: Na₂SO₄ = 100:14:2:0.05 by wt.)

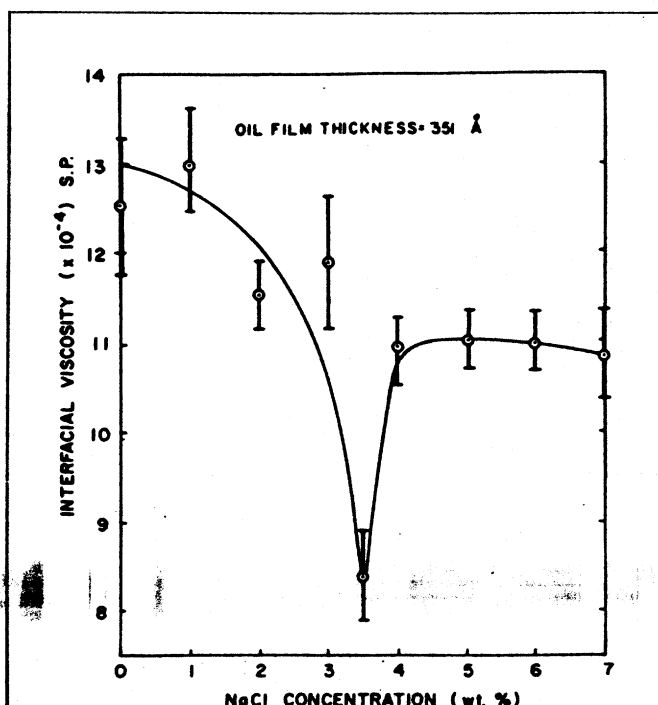


FIGURE 5. The effect of brine concentration on the interfacial viscosity of thin layers (~ 350 Å thickness) of Seeligson crude oil.

Results and Discussion

The effect of NaCl concentration on drop volume and interfacial tension is presented in Table 3 and illustrated in Figures 1 and 2. This shows that at 3.5% NaCl, there is a minimum in drop volume; consequently, there is a decrease in interfacial tension from 21 dynes/cm to 15 dynes/cm. In order to understand the mechanism for the minimum in interfacial tension, the electrophoretic mobility of crude oil droplets as a function of brine concentration was measured and the results are shown in Figure 3. It is evident that as the salinity increases from 0% to 7.0% NaCl, the electrophoretic mobility exhibited a maximum at 3.5% NaCl. This indicates that the highest surface charge density at the oil/brine interface occurred at 3.5% NaCl. Also, the migration of crude oil droplets toward the positive electrode in the electrophoretic cell indicated that the crude oil/brine interface is negatively charged at all NaCl concentrations.

In order to decide whether such a maximum in electrophoretic mobility and hence in surface charge density would exist if the composition of the brine is similar to that of the oil-field brine rather than the pure NaCl solution, a brine solution similar to that present in the Seeligson reservoir, consisting of NaCl, CaCl₂, MgCl₂, and Na₂SO₄ (weight ratios, 100:14:2:0.05), was prepared. This multi-component brine, when used at different concentrations, also exhibited a maximum at 2.75% total dissolved solids (Fig. 4). The ionic strength of brine when maximum electrophoretic mobility occurs (Figs. 3 and 4) was respectively 0.605 and 0.577. Therefore, it is clear that the maximum surface charge is developed at a specific ionic strength, whether in a single-component brine (e.g., NaCl) or in a multi-component brine.

After having established the correlation between electrophoretic mobility and interfacial tension, the effect of brine on the interfacial viscosity of crude oil film was measured. Figure 5 shows that at 3.5% NaCl, there is a minimum in interfacial viscosity. This is expected, because high surface charge density would cause repulsion between molecules at the interfaces.

Few screening methods for oil recovery efficiency involving the oil, brine and quartz surface have appeared in the literature. Reisberg and Doscher⁽¹⁷⁾ used the technique of dipping a microscope slide in the crude oil; Hill *et al.*⁽¹⁸⁾ used a microscope to observe the behaviour of an oil droplet displaced by water or surfactant solution

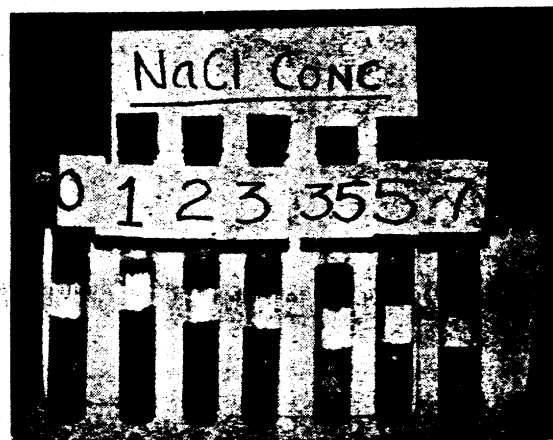


FIGURE 6. The effect of NaCl concentration on the Seeligson crude oil in the sand shaking experiment.

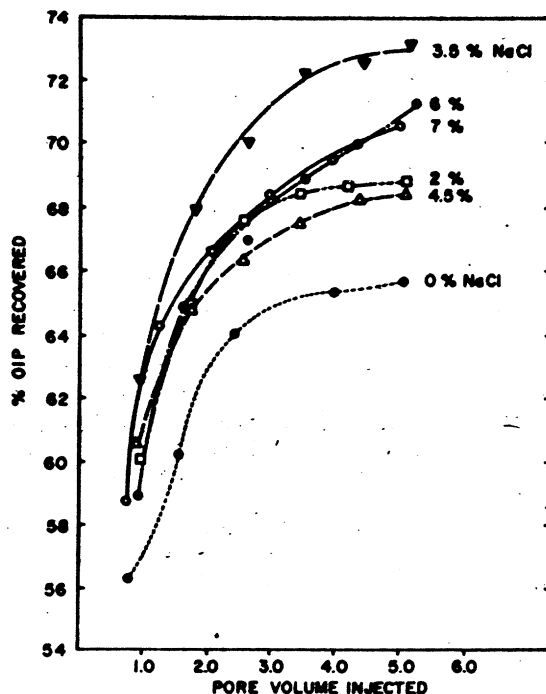


FIGURE 7. The effect of NaCl concentration on per cent oil-in-place recovered for each pore volume injected in sand packs.

between two glass slides. We used a simple sand-shaking technique. The result is shown in Figure 6. Here, it is clear that at 3.5% NaCl solution, there is a maximum amount of oil aggregated at the top, and also the cleanest sand remaining on the bottom.

This encouraging result led us to perform the oil displacement tests. Figure 7 shows the per cent OIP recovered as a function of pore volume of brine injected in sand packs. The flooding history is similar to that reported in the literature⁽¹⁷⁾; eighty-five per cent of the total recovered oil was displaced by the initial 1 PV brine-injection. Figures 8 and 9 show the OIP recovered as a function of salinity in sand packs and Berea cores respectively. In sand packs, a maximum of 73 per cent OIP was recovered at 3.5% NaCl concentration of injected brine. In Berea cores, also, a maximum of 58 per cent OIP was recovered by 3.5% NaCl brine. Therefore, for both sand packs and Berea cores, a significant improvement in oil recovery is observed when 3.5% NaCl is injected.

In order to account for such an increase in oil displacement, wettability alteration of the porous media must be considered. Figure 10 shows the results of the contact-angle measurements of oil drops on a quartz surface immersed in brine of various NaCl concentrations. The angle θ was measured through the oil drop, as shown on the same figure. As salinity increased from 0% to 7% NaCl, the contact angle, θ , decreased gradually from 166 to 160 degrees without any abrupt change at 3.5% NaCl. As the measured angles are all greater than 140 degrees, it is considered to be a water-wet system⁽¹⁸⁾, as one would expect for the quartz-brine-oil system. However, it is clear that the wettability of the quartz surface did not change as brine salinity changed. Therefore, the mechanism causing the increase in oil recovery by 3.5% NaCl must be other than the wettability change of the sand surface.

It was then conjectured that the change in interfacial

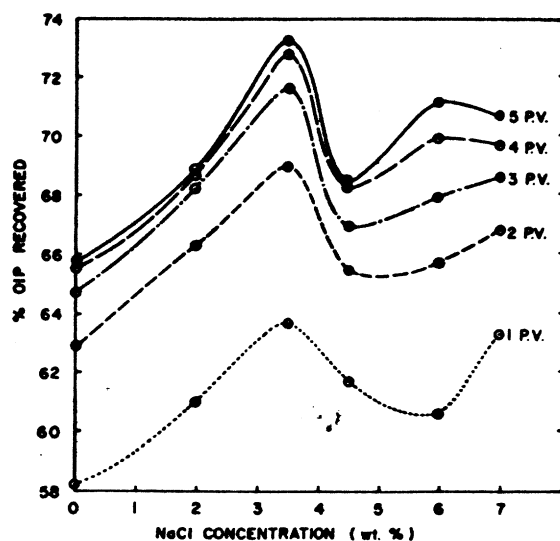


FIGURE 8. The effect of NaCl concentration on per cent oil-in-place recovered for each pore volume injected in sand packs.

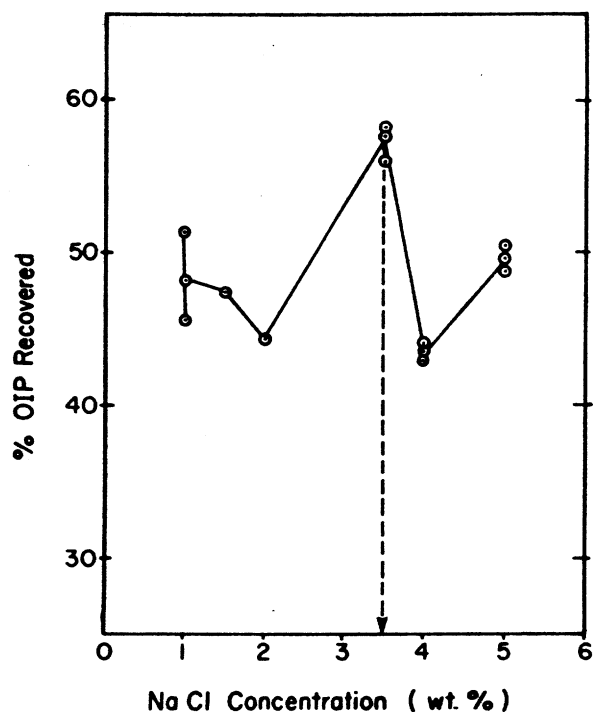


FIGURE 9. The effect of NaCl concentration on per cent oil-in-place recovered in Berea cores.

properties and oil displacement efficiency at 3.5% NaCl might be caused by the materials within the crude oil itself. From different crude oils, Bartell and Niederhauser⁽²⁰⁾, Reisberg and Doscher⁽¹⁷⁾, and Denekas *et al.*⁽²¹⁾ extracted materials which were surface active.

Surface-active materials in Seeligson crude oil were isolated by column chromatography and quantified by the methylene-blue colorimetric method, as discussed in the

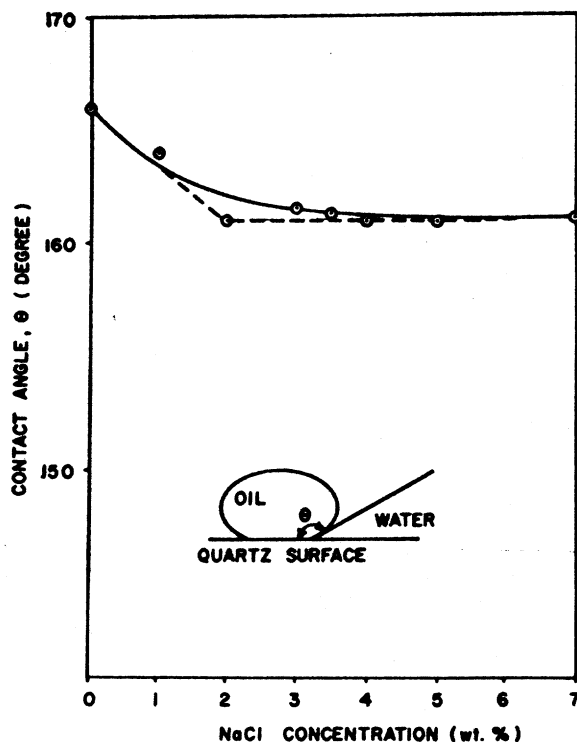


FIGURE 10. The effect of NaCl concentration on the contact angle for crude oil/NaCl solution on a quartz surface.

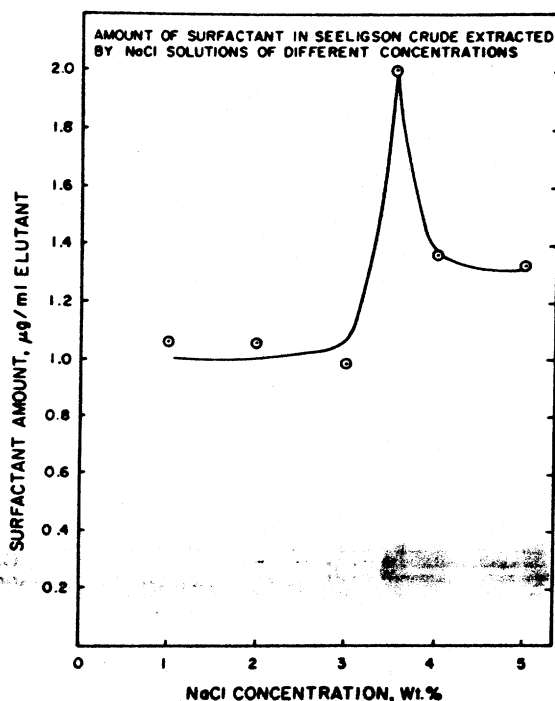


FIGURE 11. The effect of NaCl concentration on the amount of natural surfactant in Seeligson crude oil extracted by column chromatography.

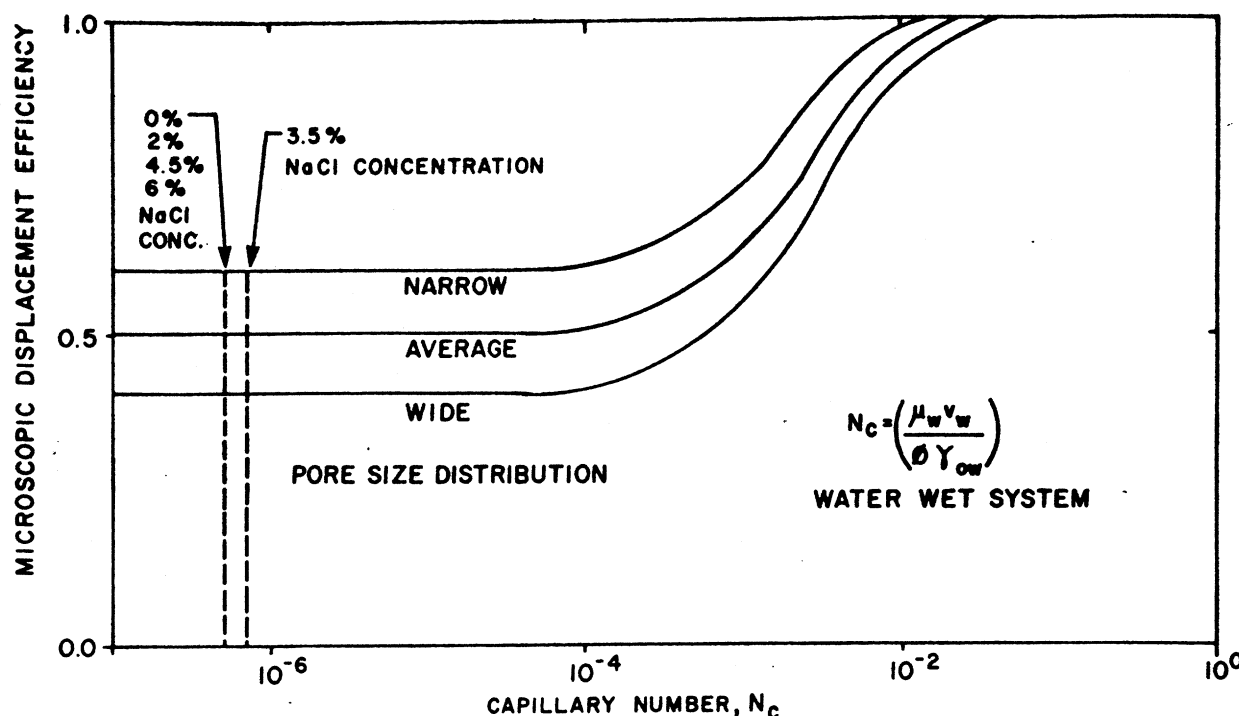
"methods" section. The results, shown in Figure 11, indicate that at 3.5% NaCl concentration, a maximum amount of surface-active materials is present at the oil/brine interface. No effort was made to separate and identify these materials.

The following is our proposed explanation to account for the observed effects. We propose that increasing the salt concentration facilitates the adsorption of surface-active molecules at the oil/brine interface up to 3.5% NaCl due to shielding of negative charges by sodium ions. At 3.5% NaCl concentration, the maximum in electrophoretic mobility corresponds to the maximum surface concentration of surface-active molecules. Above 3.5% NaCl, either the negative charges are neutralized by the Na^+ ions or surfactant molecules are being desorbed from the interface. Therefore, the electrophoretic mobility decreases and the interfacial tension increases. It is known from the electro-capillary curve⁽²⁰⁾ that a maximum in surface charge density should create a minimum in interfacial tension, which also was observed at 3.5% NaCl (Figs. 2 and 3).

We believe that the displacement of micro-droplets of oil or oil ganglia in porous media is facilitated by the negative charges at the crude oil/brine interface and those on the sand particles. Although the interfacial tension was at its minimum at 3.5% NaCl, its value is about 15 dynes/cm, which is too high to have any significant effect on capillary number, N_c , or oil recovery efficiency. To illustrate this point more clearly, the dimensionless number, N_c , at various salt concentrations was calculated. The result is added to the graph of Melrose and Brandner⁽²¹⁾, reproduced in Figure 12. For crude oil-brine systems at all salt concentrations, capillary numbers are below 10^{-4} . The small difference in capillary numbers for all NaCl concentrations cannot account for the increased oil recovery efficiency at 3.5% NaCl. Hence, the increase at 3.5% NaCl is neither due to the capillary number nor the wettability change, as proposed by others^(6,7) in this system.

Figure 13 illustrates our concept of the role of interfacial charge in oil displacement processes. We proposed that at 3.5% NaCl, the high surface charge density at the crude oil/brine interface minimizes the re-attachment of crude oil droplets to the negatively charged sand particles, and hence more droplets would come out of the porous media. As seen in the interfacial viscosity plot (Fig. 5), a minimum also occurs at 3.5% NaCl. Therefore, the minimum interfacial tension and interfacial viscosity would increase the deformability of drops to come through narrow necks of pores, and also promote the coalescence of droplets, thus resulting in a higher oil recovery efficiency.

The importance of surface charge at the crude oil/brine interface was also shown to be relevant to the caustic flooding process⁽²²⁾. The minimum in interfacial tension and the maximum in electrophoretic mobility occurred in the same caustic concentration range⁽²³⁾. For various surfactant systems, we have shown^(22,24) that the minimum in interfacial tension always corresponds to the maximum in electrophoretic mobility. A greater emphasis on surface charge is more meaningful to elucidate various interactions in oil displacement processes. It is conceivable that a surfactant system that may produce ultra-low interfacial tension (and hence a maximum surface charge density) may not mobilize oil ganglia if positively charged minerals are in the reservoir rocks. Hence, consideration of surface charge at the oil/brine interface brings into focus the role of surface charge on the rock/brine interface in relation to the oil displacement process. The surface charge concept is also important in understanding the effect of sacrificial agents and preflush chemicals.

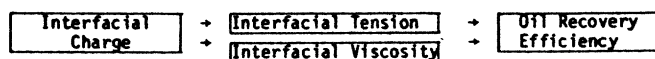


Melrose, J.C., and Brandner, C.F., J. Canadian Petr. Tech., Oct.-Dec., 1974 p. 58

FIGURE 12. Capillary numbers of the Seeligson crude oil-brine system at various NaCl concentrations.

In conclusion, we believe that surface charge density is a very important, but so far neglected, parameter in oil displacement processes. The importance of the results presented here is that they establish a mechanism which may be utilized to increase the oil recovery efficiency during water flooding in suitable reservoirs. It should be emphasized that 3.5% NaCl is by no means a universal brine concentration for improved oil recovery by water-flooding. The specific brine concentration is related to the structure and composition of surface-active components of the crude oil. Thus, it is expected that the optimal brine concentration may vary for different crude oils. It must be pointed out that we are not implying that every crude oil must have a specific optimal brine concentration, such as that observed in this study.

In summary, we propose that the following chain of events seems to occur in the oil displacement process by brine solutions.



Conclusions

Based on the experimental results and discussion presented in this paper, the following conclusions can be drawn:

(1) For Seeligson Field crude oil, sand-pack and Berea core studies show that maximum oil displacement efficiency correlates with minimum interfacial tension, minimum interfacial viscosity and maximum electrophoretic mobility at 3.5% NaCl concentration brine.

(2) Maximum crude oil surface charge density was also found in the presence of multicomponent brine similar to that of the oil field.

(3) Wettability of quartz surfaces by oil and brine, as indicated by the contact-angle measurement, did not show any change at 3.5% NaCl concentration brine.

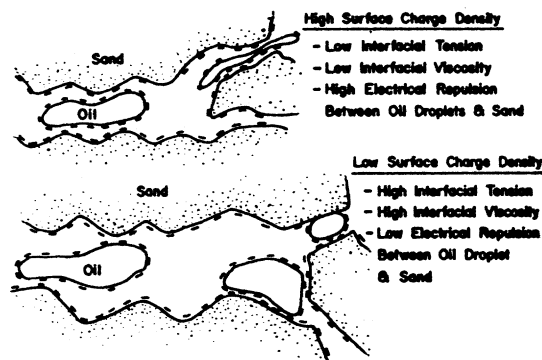


FIGURE 13. The role of surface charge in oil displacement process.

(4) The improved oil recovery for this system cannot be accounted for by either the small change in capillary number or by the alteration of wettability.

(5) By column chromatography, it was shown that the maximum amount of surface-active material is adsorbed at the oil/brine interface at 3.5% NaCl concentration.

(6) The changes in interfacial properties at the crude oil/brine interface, as well as the improved oil recovery efficiency, are explained in terms of interfacial charge density at the crude oil/brine interfaces.

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