Ultralow Oil-Water IFTs Using Neutralized Oxidized Hydrocarbons as Surfactants

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Surfactants that may be suitable for application in enhanced oil recovery have been produced from C_{22} and C_{26} paraffinic and naphthenic petroleum fractions by a two-step process. The hydrocarbon feed stocks were first oxidized in the vapor-phase, followed by neutralization of the oxidized products with aqueous alkali. As a result, dilute solutions of organic acid salts were produced that achieved ultralow ($< 10^{-2}$ dyne/cm) interfacial tensions against a synthetic oil. Surfactant solutions that exhibited the lowest interfacial tensions (IFTs) were prepared from neutralizations that used low concentrations of sodium hydroxide rather than sodium silicate, sodium tripolyphosphate, or sodium carbonate. Neutralizations that used sodium silicate or sodium carbonate resulted in surfactant solutions having IFT profiles that were less sensitive to the electrolyte concentration. When sodium hydroxide was combined with either sodium silicate or sodium tripolyphosphate in the neutralizations, solutions having intermediate IFT properties were produced. The amount of alkali used in the neutralizations was observed to affect the IFT properties of the resultant surfactant solution. The electrolyte concentration at which the minimum IFT occurred was inversely related to the pH of the surfactant solution. For surfactant solutions of common pH prepared from different concentrations of oxidized product, the minimum IFTs all occurred at the same concentration of electrolyte. Surfactant solutions remained interfacially active even in the presence of significant concentrations of calcium chloride. One pore volume of a solution containing only about 1% of active surfactant recovered 42.0% of the residual oil in a tertiary core-flood experiment.

The ability to lower the interfacial tension (IFT) between oil and water is a requirement of surfactant systems being considered for application in enhanced oil recovery (EOR) techniques. Candidates for this use are typically sodium petroleum sulfonates produced from alkyl aryl feed stocks (which are expensive), using sulfur trioxide or sulfuric acid (which are undesirable based on handling and waste disposal considerations). The surfactants are often combined with alcohols and used in sufficient concentration to form microemulsions, thus further adding to the cost.

The purpose of this research was to develop a simple procedure that could be used in a producing oil field to economically convert a portion of the recovered hydrocarbons to surfactants. These surfactants then could be used as the surface-active agents for EOR after oil production rates had sufficiently declined. Thus, large savings in transportation and raw material costs could be realized. Further, it was desirable to be able to use non-aromatic hydrocarbons as the feed stocks. This technology could then be used to recovery crude oils like those found in Pennsylvania (noted for their superior lubrication properties) and Daqing (the largest oil field in China), which contain very little aromatic hydrocarbons.

In the two-step procedure that was developed, surfactants were produced by vapor-phase oxidation of the hydrocarbon feed stocks, followed by neutralization of the oxidized products. In actual field applications, the unconverted portion of the feed stock could be recycled. The oxidized molecules that are not converted to surfactant make potentially good cosurfactants (1).

This paper describes how dilute, aqueous solutions of oxidized hydrocarbons, the alkali, and electrolytes may be used to generate ultralow IFTs ($< 10^{-2}$ dyne/cm) against a synthetic oil. The discovery of the interfacial activity of such solutions was first presented by Duda and coworkers from this laboratory (2). These initial results also were described by Arf in her doctoral work (1).

The oxidized hydrocarbons used were produced from paraffinic and naphthenic petroleum fractions of the C_{22} and C_{26} average molecular size ranges. The C_{22} and C_{26} hydrocarbons were selected because the produced surfactants were of the desired equivalent weight range for correct oil-water solubility properties for EOR. In actual field applications, hydrocarbons in the desired range could be obtained from the produced crude oils by distillation. if necessary. The energy required for such distillations could possibly be reclaimed from the highly-exothermic oxidation steps. For the low temperature ($< 400°C$) oxidations used in this work, the oxidized products were expected to be of the same molecular size as the feed stock, based on the work of previous researchers from this laboratory (3-6). The synthetic oil used was composed of 38.8 vol % isopropyl benzene and 61.2 vol % n-decane. This combination gave an equivalent alkane carbon number (EACN) of seven, which is characteristic of Pennsylvania crude.

EXPERIMENTAL

Oxidation of the hydrocarbon feed stocks was carried out in the vapor phase in a non-catalytic tubular reactor operating at atmospheric pressure. Air was used as the oxidant, and steam (and in some cases nitrogen gas) were used as diluents. The reactor and the effect of reaction variables on product distribution have been described by other workers from this laboratory (6,7).

The products consisted of a gas (CO, CO_2, N_2, and light hydrocarbons), an aqueous layer (containing some low molecular weight oxygenated compounds), and an organic layer (comprising the major products). The aqueous layer was removed and the remaining organic phase was taken as the oxidized product. In this paper, the term "oxy" is used to refer only to the oxygenated molecules; the term "oxidized product" refers to the entire organic phase obtained directly from the oxidation, which contains both oxygenated material plus unreacted feed stock. The oxy content of the oxidized product was typically 60-70% by volume.

A surfactant solution was then prepared by refluxing the oxidized product with aqueous alkali. The refluxing mixture was well-stirred throughout the reaction. It was determined by titration that about 20% of the oxys were neutralized to surface-active organic acid salts by this procedure.

After the neutralization step, the reaction mixture was allowed to separate. Then the insoluble organic layer was removed along with the oil-water interface. The surfactant and excess base were contained predominantly in the remaining aqueous phase. Electrolyte was added to portions of the aqueous phase to obtain the desired salinity.

In preparation for IFT measurement, 5 ml of synthetic oil was added to 5 ml of surfactant solution in a sample bottle. The contents were shaken for one hour in a Burrell wrist-action shaker set at maximum intensity, and then allowed to separate for 24 hours. Typically, no middle phase was produced, and the oil and aqueous phases appeared clear. A spinning drop interfacial tensiometer was used to determine the IFT between aqueous surfactant solutions and the synthetic oil. All steps were conducted at room temperature, and IFT measurement was continued until a constant reading was obtained.

RESULTS AND DISCUSSION

The properties of the hydrocarbon feed stocks used in the oxidations are listed in Table 1. The reaction conditions and acid solubility for each of the oxidized products are summarized in Table 2. The acid solubility data represent the portion of oxys present in the oxidized products; the acid-insoluble material is a result of the remaining unconverted hydrocarbons. The oxidized products in Batches 2 and 5 are each mixtures from more than one oxidation run.

Infrared spectroscopy was used to identify the functional groups present in the oxidized products. The oxy material was first concentrated by methanol extraction of an oxidized product from those combined in Batch 2. The acid solubility of the concentrated oxy material was 91%. A few drops of the oxy material were placed between two potassium bromide windows, and the IR spectrum is shown in Figure 1. The peak at 1724 cm^{-1} indicates the presence of the carbonyl group; this peak falls into the frequency range characteristic of aldehydes, ketones (1740-1710 cm^{-1}), and carboxylic acids (1725-1700 cm^{-1}). The broad peak between 3600 and 3200 cm^{-1} indicates the presence of the hydroxyl group, such as for an alcohol or carboxylic acid.

TABLE 1

Properties of the Hydrocarbon Feedstocks for Vapor Phase Oxidation

Hydrocarbon	Carnation white oil	MLO-7591
Average carbon number	22	26
Average molecular weight	335	336
Normal B.P. range, °C	220-420	390-460
Carbon in aromatic rings (wt%)	0.97	2.8
Carbon in naphthenic rings (wt%)	31.9	30.2
Carbon in paraffinic chain (wt%)	67.1	67.0

The sodium salts of the organic acids also were analyzed by IR. A mixture of the oxidized product and water was titrated to pH 7 at room temperature with aqueous sodium hydroxide. About 7% of the oxys were neutralized by this procedure. The aqueous phase was separated from the oil, roto-evaporated, and the remaining organic acid salts were dissolved in methanol. A few drops of this solution were placed on a potassium bromide window and the methanol evaporated. The spectrum of the resultant film is shown in Figure 2. Note that the position of the carbonyl peak was shifted to 1568 cm^{-1} in Figure 2, and is in the range characteristic of soaps (1650-1550 cm^{-1}).

It is suggested that refluxing the oxidized product with aqueous base produces sodium carboxylate solutions; the peak at 1568 cm^{-1} in Figure 2 is consistent with this suggestion. Also, the fact that the carbonyl peak (at 1568 cm^{-1}) is relatively high as compared to the other peaks in Figure 2, is expected because the spectrum is for concentrated surfactant. The height of the carbonyl peak (at 1724 cm^{-1} in Figure 1) in the oxidized product is lower relative to the other hydrocarbon structure peaks indicated, as the organic acid fraction of the oxys as determined by direct titration is approximately 7%. The difference in the other peak heights between Figures 1 and 2 may be because the samples were in two different forms during IR analysis—the oxidized products were prepared as a liquid, while the sodium salts were prepared as a solid film.

IFT profiles for each of the oxidized products are shown by the data of Figure 3 at optimum concentrations of sodium hydroxide. For consistency, the concentrations shown are those used in the preparatory steps rather than those determined from the final solutions. In other words, the proportions of oxy and sodium hydroxide are the concentrations that were present in the neutralization step. These concentrations are also used to calculate the sodium-to-oxy ratio. As was mentioned previously, the surface-active organic acid salts account for about 20% of the oxy after neutralization. For example, a 5% oxy concentration represents about 1% of active surfactant. The amount of sodium carbonate is the electrolyte concentration prepared just prior to equilibrating the surfactant solution with synthetic oil.

As the data of Figure 3 show, the minimum (optimum) IFTs occurred between 0 and 1% sodium carbonate (electrolyte) concentration. The IFTs increased sharply for electrolyte concentrations on either side of the optimum, particularly at lower electrolyte concen-

TABLE 2

Properties of the Products from Vapor Phase Oxidation

Batch number	2	3	5
Average carbon number	26	26	22
Sulfuric acid solubility (vol %)	60.8	69.2	66.6
Average reaction temperature (°C)	370–385	306	350–365
Mole O_2/mole feed	3.8–3.9	1.7	3.1–4.4
Mole N_2/mole feed	0	0	11.7–16.5
Mole H_2/mole feed	2.2–3.9	22	14.2–74.6
Average contact time(s)	11–22	11	3.5–16.5
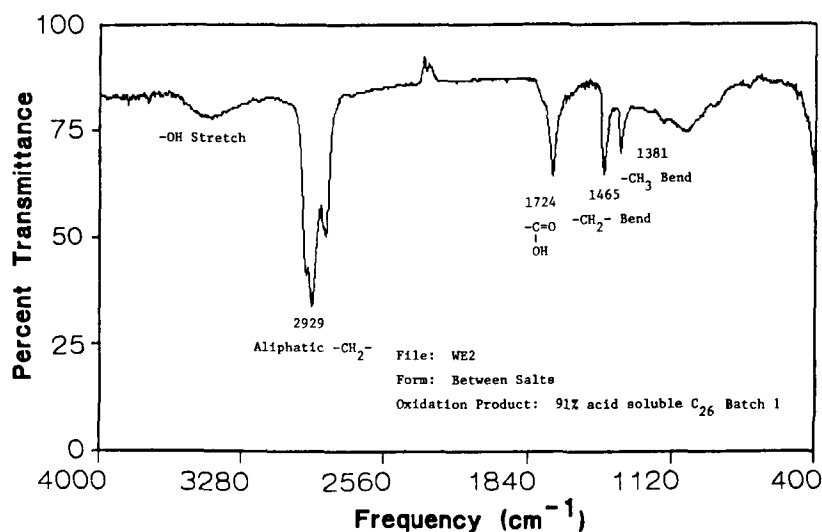
FIG. 1. Infrared spectrum of the oxidation product.
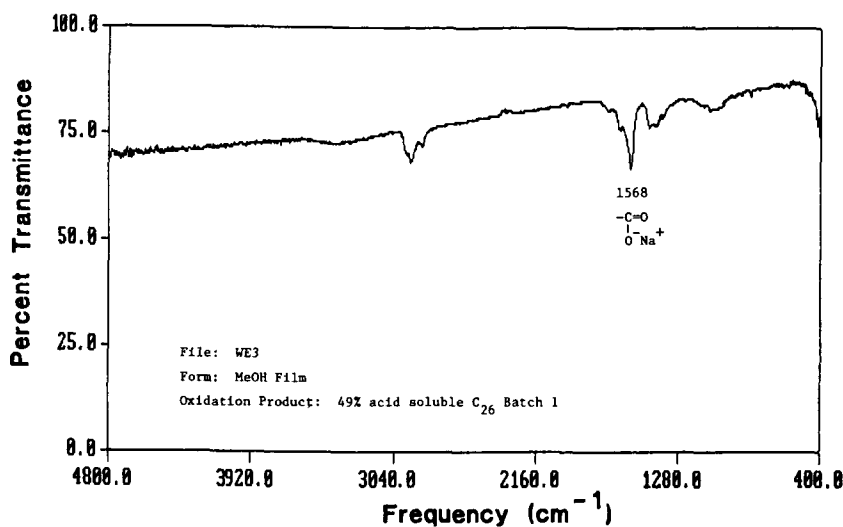
FIG. 2. Infrared spectrum of the organic acid salt.

trations. The dotted lines in Figure 3 indicate that in this region the IFTs were higher than could be measured by the spinning drop technique. The pHs are of electrolyte-free solutions.

If the amount of sodium hydroxide used in the neutralization differed from that shown for each of the oxidized products in the data of Figure 3, the IFT profile would be higher. For example, for a 5.0% oxy concentration from the Batch 3 oxidized product, the lowest IFT profile was obtained in the 0.19—0.22% sodium hydroxide concentration range. Neutralizations that used a concentration of sodium hydroxide above or below this range resulted in aqueous solutions that exhibited higher IFTs against oil. The data of Figure 4 show these results for small increments of sodium hydroxide concentration for 0.16—0.25% and at 2.0%.
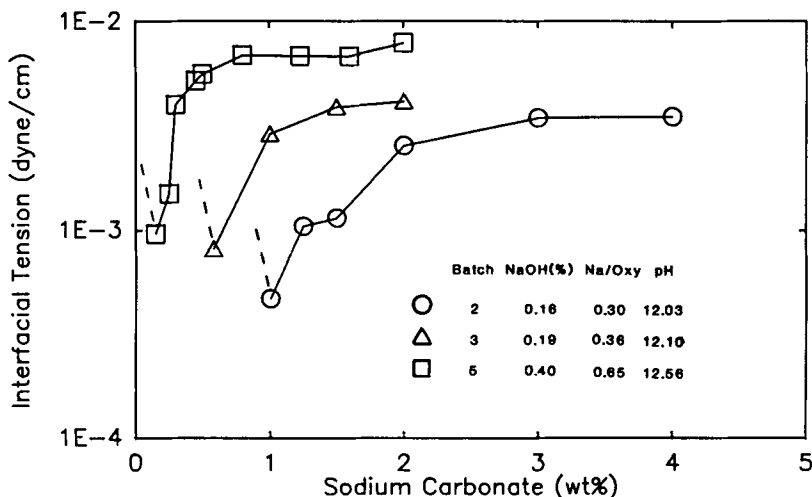
FIG. 3. The IFT profiles of various oxidized products at 5.0% oxy concentration neutralized with sodium hydroxide.
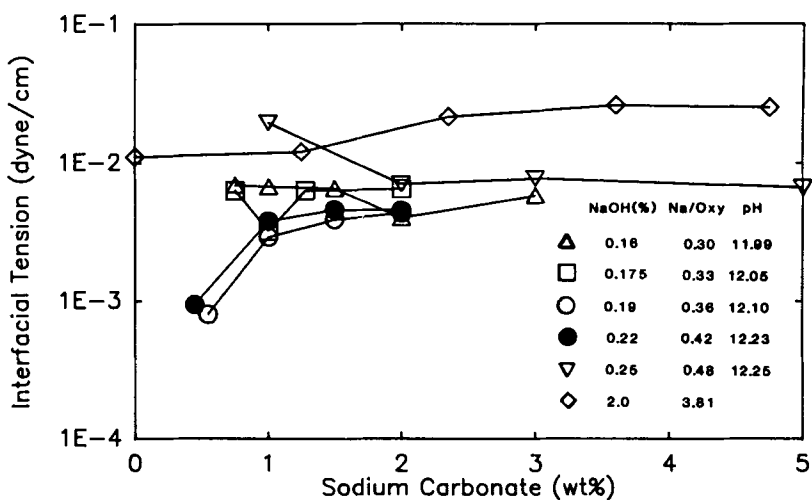

FIG. 4. Effect of sodium hydroxide concentration during neutralization of 5.0% oxy (Batch 3) on solution pH and IFT.

Sodium carbonate was used as the electrolyte in concentrations ranging from 0–5.0%.

While a sufficient concentration of base is desirable to neutralize all of the organic acids from the oxidized products, it was determined that an excess of sodium hydroxide would cause some of the more oil-soluble surfactant molecules to partition back into the organic phase during neutralization. As the organic phase was removed after the neutralization step, any surfactant it contained was lost. Therefore, the solutions neutralized with the concentrations of 0.19 and 0.22% sodium hydroxide (which achieved the lowest IFTs in Figure 4) may have contained intermediate distributions of oil-soluble and water-soluble surfactant molecules. This range of minimum IFT may correspond to the onset of micellization (8).

Furthermore, surfactant solutions that achieved the lowest IFTs were prepared from neutralizations

using sodium hydroxide rather than sodium silicate, sodium tripolyphosphate, or sodium carbonate. When sodium hydroxide was used as the alkali, it is likely that more surfactants were produced and retained in the aqueous solution following neutralization. As sodium hydroxide was the strongest base used, the weak organic acids were more completely converted to their surface-active sodium salts, and less alkali was required in the neutralization. It is reasoned that with less sodium hydroxide in solution, less surfactant would partition back into the insoluble organic phase during the neutralization step.

In another study, the concentration of oxy material used in the neutralizations was varied, while the amount of sodium hydroxide used was such that the surfactant solutions exhibited the same pH. Figure 5 shows the IFT profiles for surfactant solutions prepared from 0.5—5.0% oxy (Batch 2), where the pHs of
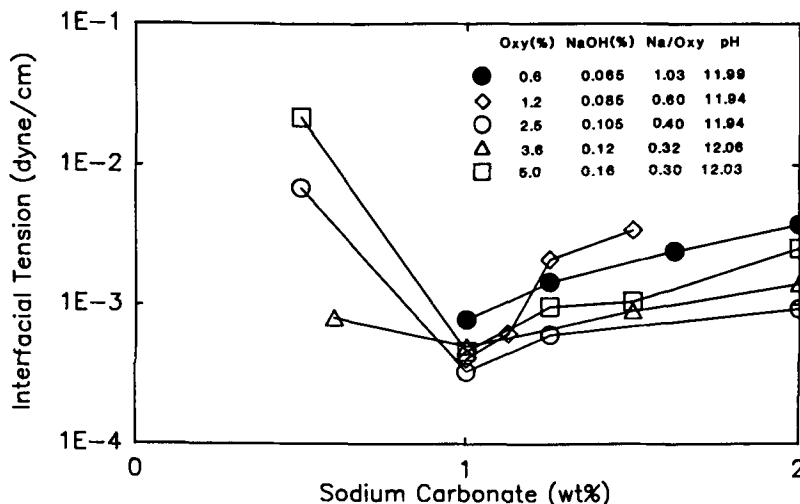
FIG. 5. The effect of oxy (Batch 2) concentration on the IFT profile at constant pH for neutralization with sodium hydroxide.

the final solutions were about 12.0. Each of the solutions exhibits similar IFT behavior, and the optimum IFT values all occur at 1.0% sodium carbonate. Also, the values of the optimum IFTs only vary between about 3×10^{-4} to 8×10^{-4} dyne/cm over the range of oxy concentration shown.

While keeping in mind that neither the actual concentrations nor the nature of the surfactants were not established for these solutions, these data demonstrate that the surfactant solubility in the aqueous phase may be limited by the amount of excess sodium hydroxide (indicated by the pH of the final solution) used in the neutralization. As a result, all the solutions in Figure 5 may contain similar concentrations of surfactant. For solutions produced from higher oxy concentrations, the additional surfactant may have partitioned back into the organic phase during the neutralization step. A technique to recover and utilize the partitioned surfactants was developed and will be reported separately.

In another experiment it was shown that if the oxy concentration was varied and the final solution pH was not constant, then the IFT behavior varied and the optimum IFTs did not occur at a common electrolyte concentration. For example, the data of Figure 6 show such results for 0.5-5.0% oxy (Batch 5). Generally, the higher oxy concentrations were neutralized with a sufficient excess of sodium hydroxide to yield final solutions of higher pH. Also, the concentration of electrolyte at the optimum IFT was inversely related to pH. The solutions prepared from 2.0 and 3.0% oxy material had an essentially identical pH, and their optimum IFTs occurred at a common electrolyte concentration. The optimum IFT values vary from about 2×10^{-4} to 1×10^{-3} dyne/cm.

One of the primary concerns when using the sodium salts of organic acids (rather than sulfonates) is their ability to remain interfacially active in the presence of divalent metal cations. As only the sodium and potassium salts are water-soluble, ion exchange with

calcium or magnesium would cause precipitation of the surfactant.

The calcium chloride tolerance of three surfactant solutions was evaluated. In each case, 3.0% oxy was employed, sodium hydroxide was used in the neutralization step, and sodium carbonate was added as an electrolyte. Then calcium chloride was added to these solutions in concentrations of up to 1000 ppm. The IFTs generated by these solutions are plotted in Figure 7. These data demonstrate that the surfactants produced from the oxidized products are unaffected in the presence of 100 ppm calcium chloride and remain rather effective at concentrations of 1000 ppm. Comparing the two surfactant solutions produced from the Batch 2 oxidized product, the IFT increased more gradually for the solution containing the lower concentration of electrolyte. The solutions derived from Batch 2 (C_{26}) and Batch 5 (C_{22}) oxidized products were about equally effective.

Sodium silicate has been reported to be an effective agent for reducing adsorption losses in surfactant flooding applications (9). When the oxidized products were neutralized with sodium silicate, the resultant surfactant solutions exhibited somewhat higher IFTs and were less sensitive to electrolyte concentration than surfactant solutions prepared from neutralizations with low concentrations of sodium hydroxide.

The data of Figure 8 show the IFT results for surfactant solutions prepared from the Batch 3 oxidized product using sodium hydroxide, sodium silicate, and a combination of these two bases in the neutralization step. The latter solution produced an IFT profile that was approximately intermediate to the other two, except in the range of 0-0.5% sodium carbonate, where it achieved the lowest IFTs.

The data in Figure 9 show the changes in the IFT profile brought about by using varying proportions of sodium hydroxide (0.19 and 0.24%) and sodium silicate (0.75 and 2.8%) together in the neutralization step. The data show that increasing the concentration of
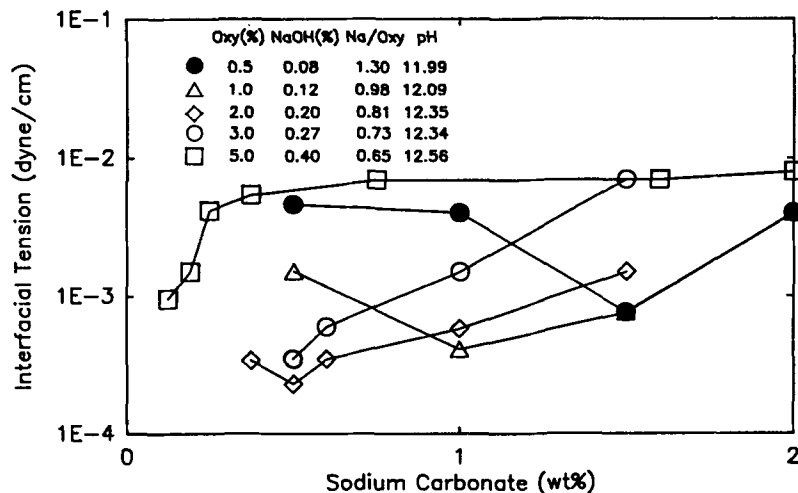
FIG. 6. The effect of oxy (Batch 5) concentration on the IFT profile after neutralization with sodium hydroxide at various sodium/oxy ratios.
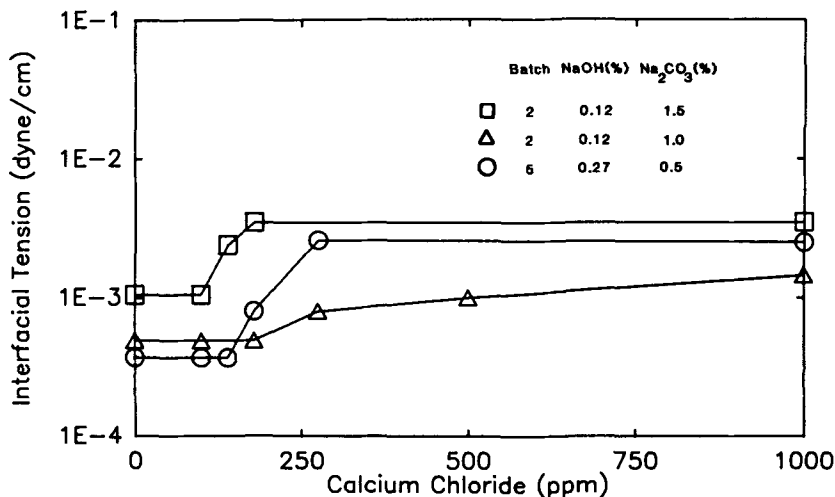

FIG. 7. The effect of calcium chloride concentration on IFT after neutralization of 3.0% oxy with sodium hydroxide.

either base caused a decrease in the electrolyte concentration where the optimum IFT occurred. Relatively flat IFT profiles were exhibited by the two solutions that contained 0.75% sodium silicate.

In another experiment, dilution was used to investigate the effect of surfactant concentration on the IFT profile. Dilution has the advantage that the concentration of surfactant can be changed in a precise way without affecting the molar ratio of the surfactant to other components in the solution. For this purpose, a large volume of surfactant solution was prepared from 5.0% oxy (Batch 3) using 0.19% sodium hydroxide and 0.75% sodium silicate in the neutralization step. Since about 20% of the oxy is converted to surface-active material, a surfactant solution containing about 1% active material was anticipated. Surfactant solutions ranging from about 0.2 to 1% active were then obtained by dilution. Over the range of the data of

Figure 10, progressively lower optimum IFTs were obtained as the concentration of active material was reduced. Furthermore, the electrolyte concentration where the optimum IFT occurred was directly proportional to the surfactant concentration for dilutions from 1 down to 0.4% active. The optimum IFT begins to occur at a slightly higher electrolyte concentration for the 0.2% active solution, possibly because of this solution's lower ionic strength.

Sodium tripolyphosphate was chosen as a base in the neutralization of the oxidized products as it was documented in the literature to be an effective agent in the reduction of surfactant losses by adsorption in alkaline systems (9). IFT profiles obtained by the neutralization of 5.0% oxy (Batch 3) with 1.7% sodium tripolyphosphate are shown in Figure 11. Similar results were obtained using either sodium chloride or sodium carbonate as an electrolyte, although a flatter
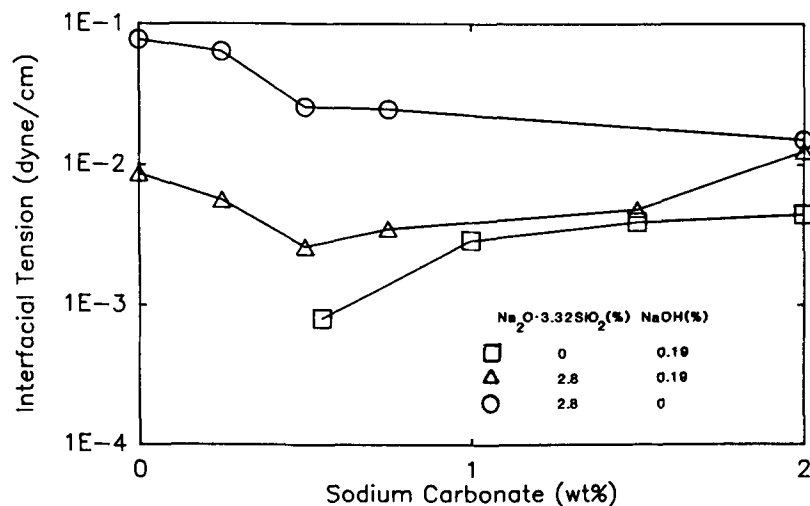
FIG. 8. The effect of neutralization of 5.0% oxy (Batch 3) with both sodium silicate and sodium hydroxide on the IFT profile compared to neutralization with these bases individually.
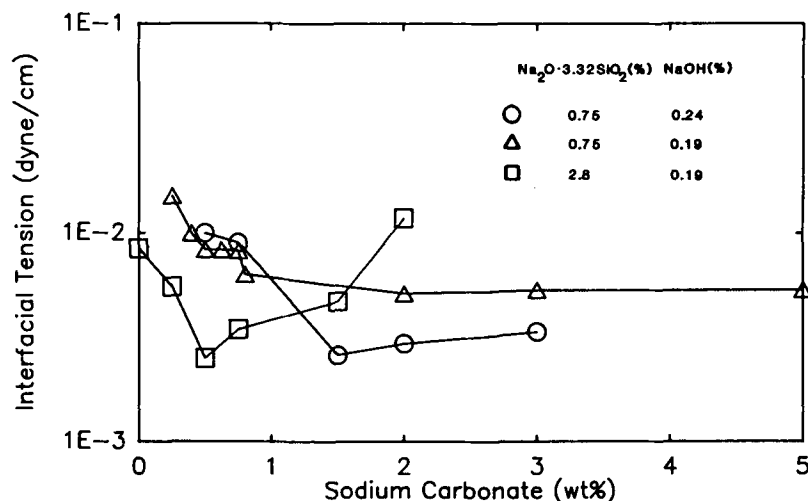

FIG. 9. The effect of neutralization of 5.0% oxy (Batch 3) with various concentrations of sodium silicate and sodium hydroxide on the IFT profile.

IFT profile was obtained in the latter case. The lowest IFT was obtained when no electrolyte was added.

Figure 12 shows the IFT results obtained by using sodium hydroxide (0.19%) and sodium tripolyphosphate (0.85%) together in the neutralization of 5.0% oxy (Batch 3) and using sodium carbonate as the electrolyte. The sodium carbonate scan from the previous figure is included for comparison. The reduction in sodium tripolyphosphate (from 1.7-0.85%) was made in an effort to increase the salt tolerance of the surfactant solution relative to that shown in Figure 11. Furthermore, it was predicted that there would be a greater need to reduce the sodium tripolyphosphate concentration due to the addition of sodium hydroxide. These steps resulted in a much improved salt tolerance, as can be seen by the lower IFT profile in Figure 12.

Besides its role as an electrolyte, sodium carbon-

ate was found to be an adequate base for use in the neutralization step. The data of Figure 13 show the IFT profiles obtained from the neutralization of 3.0% oxy (Batch 5) with 1.0% sodium carbonate, while using either sodium chloride or additional sodium carbonate as electrolyte. While the IFT values in Figure 13 are higher than some shown in previous figures, they are comparable at higher concentrations of electrolyte and are not out of the range of interest for EOR applications. In fact, these data could be the most economically significant if raw mined sodium carbonate could be used with similar results.

To test the oil-recovery potential, a surfactant solution was prepared from 5% oxy (Batch 3) by neutralization with 0.19% sodium hydroxide and 0.75% sodium silicate. After separation of the insoluble organic layer, an aqueous solution containing about 1% surfac-
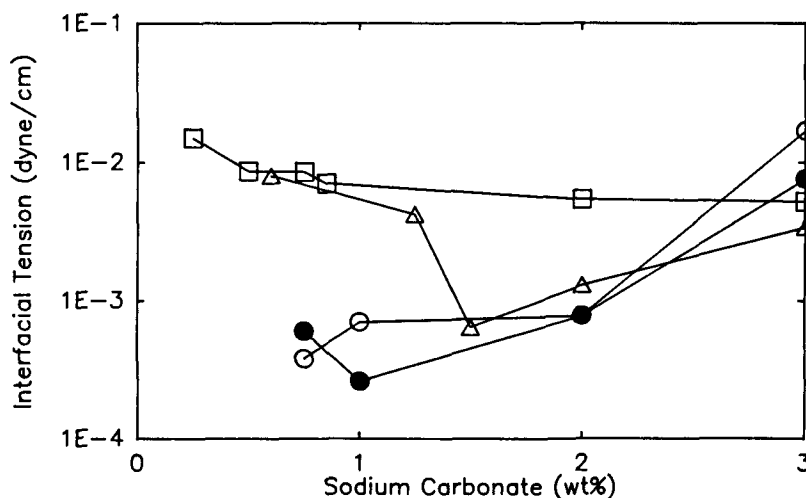
FIG. 10. The effect of oxy concentration on the IFT profile at constant sodium/oxy by dilution of a 1.0% active solution produced by neutralization of 5.0% oxy (Batch 3) with 0.75% sodium silicate and 0.19% sodium hydroxide. The resulting solutions were 1.0% (□), 0.8% (△), 0.4% (●), and 0.2% (●) active.
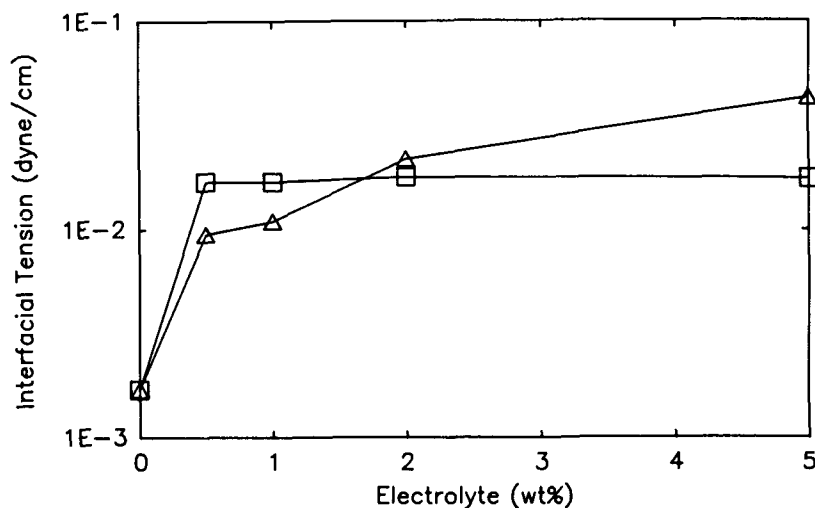

FIG. 11. The effect of sodium carbonate (□) and sodium chloride (△) electrolytes on the IFT after neutralization of 5.0% oxy (Batch 3) with 1.7% sodium tripolyphosphate.

tant was expected, and 1.2% sodium carbonate was added as an electrolyte. (This solution was chosen based on affirmative adsorption test results. The development of the adsorption test and its use in predicting oil-recovery potential will be reported separately). Core testing was performed by Yeager (10) in the Department of Petroleum and Natural Gas Engineering at the Pennsylvania State University.

A two-foot-long Berea sandstone core (304 mD permeability and 22.2% porosity) of a two-inch diameter,

round cross-section was saturated with the synthetic oil (EACN 7). Beginning with an initial oil saturation of 54.7%, the core was preflushed with brine (0.75% sodium silicate and 1.2% sodium carbonate) to simulate secondary recovery and to precondition the core for surfactant flooding. The brine was injected until the oil content of the produced fluids was less than 1 vol %. The residual oil saturation was 29.6% after brine flooding. A 1 pore volume (PV) slug of surfactant solution injected at 5 cm³/hr (1 ft/day) recovered 42.0%
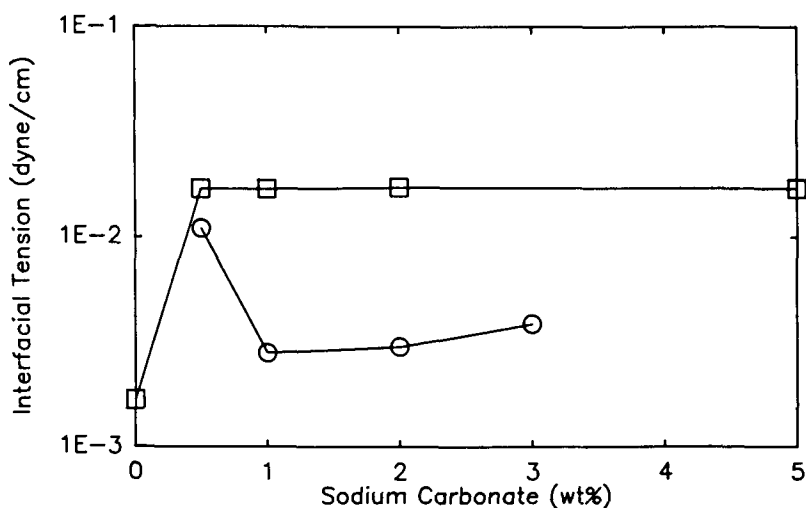
FIG. 12. The effect of neutralization of 5.0% oxy (Batch 3) with 0.85% sodium tripolyphosphate and 0.19% sodium hydroxide (O), as compared to neutralization with 1.7% sodium tripolyphosphate (□).
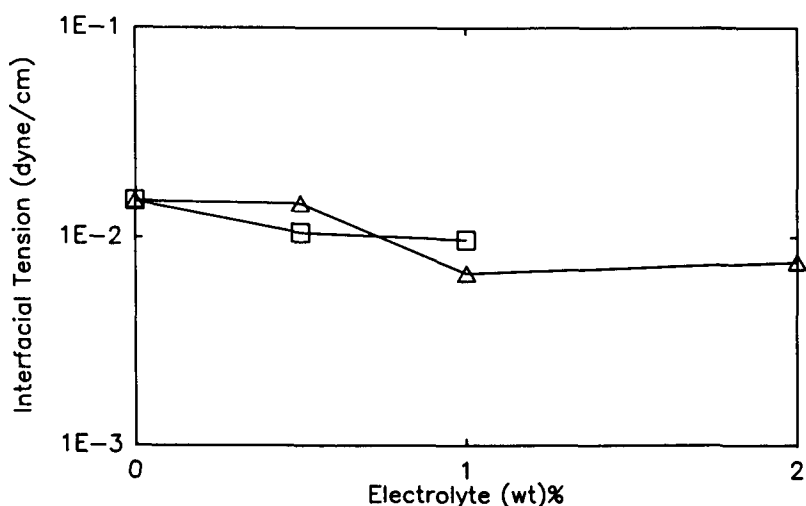

FIG. 13. The effect of sodium carbonate (□) and sodium chloride (△) electrolytes on the IFT profile after neutralization of 3.0% oxy (Batch 5) with 1.0% sodium carbonate.

of the residual oil. The surfactant was followed by 1 PV mobility buffer (40% brine and 60% glycerol) that brought the total recovery to 45.8% of residual oil. This recovery is encouraging, taking into account the low concentration of actual surfactant required.

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