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A Review on Interfacial and Phase Behavior Applications on an Oil Wet Cores

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Abstract: A laboratory study of the Alkaline surfactant polymer (ASP) process was conducted. It was found from phase behavior studies that for a given synthetic surfactant and crude oil containing naphthenic acids, Optimal salinity depends only on the ratio of the moles of soap formed from the acids to the moles of the synthetic surfactants present. Adsorption of anionic surfactants on carbonate reservoirs will decrease by sodium carbonate. The magnitude of the reduction with sodium carbonate decreases with increase in salinity.

Particular attention was given to a given surfactant blend of a PO sulfate C16-C17 hydrocarbon chain and an internal olefin sulfonate, alkaline solutions of this blend containing neither alcohol nor oil, were single phase micellar solution at all salinities up to approximately optimal salinity with representative oils. Solubilization of oil and brine for this system was high, leading to low IFT over a wide salinity range and to excellent oil recovery in both dolomite and silica sandpicks. In this paper laboratory results on phase behavior, IFT, adsorption and oil displacement in unconsolidated sand packs for an ASP process using surfactant PO sulphate having a slightly branched C16-17 hydrocarbon chain were emphasized.

I. INTRODUCTION

Most of the work directed towards developing micellar polymer process to recover residual oil from sandstone formations using anionic surfactants. Most cases soaps formed by injecting alkali would not be at the optimal conditions needed to achieve low tensions. A relatively small amount of a suitable surfactants be injected with alkali so that the surfactant soap mixture would be optimal at reservoir conditions [1]. With polymer added for mobility control, the process would be an ASP flood. The use of alkali also reduces adsorption of anionic surfactant on sandstones because the high pH reverses the charge of the positively charged clay sites where adsorption occurs. When the oil was a West Texas crude oil and the formulation included sodium carbonate to convert naphthenic acids in the crude oil to soaps, salinity scans revealed that small amounts of some cationic surfactants increased solubilization of oil and brine in the microemulsion phase near "optimal" salinity, where equal volumes of oil and brine are solubilized and interfacial tensions (IFT's) are low [2].

Carbonate reservoirs are typically mixed wet and often fractured as well. Cationic surfactants are suitable to promote desorption of acids from carbonate rock surfaces, making the rock more water wet. In some investigations the effectiveness of various surfactants alter the wettability showed that if Na₂CO₃ was used as the alkali and injected with a suitable anionic surfactant the usual positive charge of carbonate rock would be reversed, with the result that the surfactant adsorption was greatly decreased and oil wet surfaces were modified to intermediate wet. The wettability modifications allowed the surfactant solutions to enter, and the resulting low IFT reduces capillary forces to the point that the oil rose to the top of the core, where it was released. No oil was recovered when a NaCl solution was used instead [3]. Such type of alkaline surfactants solutions are preferred to inject into fractured carbonate formations to increase recovery.

The PO provides increased tolerance to Salt and Divalent ion. The branched hydrocarbon chain mitigates the formation of liquid crystalline phases in the absence of oil, thereby permitting surfactant injection as a single phase micellar solution at ambient temperature with no added alcohol or oil below or at optimal salinity for many oils. In contrast alkyl/aryl sulphonates exhibit's liquid crystal formation well below and at optimal salinity in the absence of substantial amounts of alcohol or oil. More over the long hydrocarbon chain and attached PO chain allow this new surfactant to have high solubilization and hence low IFT over a wide range of conditions.

II. METHODOLOGY

A. Two Crude Oil Samples from same well with very Similar Properties

1) API gravity is 28

- 2) Acid no. 0.20mgKOH/g
- 3) Anhydrous Na₂CO₃ powder (99.8% purity with 0.005% calcium)

The two surfactants studied were ammonium C16-17 7PO sulphate and IOS.

Surfactants solutions and oils were mixed at specific water/oil ratio (WOR) in glass vials or pipette. They were first shaken well by hand for 1 minute and mixed on a rotating shaker for 24 hours. Afterward they were put it in a upright position and allowed to settle. IFT were determined by spinning drop tensiometer. Dolomite sand and silica sand were used for the sand pack experiments.

B. Effect of Salt

Below figure.1 shows the phase behavior at ambient temperature of aqueous solution containing 3wt% (active) mixtures of N67 and IOS as a function of added NaCl for a fixed 1wt% concentration of Na₂CO₃, but no alcohol at ambient temperature [4]. IOS exhibits precipitation above 4wt% NaCl. In contrast no precipitation occurs and a surfactant rich liquid phase less dense than brine forms as NaCl content increases for solutions containing N67 and its mixtures having up to 75% IOS. The phase transition occurs at higher salinities as IOS is initially added to N67, reaching a maximum near 8wt% NaCl for a 1/1 blend.

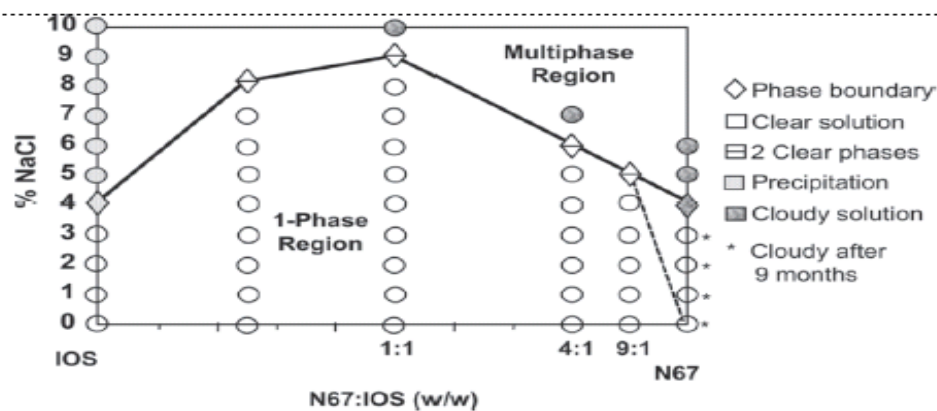


Figure.1 Effect of NaCl on phase behavior of 3 wt% solutions of N67/IOS containing 1 wt% Na₂CO₃

The significance of the above figure.1 is that N67/IOS mixtures can be injected as a single phase micellar solution of relatively low viscosity at ambient temperatures at salinities approaching or in some cases even exceeding optimal salinity for many oils without addition of alcohol or oil.

As in petroleum sulphonate system, addition of high molecular weight polymer can cause phase separation. Below figure.2 shows increasing NaCl content from 2 to 4wt% produces phase separation in a solution containing 0.5 wt% NI blend, 1 wt% sodium carbonate and 0.5wt% partially hydrolyzed polyacrylamide polymer. Larger micelles are expected at the higher salinity, which promotes separation into polymer rich and surfactant rich phases.

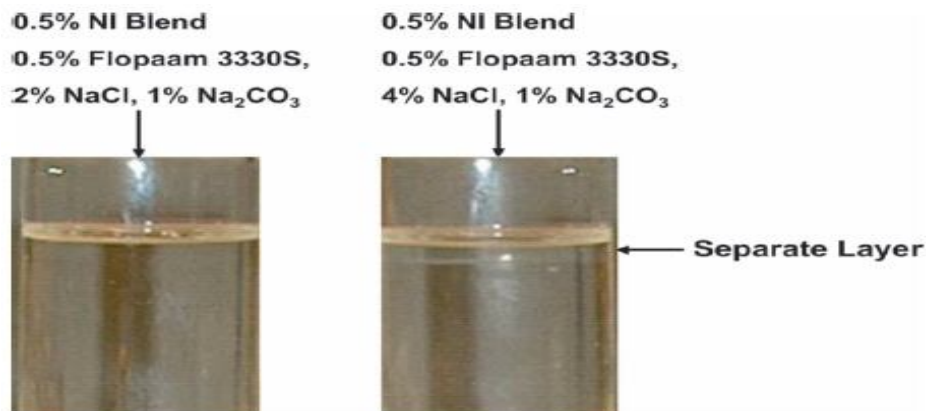


Figure.2 phase separation caused by increasing NaCl content for aqueous solution of 0.5 wt% NI blend, 1 wt% Na₂CO₃, and wt% Polymer

C. Phase Behavior with Oil Importance of Soap-to-Surfactant ratio

Below figure.3 shows variations of phase behavior with NaCl concentration with alcohol free solutions containing 0.2 wt% (active) NI blend and 1% Na₂CO₃ mixed with crude oil at water to oil ratio of 3% and stored at ambient temperature for 40 days. From the report acid no. of crude oil (0.2 mg KOH/g), Soap-to-Surfactant Ratio was calculated to be 0.35.

Observation over time of the samples below optimal salinity revealed that the particles or materials less dense than the lower phase micro emulsion rose to the oil micro emulsion interface over time. As a result a thin layer of a colloidal dispersion formed as shown above for a similar sample with 2 wt% NaCl, but with 23 days settling [5]. The materials in the colloidal dispersion is essential for achieving ultralow IFT. It is not simply a collection of particles having the same composition as the crude oil that have not yet coalesced with the excess oil phase, because such particles do not effect IFT. The low density of dispersed material suggests a high ratio of oil to brine than in the lower phase. The latter results suggests that the dispersed materials has a higher soap to surfactant ratio than the lower phase and hence more lipophilic than the lower phase, with the capability of solubilizing more oil but less brine.

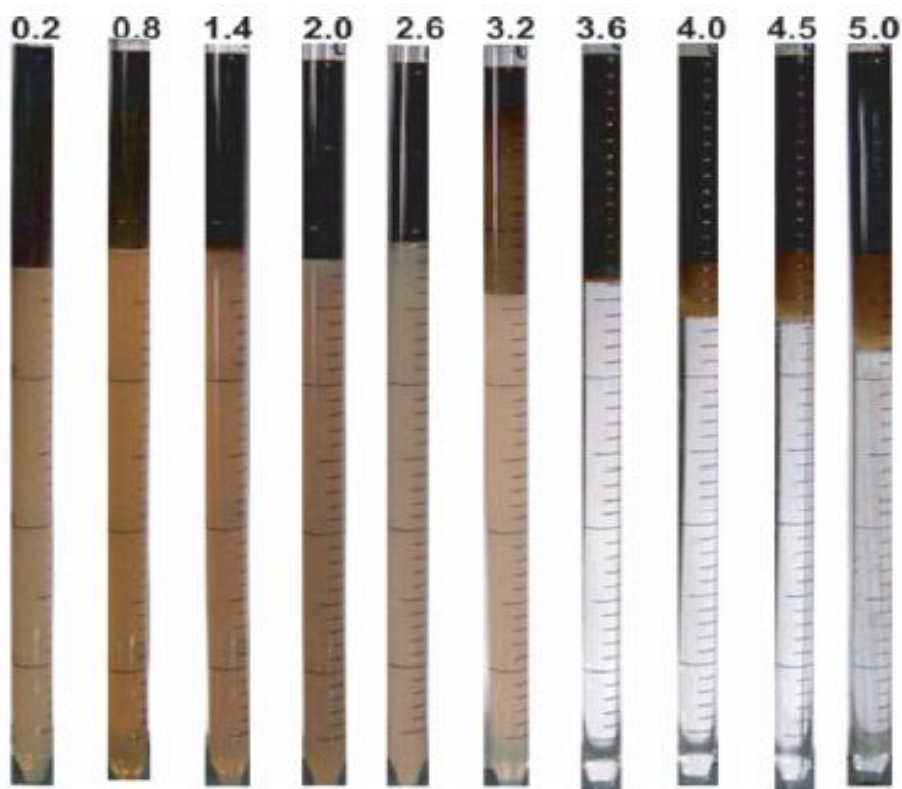


Figure.3 Salinity scan for 0.2%NI blend, 1% Na₂CO₃

As shown in the following optimal salinity for the salt scan of above figure.3 as defined by conditions for equal solubilization of oil and brine, is approximately 3.5% NaCl. Below figure.5 the same scan as seen when the samples are placed between perpendicularly oriented sheets of polarizing material, shown that slightly below optimal salinity at 3.2% NaCl the lower phase becomes birefringent [6].

Equal oil and brine solubilization corresponds to conditions when surfactant films have no tendency to curve toward either an oil continuous or brine continuous configuration and thus is favourable for formation of the lamellar liquid crystalline phase, which consists of many parallel surfactant bilayers and exhibits birefringence. In view of its low overall surfactant concentration and viscosity, the birefringent region seen at 3.2% NaCl is likely the dispersion of lamellar of the lamellar phase in a water continuous microemulsion. That the dispersion has not separated after 40 days indicates that the two phases have nearly equal densities. At higher salinities, the thin birefringent region is probably a lamellar phase. Interfaces in overoptimum samples remained mobile after 40 days.

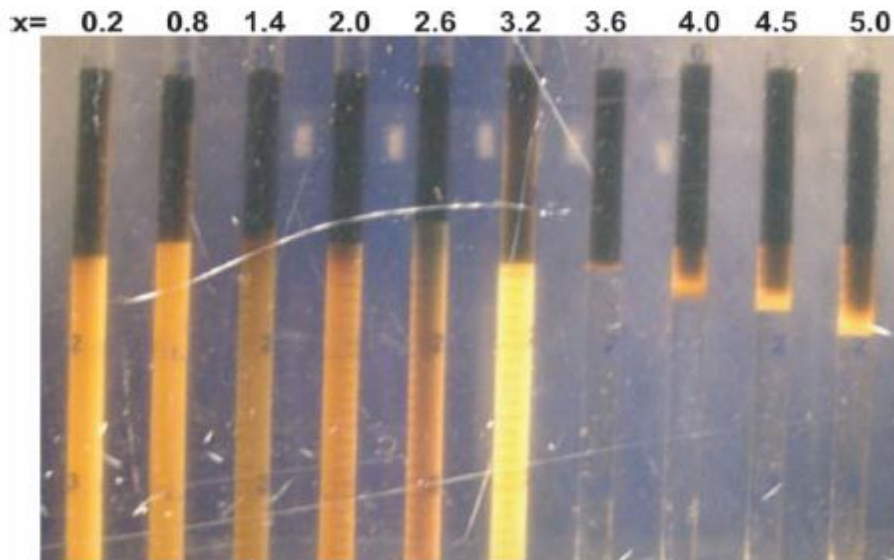


Figure.5 Salinity scan between perpendicularly oriented

D. Interfacial tension

A key requirement of alkaline /surfactant process is achieving ultralow IFT. If such tensions correlate with optimal phase behavior and high solubilization, they must depend on the soap-to-surfactant ratio [8]. Because the amount of soap present for a given volume of crude oil is dictated by its acid no.

For the scan 0.2 wt% NI blend, it was found that below optimal salinity, measured tensions between the lower phase and excess oil depended on the settling time between the end of the mixing process and sampling of the lower phase (well below the interface) and excess oil. Below figure.6 shows that for the sample containing 2 wt% NaCl, low tensions (below 0.01mN/m) were achieved only for settling times of approx. 4 hours or less. The results suggest that low tensions were not obtained once most of the colloidal material dispersed in the lower phase had risen to the vicinity of the interface and thus was not sampled.

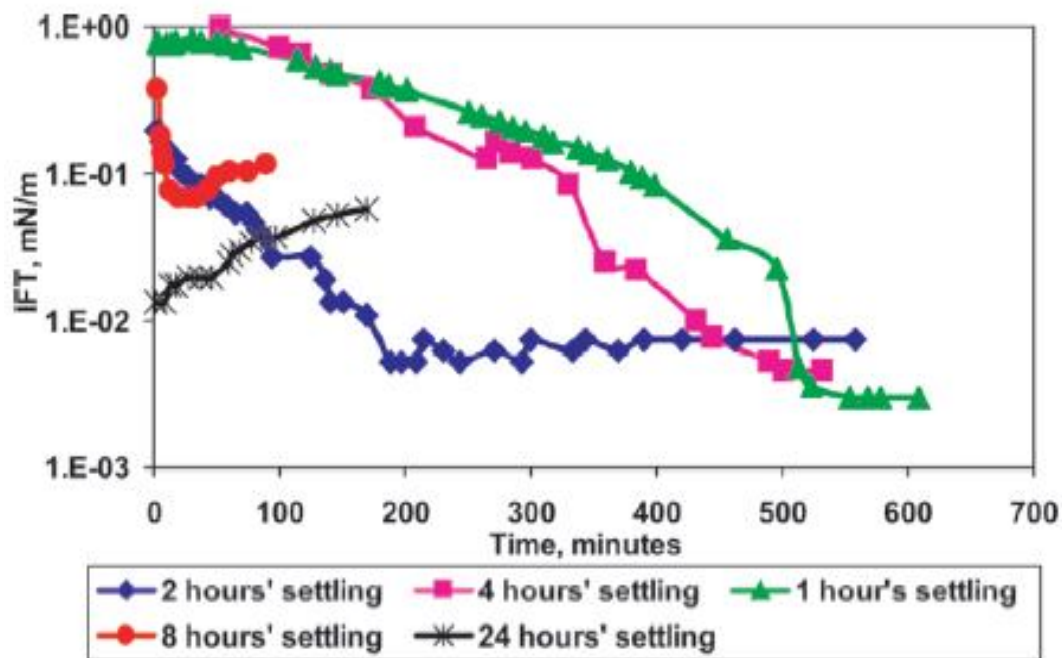


Figure.6 IFT on Settling Time

For salt scan identical to that of figure.7 but with no sodium carbonate present (and hence minimal soap), less colloidal dispersion was seen [9]. Moreover, IFT values were below 0.01mN/m over a much narrower range of NaCl concentration. The results indicates that the wide range of low tensions with alkali present is a consequence of formation of naphthenic soaps.

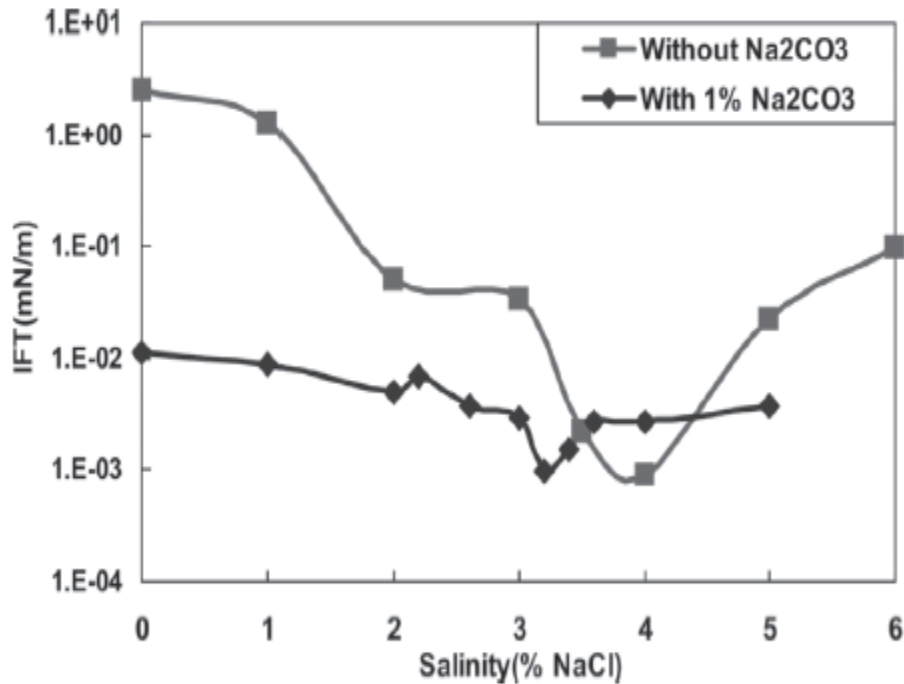


Figure.7 IFT for Salt with and without Na₂CO₃

Below figure.8 shows the show adsorption isotherms of N67 and IOS on calcite powder for solutions containing no NaCl and either 0% or 1% Na₂Co₃.

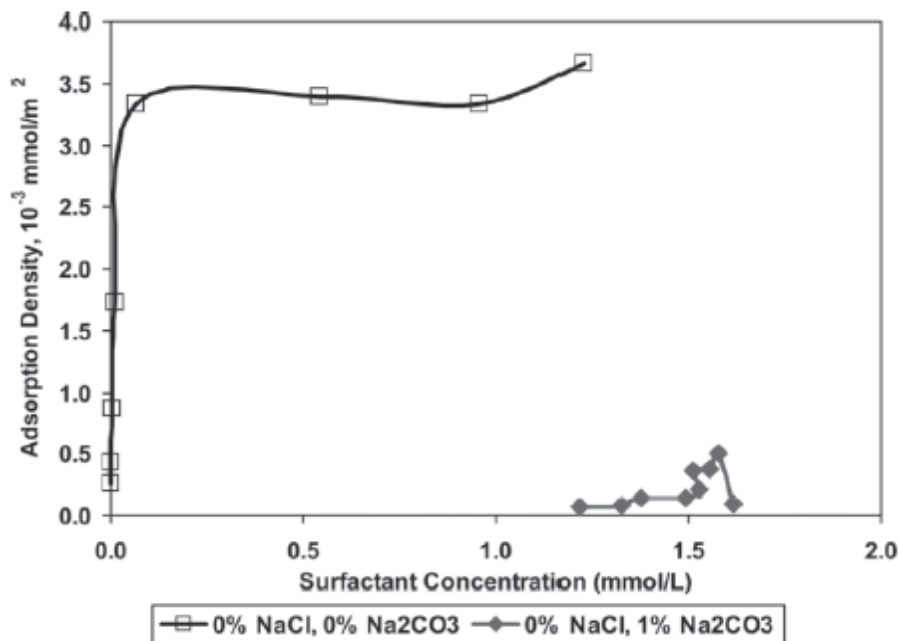


Figure.8 Adsorption of N67 on calcite Powder

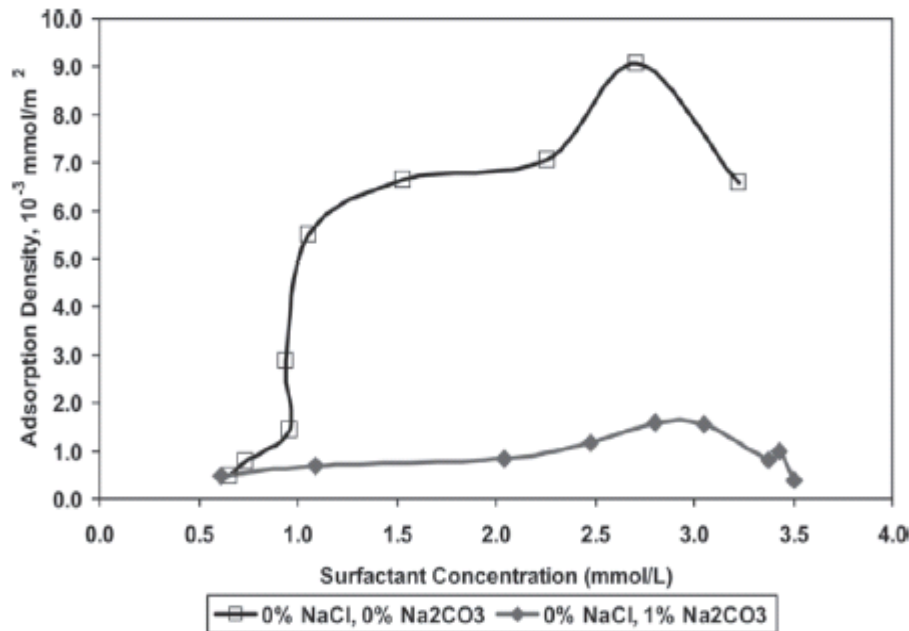


Figure.9 Adsorption of IOS on Calcite Powder

The plateau region for each surfactant represents concentrations well above the CMC, where micelle composition is constant even for these commercial surfactants with numerous individual species because virtually all the surfactant is present in the micelles. The plateau region extends to lower surfactant concentrations for the more lipophilic N67 owing to its lower CMC [10].

The most striking feature of above figure.9 is the large reduction in adsorption produced by addition of Na₂CO₃- more than an order of magnitude for N67 and several fold for IOS [11]. Carbonate is a potential determining ion, which reverses the charge of the calcite surface from positive to negative, leading to the repulsions of anionic surfactant ions. Hydroxide is not a potential determining ion for carbonate surfaces and using NaOH instead of sodium carbonate as the alkali produced no significant change in adsorption of the TC blend.

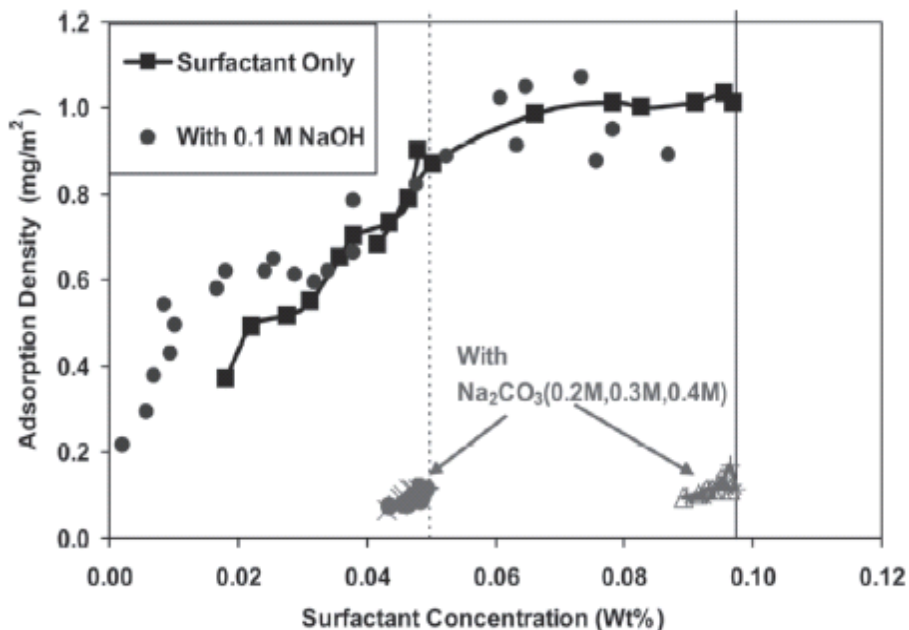


Figure.10 Adsorption of TC blend on Dolomite powder

While the results of the above figure.10 are for dolomite powders, a series of experiments with the TC blend showed that the adsorption per unit areas were nearly the same for calcite and dolomite powders.

Below, figure.11 shows adsorption isotherm of the NI blend of calcite at different NaCl concentrations with and without 1 wt% Na₂CO₃. in the absence of NaCl adsorption is comparable to that of N67 alone. As NaCl concentration increases, the beneficial effect of Na₂CO₃ is reduced, presumably because the screening effect of the additional electrolyte decreases electrostatic repulsion between surfactant ions in solution and the calcite surface. Nevertheless sodium carbonate reduces adsorption more than a factor of 3 for 3wt% NaCl. Additional experiments showed that only 0.1-0.2 wt% sodium carbonate was sufficient to produce the same decreases in adsorption as shown in fig. below for 1% Na₂CO₃.

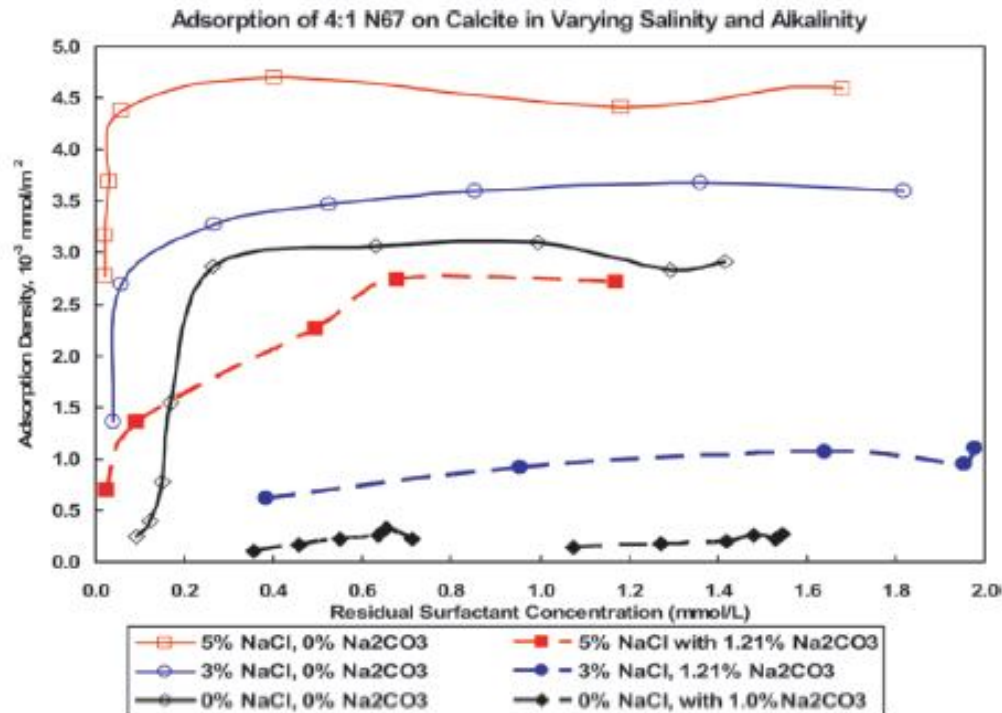


Figure.11 Adsorption of NI on Calcite as a function of NaCl with and without Na₂CO₃

III. CONCLUSION

Interfacial tension is an important parameter for improving effectiveness in oil recovery. It has been affected by the composition of NaCl and Na₂CO₃ ultimately recovery. Adsorption of surfactants onto sandstone makes recovery less Effective. Before application of Surfactant onto any reservoir careful investigation has to be done for adsorption. Adsorption of surfactant purely depends on mineral composition of adsorbed surface. By monitoring these parameters the recovery may improve. These observations can be extended to other reservoirs like limestones and shales.

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