

Alkalines Can Improve Miscibility of a Surfactant-Oil-Brine System and Areal Sweep Efficiency of Oil

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ABSTRACT

This paper deals with the effect of alkali on the phase behavior of some available surfactants (Petrostep HMW) – Safaniya crude oil-brine system and the phase relations were obtained after equilibrium at 25 and 70 °C. New results of the areal sweep efficiency in alkaline flooding is presented. It was found that the miscibility increases when using NaOH and with increasing concentration from 0.5 to 1.0 % for reservoir salinity of 23 % NaCl. Increasing NaCl concentration from 3.84 to 23 % decreases the system miscibility. Temperature increase decreases miscibility. It was also found that waterflooding oil sweep efficiency increases with adding NaOH in the flooding water. A composite slug of alkaline and polymer additives improved oil displacement efficiency. Areal sweep efficiency increased with increasing NaOH concentration. Areal sweep efficiencies in the homogeneous sandpack were found to be much better than in the non-homogeneous sandpack.

1. INTRODUCTION

Since the surfactant solution flood rely on a prolonged miscible displacement, information on the phase equilibrium of these solutions is necessary to formulate systems that exhibit small two phase regions. Also for the low tension immiscible fluid may be possible to decrease surfactant requirement as the area of the two phase region is diminished.

A serious limitation on the use of surfactant solutions is their incompatibility with and/or sensitivity to reservoir fluids and rocks. It was found [1 – 4] that divalent ions are notorious, particularly calcium ions which may exchange the sodium ions of the petroleum sulfonates increasing their molecular weight.

Alkaline chemicals have been used in the preflushes for most of the chemical flooding process. Alkali, as a preflush, are effective for removing a major portion of the multivalent cations ahead of the surfactant front. Therefore, the inclusion of the alkaline chemicals directly in the surfactant slug is intended to give further protection of the surfactant [5].

Displacement of oil by alkaline solutions is an important process. Both laboratory investigations and actual field tests of this oil recovery process have established its importance as an enhanced oil recovery method [6 – 12]. These studies demonstrated the increase in oil recovery by alkaline additives. Different mechanisms have been proposed to explain the displacement process of oil by alkaline solutions. In all of these mechanisms, reaction between the alkaline solution and certain organic acids present in some crude oils results in the formation of soaps. The for-

mation of these soaps enhances emulsification. The interfacial tension is lowered with the emulsification process. Under certain conditions, the rock wettability may be altered either from oil-wet to water-wet or the reverse. This wettability change results in an increase in oil recovery regardless of the direction of wettability reversal.

The main objective of this study was to investigate the effect of alkaline and polymer on the phase behavior of surfactant-oil-brine system and to determine the areal sweep of oil displacement by using alkaline solutions.

2. EXPERIMENTAL WORK

Phase behavior experiments were performed in order to establish ternary relations between surfactant, Safaniya crude and brine solutions. The composition of the phases were measured when equilibrium was obtained at 25 °C and at 70 °C. The volumes of the aqueous and oleic

Table 1 Surfactant Composition and Fluid Properties

(a) Composition of HMW Surfactant				
Sulphonate actives		50.7 %		
Free oil		24.4 %		
Water		22.1 %		
Inorganic salt		2.8 %		
Equivalent weight range		500 – 530		
Density (lb/gal at 120°F)		9 – 9.4		
(b) Physical Properties of Fluids Used at 23 °C				
Fluid type	Density, g/cm ³	Viscosity, cp	Concentration	pH
Crude oil	0.9178	50.0	–	–
Brine	1.0002	1.26	3.5 % NaCl	9.50
Alkaline	1.0002	1.235	0.5 % NaOH	12.30
Alkaline	1.032	1.235	1 % NaOH	12.50
Polymer	1.002	s. Fig. 1	500 ppm	7.91
Alkaline-Polymer	1.002	s. Fig. 1	500 ppm	12.33
Composite			0.5 % NaOH	
Isopropyl	0.7845	2.00	– 8.14	

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improved as shown in Fig. 12. Hence, this minimum mobility value can establish adequate mobility control at very low rates; thus, an improvement in the displacement efficiency was achieved.

Minimum rate point, which is defined as the flood advance rate at which the tertiary oil recovery was a minimum, was shifted toward the right of the minimum rate point of the 2-ft cores as the core length increased as shown in Figs. 1 and 2. This behavior could be explained in the light of the mechanisms discussed previously. It has been established that the mobility of the Kelzan buffer that moved ahead of the brine was reduced by flow rate. For a given porous medium having the same cross-sectional area and the same injection rate, the pressure difference was higher in the longer cores. This allows the effect of mobility control by the buffer solution to appear early in the 4-ft cores. Therefore, it can be seen that the minimum rate point is shifted toward the right when core length is increased. Actually, what has been said will depend on the system used.

Effect of Rate on Formation of Stabilized Oil/Water Bank

The production histories for the 10% PV slug displacements in 4-ft-long cores at different rates are shown in Fig. 17. Cumulative oil recovery is expressed as a percentage of tertiary oil in place. Production histories for rates of 4.35 and 0.5 ft/D show that there is a wider stabilized oil/water bank (0.43 to 0.57) compared with that for a rate of 0.94 ft/D (0.27). Although at 0.5 ft/D the micellar solution production was small, the oil recovery increased. This could be explained by the low mobility of the buffer at this rate or the much lower interfacial tension inside the core than the externally measured values, which implies an improvement in the displacement efficiency.

It is evident from the production histories for different rates but same slug size and core length that the stabilized oil/water bank breakthrough varies with rate.

This can be explained by the bypassing of the core resident oil and water by the micellar slug front. This observation agreed with what has been published in the literature.^{6,10,13}

Implications of Very Low Flood Advance Rates

The Lawry-Penn Grade-DOE project is a field test to demonstrate the efficiency and economics of the tertiary recovery of oil by micellar solutions from a low-permeability (7-md) depleted waterflooded reservoir. The field advance rates in this project are comparable with our laboratory low rates (on the order of 0.10 ft/D). This flood is still in progress, and the response is yet to come.

An understanding of the effect of the flood advance rate will be of value in the design of micellar solutions and mobility buffers. A mechanistic and quantitative basis for interpreting the field test results then could be obtained. In addition, useful

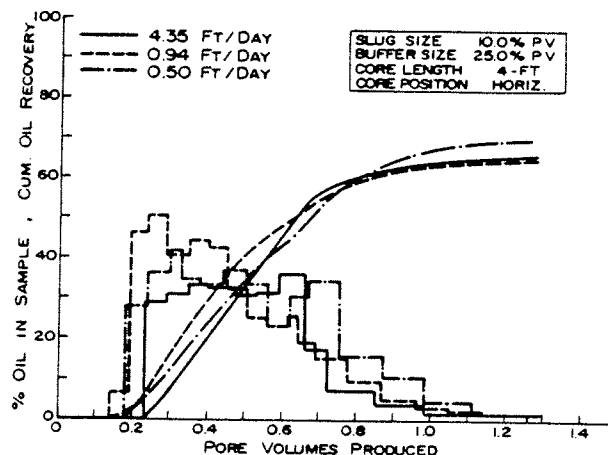


Fig. 17 - Production histories for 10% PV slug displacements in 4-ft cores at different flood advance rates.

correlations of the final oil saturation with rate are now available from the laboratory tests.

Conclusions

Experiments were carried out where micellar slugs used in the Pennsylvania field tests were injected at rates of 0.10 to 5.20 ft/D into waterflooded 2- and 4-ft Berea sandstone cores. The following conclusions can be derived from this work.

1. Oil recovery by micellar solutions was found to be rate dependent for all slug sizes tested.
2. Oil recovery tends to decrease with decreasing rate up to a point; thereafter, it shows a small increase with further decrease in rate.
3. On the basis of the viscosity/shear characteristics of the polymer employed, mobility control by the buffer is rate dependent.
4. Mobility of the buffer solution decreases with decreasing rate.
5. Oil recovery is a function of the ratio between viscous and capillary forces, and it was found that the high value of this ratio was the controlling parameter in increasing the fractional flow of oil in the stabilized bank.
6. Sulfonate adsorption on Berea sandstone increases with solution concentration. For the same concentration, a noticeable change in adsorption was observed for different rates.
7. Reduced sulfonate adsorption was observed on the crushed Berea sandstone under static conditions in the presence of the polymer solution.
8. The stabilized oil/water bank size and its breakthrough time were rate dependent.
9. The micellar slug was affected by its breakdown to an extent that depended on flow rate.

Nomenclature

- A = area of core cross section, sq ft
- c = parameter found from drop dimensions
- d = measured diameter of drop, cm
- f = fractional flow, dimensionless
- k = absolute permeability, darcy

TABLE 2 - PROPERTIES OF POROUS MEDIA

Type	Core Length (ft)	Core Diameter (in.)	Porosity (%)	Permeability (md)
Berea sandstone (Core A)	4	2	20	107 to 332
Berea sandstone (Core B)	2	2	20	71 to 239

TABLE 3 - COMPOSITION OF MICELLAR SOLUTIONS

Component	Composition (vol%)
Richburg micellar slug	
Water	68.03
Diesel oil	17.97
Sulfonate TRS 16*	5.46
Sulfonate TRS 40*	5.51
Amyl alcohol	2.37
Butyl alcohol	0.66
Bradford micellar slug	
Water	59.65
Sulfonate TRS 16	4.04
Sulfonate TRS 48*	4.92
Crude oil	27.58
Neodahl	0.87
Amyl alcohol	1.30
n-butyl alcohol	1.64

*Witco Chemical Co., Bradford, PA.

TABLE 4 - PHYSICAL PROPERTIES OF LIQUIDS

Liquid	Viscosity (cp)	Specific Gravity	Refractive Index
Bradford crude	3.4	0.794	1.454
Richburg slug	11.8	0.968	1.368
Bradford slug	7.0	0.809	1.370
2% NaCl brine	1.02	1.010	1.332
350-ppm Kelzan buffer	5.0 to 6.0	1.00	1.3325

k_r = relative permeability, dimensionless

\bar{K} = constant

L = length of core, ft

n = Ostwald-de Waele power law index

N_c = capillary number, dimensionless

\bar{p} = tensiometer period read off counter, ms/RRV

Δp = pressure difference, psi

R_F = flow resistance

t = time variable, days

v = frontal velocity, ft/D

w = speed of revolution radius, rad/s

γ = interfacial tension, dyne/cm

$\dot{\gamma}$ = shear rate, seconds⁻¹

λ = mobility, cp⁻¹

μ = viscosity, cp

$\Delta\rho$ = density difference between the two phases, g/cm³

ϕ = porosity, dimensionless

Subscripts

b = stabilized bank

o = oil or oleic

p = polymer solution

t = total

w = water or aqueous

Acknowledgment

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APPENDIX A

Material, Apparatus, and Experimental Techniques

The properties of the porous medium used in the experimental investigation are given in Table 2. The micellar solutions being used in the Pennsylvania field tests were employed for this work. These micellar solutions are referred to as the Richburg and Bradford slugs. The compositions of the two micellar solutions are shown in Table 3. The mobility buffer

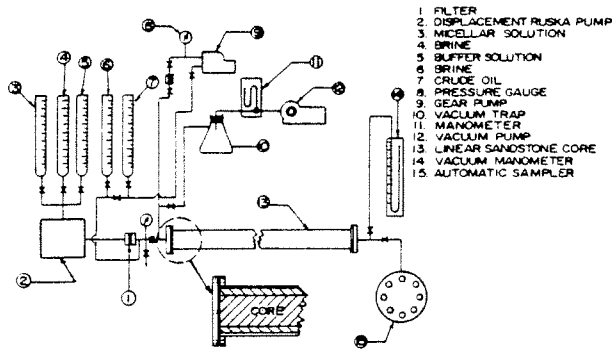


Fig. 18 - Experimental apparatus.

consists of 350-ppm Kelzan. The physical properties of the different fluids used in this research are shown in Table 4.

The experimental apparatus is shown schematically in Fig. 18. The sandstone cores initially were saturated with 2% sodium chloride brine, then flooded with crude, and thereafter waterflooded with brine. The core then attained the residual oil saturation, and a tertiary micellar flood then could be initiated. A new core was used for each run. The same brine was used for driving the mobility buffer.

The method used in finding the interfacial tension was the spinning drop technique¹⁴ based on measuring the length L and width h of the drop. If $0 \leq L - h < 3h$, the following equation was used.¹⁴

$$\gamma = \frac{\Delta p w^2}{4C} \dots \dots \dots (A-1)$$

On the other hand, if the drop length was greater than four times the width (i.e., $L > 4h$), the interfacial tension was determined by¹⁴

$$\gamma = 5.2203 \times 10^5 \frac{\Delta \rho d^3}{p - 2} \dots \dots \dots (A-2)$$

Rheological Behavior of Micellar Solutions and Mobility Buffers

The micellar solutions used exhibited the rheological behavior of a Newtonian fluid shown in Fig. 19. The viscous properties of the Kelzan buffer as measured at room temperature in a Brookfield viscometer are shown in the same figure. The laboratory tests showed that the viscosity of the mobility buffer decreases with mechanical shear.

APPENDIX B

Mobility of Buffer Solution

The total mobility of the stabilized oil/water bank is defined as

$$\lambda_t = \lambda_o + \lambda_w = \frac{k_{ro}}{\mu_o} + \frac{k_{rw}}{\mu_w} \dots \dots \dots (B-1)$$

The mobility ratio between the buffer bank and the stabilized bank can be written as

$$M = \frac{k_p}{\mu_p} \left(\frac{k_{ro}}{\mu_o} + \frac{k_{rw}}{\mu_w} \right)^{-1} \dots \dots \dots (B-2)$$

or

$$M = \frac{k_p}{\mu_p} \cdot R_F, \dots \dots \dots (B-3)$$

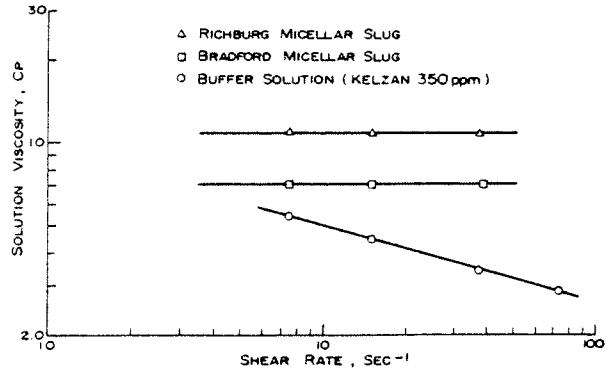


Fig. 19 - Rheological behavior of micellar solutions and Kelzan buffer (350 ppm).

where R_F is the flow resistance.

To obtain adequate mobility, the mobility of the buffer bank displacing the micellar slug must be equal to or less than the total mobility of the oil/water bank - i.e.,

$$\left(\frac{k_p}{\mu_p} \right) R_F \leq 1 \dots \dots \dots (B-4)$$

Fig. 19 shows that the buffer solution exhibits non-Newtonian behavior. The relationship between the apparent viscosity of the buffer solution and shear rate can be obtained as

$$\mu_p = \bar{K} (\dot{\gamma})^{n-1} \dots \dots \dots (B-5)$$

To calculate the shear rates in a reservoir, the following equation can be used.¹⁵

$$\dot{\gamma} = \frac{3v \left(3 + \frac{1}{n} \right)}{\sqrt{150 \bar{K} \phi}} \dots \dots \dots (B-6)$$

where the power law index n can be obtained from Fig. 19.

Finally, mobility of the buffer solution during a displacement process can be evaluated from Eqs. B-5 and B-6 as follows.

$$\lambda_p = \frac{k}{\bar{K}} \left[\frac{3v \left(3 + \frac{1}{n} \right)}{\sqrt{150 \bar{K} \phi}} \right]^{1-n} \dots \dots \dots (B-7)$$

or

$$\lambda_p = \frac{k}{\bar{K}} \left[\frac{v \left(3 + \frac{1}{n} \right)}{\sqrt{16.67 \bar{K} \phi}} \right]^{1-n} \dots \dots \dots (B-8)$$

SI Metric Conversion Factors

cp × 1.0*	E-03 = Pa·s
dyne/cm × 1	= mN/m
ft × 3.048*	E-01 = m
in. × 2.54*	E+00 = cm
psi × 6.894 757	E+00 = kPa
sq ft × 9.290 304*	E-02 = m ²

*Conversion factor is exact.

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Phase Behavior of CO₂ and Crude Oil in Low-Temperature Reservoirs

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Abstract

Phase behavior of CO₂/crude-oil mixtures which exhibit liquid/liquid (L/L) and liquid/liquid/vapor (L/L/V) equilibria is examined. Results of single-contact phase behavior experiments for CO₂/separator-oil mixtures are reported. Experimental results are interpreted using pseudoternary phase diagrams based on a review of phase behavior data for binary and ternary mixtures of CO₂ with alkanes. Implications for the displacement process of L/L/V phase behavior are examined using a one-dimensional finite difference simulator. Results of the analysis suggest that L/L and L/L/V equilibria will occur for CO₂/crude-oil mixtures at temperatures below about 120°F (49°C) and that development of miscibility occurs by extraction of hydrocarbons from the oil into a CO₂-rich liquid phase in such systems.

Introduction

The efficiency of a displacement of oil by CO₂ depends on a variety of factors, including phase behavior of CO₂/crude-oil mixtures generated during the displacement, densities and viscosities of the phases present, relative permeabilities to individual phases, and a host of additional complications such as dispersion, viscous fingering, reservoir heterogeneities, and layering. It generally is acknowledged that phase behavior and attendant compositional effects on fluid properties strongly influence local displacement efficiency,¹⁻⁵ though it also is clear that on a reservoir scale, poor vertical and areal sweep efficiency (caused by the low viscosity of the displacing CO₂) may negate the favorable effects of phase behavior.³

Interpretation of the effects of phase behavior on

displacement efficiency is made difficult by the complexity of the behavior of CO₂/crude-oil mixtures. The standard interpretation of CO₂ flooding phase behavior, given first by Rathmell *et al.*¹ is that CO₂ flooding behaves much like a vaporizing gas drive, as described originally by Hutchinson and Braun.⁶ During a flood, vapor-phase CO₂ mixes with oil in place and extracts light and intermediate hydrocarbons. After multiple contacts, the CO₂-rich phase vaporizes enough hydrocarbons to develop a composition that can displace oil efficiently, if not miscibly. The picture presented by Rathmell *et al.*¹ appears to be consistent with phase behavior observed for CO₂/crude-oil mixtures as long as the reservoir temperature is high enough. Table 1 summarizes data reported for CO₂/crude-oil mixtures. Of the 10 systems studied, all those at temperatures above 120°F (50°C) show only L/V equilibria while those below 120°F exhibit L/L/V separations (Stalkup³ also reports two phase diagrams that are qualitatively similar to the other low-temperature diagrams but does not give temperatures). Thus, at temperatures not too far above the critical temperature of CO₂ [88°F (31°C)], mixtures of CO₂ and crude oil exhibit multiple liquid phases, and at some pressures L/L/V equilibria are observed.^{5,7,8}

It has not been established whether Rathmell *et al.*'s¹ interpretation of the process mechanism can be extended to cover the more complex phase behavior of low-temperature CO₂/crude-oil mixtures. In a recent paper, Metcalfe and Yarborough⁴ argued that low-temperature CO₂ floods behave more like condensing gas drives,⁶ whereas Kamath *et al.*¹³ concluded that an increase in the solubility of liquid-phase CO₂ in crude oil at temperatures near the critical temperature of CO₂ should cause more efficient displacements of oil by CO₂. Huang and

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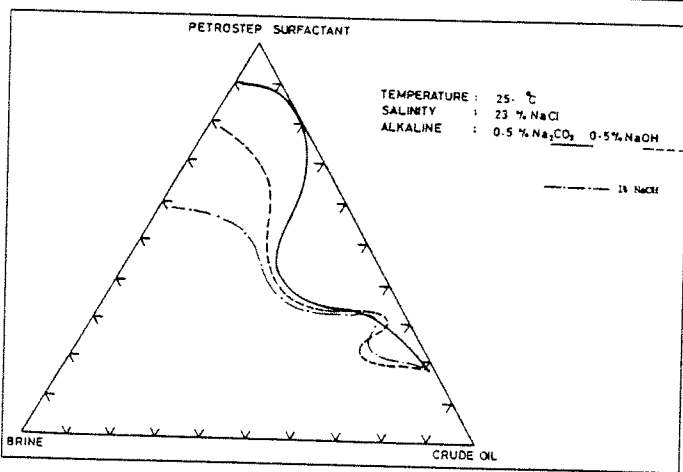


Fig. 1 Phase diagram of petrostep surfactant/crude oil/water at 25 °C for Na₂CO₃ and NaOH solutions

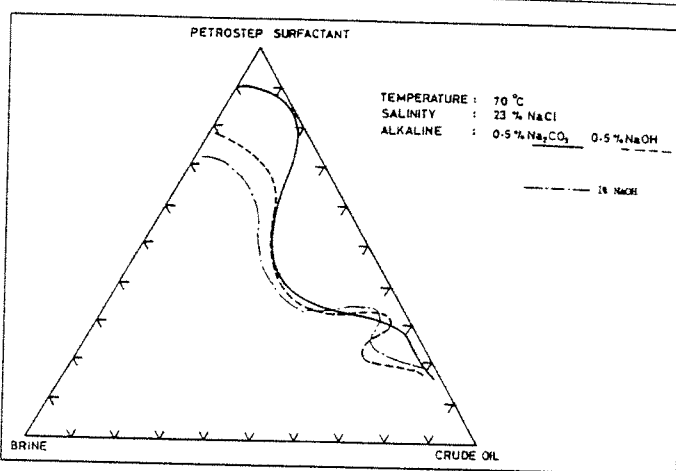


Fig. 2 Phase diagram of petrostep surfactant/crude oil/water at 70 °C for Na₂CO₃ and NaOH solutions

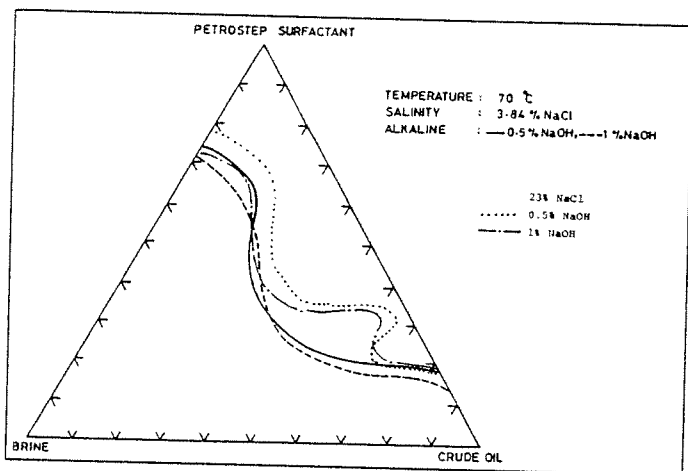


Fig. 3 Effect of NaOH concentration on phase behavior at 70 °C

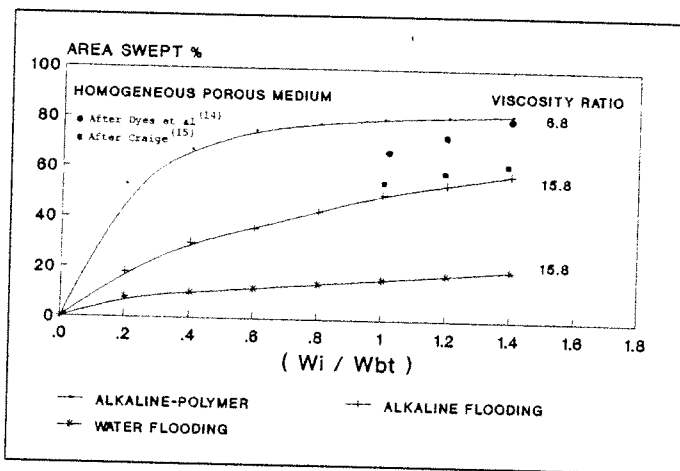


Fig. 4 Area swept vs. W_i/W_{bt} for different processes

phases were measured at the laboratory temperature (25 °C) at different times until equilibrium was obtained. The samples were then placed in an oven at reservoir temperature of 70 °C until equilibrium was obtained. The phase diagrams were obtained at these temperatures. The available composition of Petrostep HMW surfactant and the properties of the used fluids are shown in Table 1.

Safaniya crude oil is thought to be good for alkaline water flooding due to its high acidity number = 1.5. The used porous medium was a quadratic five-spot model. The model allows visual observations. The inner dimensions of the model were 28.1, 28.1 and 5 cm and has an injector and producer on the two ends of the same diagonal. The model was packed either homogeneously or non-homogeneously and was then saturated with oil by continuous injection until no water is produced. Oil was then displaced by water or alkaline or composite alkaline-polymer solution. The produced liquids were collected and the amounts of oil and water in the sample were determined and recorded with time. The area swept was outlined with time and then determined by the planimeter.

3. RESULTS AND DISCUSSION

Brines (23 % NaCl) with different alkaline solutions (Na₂CO₃ and NaOH) were added with surfactant, and crude, and mixed. The ternary diagrams were constructed. Figures 1 and 2 are ternary phase plots to show the effect of the two alkaline solutions on miscibility behavior of Petrostep HMW at 25 °C and 70 °C respectively. It is apparent from these plots that the size of the single phase region increases when using NaOH solution at both temperatures of 25 °C and 70 °C. Thus the highest miscibility conditions is obtained when NaOH is added. It is believed that this behavior is due to the effect of alkali type on solution properties such as interfacial tension. Sodium hydroxide improves surfactant's performance by minimizing the harmful effects of multivalent metal ions. The enhancement caused by these alkalines was attributed to a pH-dependent oil/water interfacial tension lowering and alkali enhanced surfactant activity.

The alkali anions of Na₂CO₃ react with multivalent ions both in solution, forming either colloidal particles or precipitates. This will cause trapping these ions or slowing the ion-exchange process, rendering

the surfaces less attractive to surfactant molecules. This may explain the improvement in miscibility conditions when using NaOH alkaline solutions.

The effect of NaOH concentration on phase behavior was investigated. Phase diagrams of Safaniya crude, Petrostep HMW, and brines (23 % NaCl) containing 0.5 and 1 % NaOH at 70 °C were obtained as shown in Figure 3. It is clear from this figure that the single phase region increases with increasing the concentration of NaOH from 0.5 % to 1 %. Figure 8 shows the pH of the aqueous phases obtained from the two-phase samples. It is seen that the higher NaOH concentration exhibits higher pH values. This explains the improvement of miscibility when concentration increased from 0.5 to 1 % NaOH. The natural surfactants containing carboxylic groups present in the crude oil react with NaOH and determine the magnitude of the charge at crude oil-caustic interface. The higher interfacial change is responsible for the minimum in interfacial in oil-caustic system. The miscibility behavior is almost similar when using 3.84 NaCl brines at 70 °C as shown in Figure 3. It is also apparent from Figure 3 that the

size of the single phase region decreases with increasing NaCl concentration from 3.84 % to 23 %. The interfacial tension is strongly dependent on the salinity of the aqueous phase. By changing the salinity of the aqueous phase, the relative solubilities of the surfactant in oil and water can be varied significantly. At low salt concentrations, most of the surfactant stays in the aqueous phase, while at high salt concentrations, the surfactant preferentially dissolves into the oil phase. At optimal concentration, however, the surfactant concentration is the same in both oil and water which produces the lowest interfacial tension. The effect of salinity, therefore, may be attributed to the effect of water salinity on interfacial tension.

Surfactant-polymer flooding studies should be performed at reservoir temperature so that the results can be applied to oil fields. Because of that, the effect of temperature on the phase relation of the surfactant-oil-brine system was studied. The effect of temperature is in the direction of decreasing miscibility with temperature increase as shown in the previous figures, which means lower surfactant effectiveness during displacement process at reservoir conditions.

This may be attributed to the thermal degradation of surfactant at 70 °C temperature. The thermal stability of surfactants at reservoir temperature is required for efficient oil displacement in porous media.

The sweep pattern for Safaniya crude oil displacement by water, alkaline and composite of alkaline-polymer solutions at breakthrough in homogeneous packs was determined. The percent of area swept Vs. Wi/Wbt (volume injected : volume injected at breakthrough) for the obtained experimental data is shown in Figure 4. It is seen from this figure that the data after breakthrough between the results obtained in this work and those obtained previously [14,15] are close. Data before breakthrough obtained in this study is available. It is clear that the areal sweep efficiency at breakthrough was improved in the case of displacing crude oil by a composite alkaline-polymer solution. The higher sweep efficiency was obtained as the viscosity ratio was decreased as shown in Fig. 4.

This means that the most important factor affecting sweep efficiency is the mobility. The buffer slug clearly provided adequate mobility control.

The reaction of sodium hydroxide solutions and the organic acids naturally present in crude oil was taken place to form emulsifying soaps. The formation of an oil-in-water emulsion in situ within the pore spaces of the rock in this case is essential first step in the displacement mechanism. The second step was entrainment of the emulsified oil in the flowing alkaline solution by the pore throats that are too small for the oil emulsion droplets to penetrate [9]. This mechanism results in a reduced water mobility (i.e. reducing water permeability) that improves areal sweep efficiency. This is especially important in waterflooding viscous oils where waterflood sweep efficiency is poor. It is seen from Figure 4 that, although the same viscosity ratio, the areal sweep efficiency in the case of using alkaline solution is much better than in the case of using water. This is due to the reduction in permeability ratio resulted from emulsifying soaps due to alkaline.

The most important challenge of any secondary or tertiary recovery method involves flooding is to increase the viscosity to decrease the permeability of displacing fluid. This leads to decrease in mobility ratio which leads to increase in areal sweep efficiency as shown in Figure 4.

4. CONCLUSIONS

For the fluid system investigated and at conditions prevailing in this study, it was found that alkaline type and its concentration have an important effect on the phase behavior of surfactant solutions tested. The miscibility increases when using NaOH and with increasing concentration from 0.5 % to 1 %. Increasing salt in presence of alkali decreases the solution miscibility. Temperature affects surfactant solution phase behavior. Miscibility decreases at 70 °C.

The sweep efficiency is strongly dependent on viscosity ratio between displaced and displacing fluids. Presence of NaOH in the flooding water improves areal sweep efficiency.

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Rate Effects in Tertiary Micellar Flooding of Bradford Crude Oil

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Abstract

Micellar flooding of the tight Pennsylvania oil reservoirs invariably is accompanied by low flood advance rates — on the order of a fraction of 1 ft/D. This investigation, therefore, was devoted to the effect of rate on tertiary oil recovery.

The experiments were conducted in 2- and 4-ft-long Berea sandstone cores at rates as low as 0.10 ft/D. All runs were tertiary in nature. The micellar solutions being used in the field tests in Pennsylvania also were used for this research. The majority of the runs were carried out in horizontally positioned cores (although a few runs used vertical cores) to determine if gravity was a factor in the observed effect.

It was found that oil recovery decreased with a decrease in the flood advance rate up to a point. Thereafter, it showed a small increase with further decrease in rate. This effect has not been reported by other investigators.

The rate effect is discussed and analyzed in terms of the system phase behavior, sulfonate adsorption, dispersion, diffusion, and mobility control. The role of the rate effect on the formation of the stabilized bank also was developed for the experimental conditions involved. The implications of very low rates are discussed in the light of field results.

Introduction

During recent years, much effort has been devoted to investigations of oil displacement by micellar solutions. This process was proposed and described in detail by Gogarty and Tosch¹ and Davis and Jones.² An analysis of the mechanism of the process is given by Bleakley.³ The micellar solutions are composed primarily of a hydrocarbon, water, a surfactant, and a cosurfactant. Micellar flooding involves sequential injection of a micellar slug, a mobility buffer, and drive water.

Since one of the significant characteristics of

Pennsylvania oil reservoirs is the low formation permeability, waterflood rates in many of these reservoirs are much less than 1 ft/D. Currently, tertiary micellar floods are being conducted in these reservoirs. Thus, it is important to investigate the recovery behavior of micellar displacement at comparable flow rates. Taber *et al.*⁴ observed that at both higher and lower rates the displacement of oil and water by an alcohol was efficient. This was confirmed later by Taber and Meyer.⁵ An increase in microemulsion displacement efficiency at high rates was observed by Healy *et al.*⁶

In our previous work,⁷ the effect of flood advance rate in micellar/polymer displacement process under a wide variety of conditions was investigated to determine (1) what effect do flow rates have on oil recovery and (2) whether flow rate itself or some other factor, such as gravity segregation, contributes to the observed behavior. Oil recovery was found to be rate dependent under these conditions.

One objective of this work is to analyze the effect of flood advance rates in terms of system phase behavior, sulfonate adsorption, mixing mechanism, and mobility control. Another purpose is to understand the effect of rate on the formation of the stabilized oil/water bank and discuss the implications of very low rates.

Experimental Results Showing Effect of Rate on Tertiary Oil Recovery

An experimental investigation was carried out to study the variation of tertiary oil recovery with rate, using different slug sizes for horizontal and vertical displacements in 4- and 2-ft-long cores. (Material, apparatus, and experimental techniques are described in Appendix A.) Summary of the results is given in Table 1. It is evident that in all cases recovery increased with an increase in slug size. Two different micellar slugs were used. Runs 1 through 29 and 31 through 34 employed the Richburg slug. The

TABLE 1 - SUMMARY OF TERTIARY MICELLAR SOLUTION FLOOD -
KELZAN-BUFFER/BRADFORD-CRUDE/BEREA-SANDSTONE CORES

Run	Core Characteristics		Rate (ft/D)	Buffer Size (% PV)	Micellar Solution		Initial Tertiary Oil Saturation	Fractional Flow of Oil/Water Bank	Micellar Recovery (% injected)	Tertiary Oil Recovery (% injected)	Remarks	
	Length (ft)	k_a (md)			Position	Size (% PV)						Type
1	4	198	horizontal	4.35	25	2.5	Richburg	23.70	0.225	-	28.13	
2	4	332	horizontal	4.35	25	5	Richburg	33.47	-0.411	43.72	60.72	
3	4	158	horizontal	0.94	25	5	Richburg	35.66	0.319	70.26	43.70	
4	4	137	horizontal	0.94	25	2.5	Richburg	33.10	0.221	1.07	24.47	
5	4	107	horizontal	0.94	25	10	Richburg	32.80	0.382	82.40	64.04	
6	4	323	horizontal	4.35	25	10	Richburg	25.70	0.322	3.79	66.73	
7	4	200	horizontal	0.50	25	2.5	Richburg	27.00	0.242	2.03	28.22	
8	4	220	horizontal	0.50	25	5	Richburg	31.40	0.312	7.64	54.46	
9	4	213	horizontal	0.50	25	10	Richburg	32.35	0.332	4.02	69.75	
10	4	210	horizontal	0.50	25	15	Richburg	33.80	0.351	7.16	71.44	
11	2	138	horizontal	0.20	25	2.5	Richburg	36.00	-	96.26	40.64	
12	2	217	horizontal	0.20	25	5	Richburg	31.80	0.200	25.36	44.44	
13	2	169	horizontal	0.20	25	10	Richburg	27.68	0.214	18.15	61.13	
14	2	239	vertical	0.94	25	10	Richburg	30.74	0.325	86.30	65.16	
15	2	239	vertical	0.94	25	5	Richburg	27.70	0.264	10.17	56.13	
16	2	71	vertical	0.94	25	2.5	Richburg	34.70	0.226	29.95	26.99	
17	2	146	vertical	4.35	25	2.5	Richburg	30.40	0.187	5.83	32.74	
18	2	146	vertical	4.35	25	5	Richburg	30.40	0.356	5.13	58.63	
19	2	146	vertical	4.35	25	10	Richburg	32.00	0.321	5.47	81.33	
20	2	146	horizontal	0.94	25	5	Richburg	32.00	0.380	10.06	52.31	
21	2	145	horizontal	0.94	25	2.5	Richburg	32.65	0.147	23.44	25.05	
22	2	146	horizontal	0.94	25	10	Richburg	31.20	0.318	13.40	64.65	
23	2	125	horizontal	0.50	25	5	Richburg	27.20	0.254	19.23	50.34	
24	2	131	horizontal	0.50	25	15	Richburg	30.20	0.527	1.55	70.53	
25	2	139	horizontal	0.94	25	5	Richburg	30.20	0.242	31.81	46.91	
26	2	125	horizontal	0.10	25	10	Richburg	28.90	0.272	2.63	63.04	
27	2	110	horizontal	0.10	25	5	Richburg	24.40	0.227	23.70	49.68	
28	2	167	horizontal	0.10	25	2.5	Richburg	33.90	0.249	39.41	47.47	
29	2	175	horizontal	4.35	25	10	Richburg	28.00	0.342	0.28	82.45	
30	2	112	horizontal	4.35	25	2.5	Bradford	32.20	0.259	30.36	44.69	
31	2	363	horizontal	1.00	25	10	Richburg	31.30	0.371	28.98	64.50	
32	2	112	horizontal	1.00	25	5	Richburg	37.00	0.378	48.78	48.78	
33	2	79	horizontal	1.00	25	10	Richburg	35.30	0.387	4.48	51.02	decomposed slug
34	2	193	horizontal	1.00	25	5	Richburg	29.30	0.282	4.12	25.43	decomposed slug
35	2	442	horizontal	2.6	25	10	Bradford	37.30	0.409	24.26	67.49	
36	2	105	horizontal	5.2	25	10	Bradford	32.30	0.422	27.46	68.16	
37	2	393	horizontal	0.25	25	10	Bradford	44.50	0.385	16.35	43.50	
38	2	257	horizontal	5.2	25	10	Bradford	31.40	0.310	10.46	68.94	
39	2	-	horizontal	0.5	25	5	Richburg	30.0	0.305	4.41	53.40	decomposed slug
40	2	272	horizontal	5.2	25	10.2	Bradford	34.0	0.355	5.69	76.40	470-ppm Kelzan
41	2	163	horizontal	0.10	25	10	Bradford	32.30	0.347	4.77	56.09	

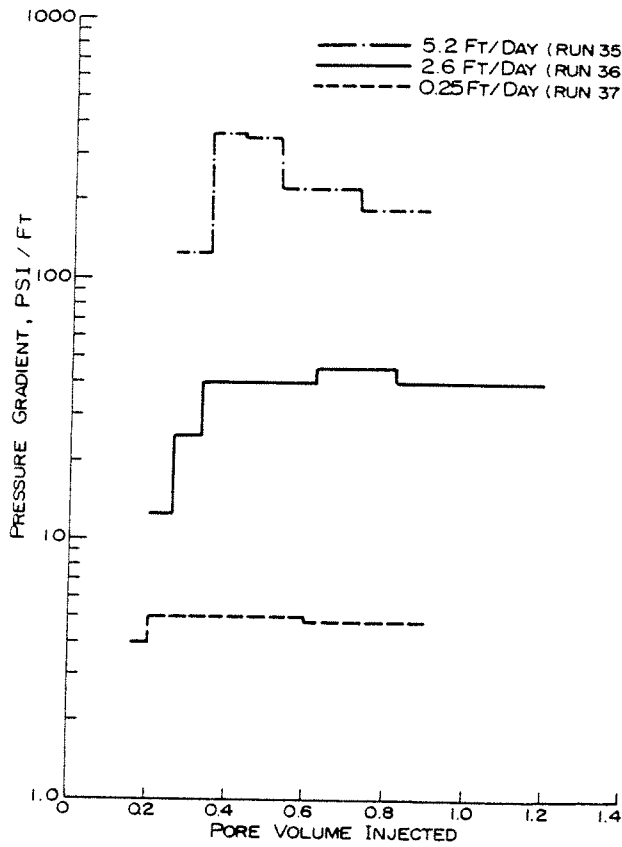


Fig. 6 - Pressure behavior at different injection rates.

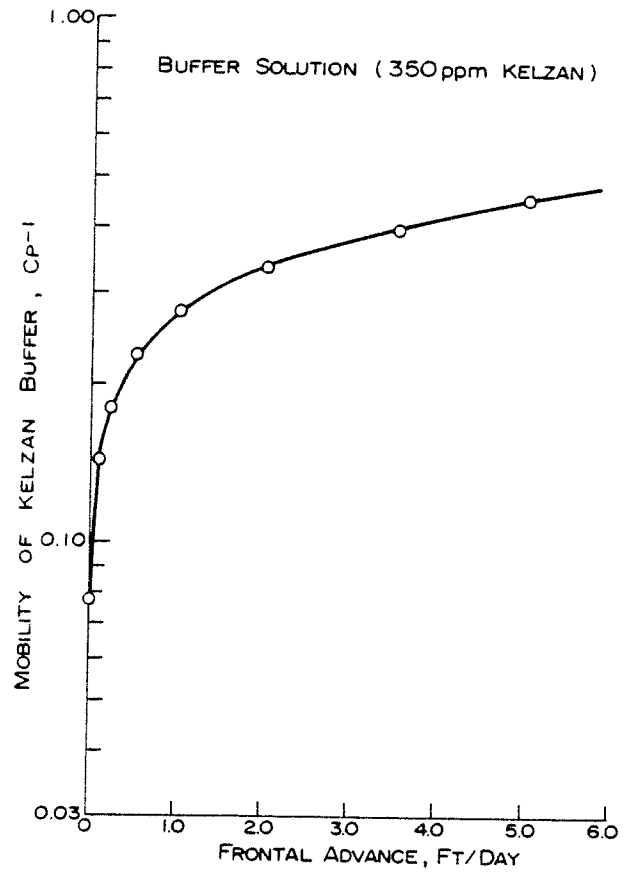


Fig. 8 - Mobility of Kelzan buffer as a function of flood advance rate.

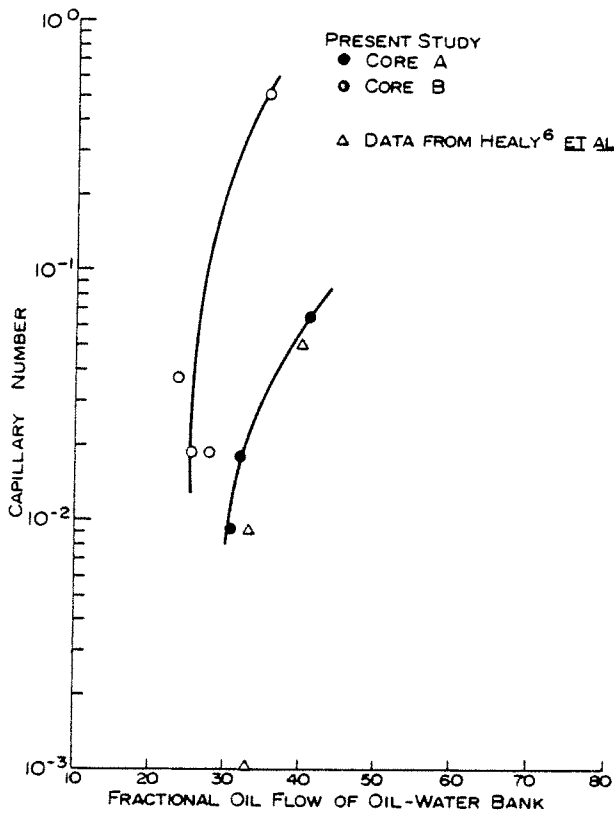


Fig. 7 - Fractional oil flow of oil/water bank as a function of capillary number.

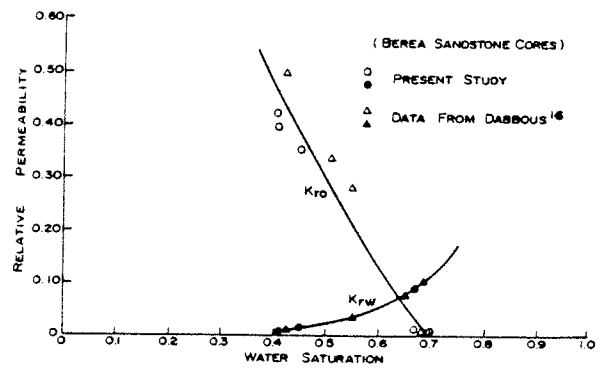


Fig. 9 - Relative permeability curves for Berea sandstone cores.

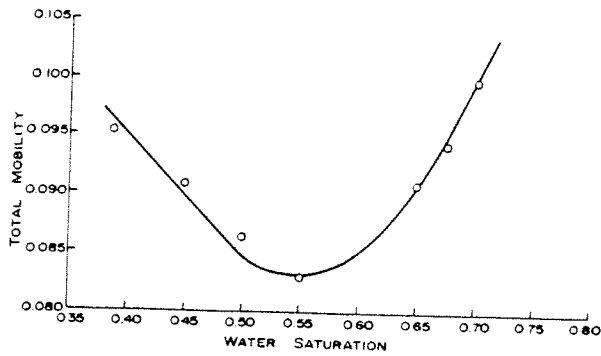


Fig. 10 - Variation of total mobility with water saturation.

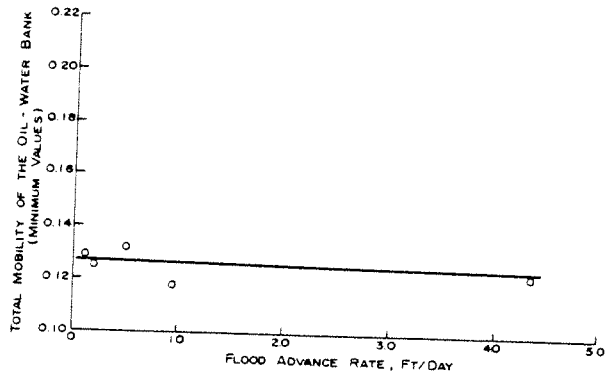


Fig. 11 - Variation of total mobility of stabilized oil/water bank with rate.

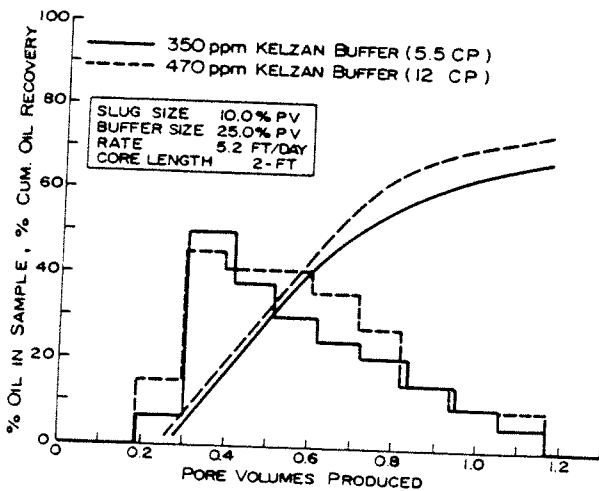


Fig. 12 - Production histories for 10% PV slug and 25% PV Kelzan buffer (350 and 470 ppm) displacements in 2-ft cores at 5.2 ft/D.

total mobility of the oil/water bank and the flood advance rate. This relationship is developed from

$$\lambda_{sob} = \lambda_w (1 - f_{sob})^{-1} \dots \dots \dots (4)$$

Since water is a Newtonian fluid, λ_w is rate independent and Eq. 4 shows the total mobility dependence of fractional flow of the stabilized oil/water bank. Fig. 11 shows that the total mobility* of the oil/water bank is rate independent within the rates used. Chang *et al.*¹¹ found that the total mobility is rate sensitive at extremely high rates (~140 ft/D)

Two important observations concerning the mobility control mechanism can be made:

1. A decrease in flood advance rates at very low values will lead to a considerable decrease in the mobility of the buffer solution as shown in Fig. 8, whereas the total mobility of the oil/water bank is rate independent as indicated by Fig. 11.

2. The minimum total mobility of the stabilized oil/water bank is established at 0.083 cp^{-1} on the basis of Fig. 10.

Two runs were carried out to study the behavior of oil recovery using 350-ppm (5.5-cp) and 470-ppm (12-cp) Kelzan buffer at 5.2 ft/D. The results indicated that the displacement efficiency was improved when using the more viscous buffer, which represented the reciprocal value of minimum mobility (0.083 cp^{-1}). Fig. 12 shows the production histories for these two runs. Since this minimum mobility value can establish adequate mobility control at very low rates, an improvement in the displacement efficiency was achieved.

However, we are not assuming that unit mobility ratio can be achieved at the higher polymer concentration. This is because of the often-observed increase in polymer solution mobility due to slug/polymer solution interaction.

Sulfonate and Polymer Adsorption

In the micellar flooding process, there can be a loss of miscibility because of either mixing or adsorption of the micellar slug. It is necessary, therefore, to determine if sulfonate adsorption varies substantially with the flood advance rate. Theoretically, if the residence time ($\tau = L/v$) of the micellar slug is long enough (low rates), adsorption on the rock surface may occur.

A series of experiments using a constant weight of crushed Berea sandstone and different concentrations of the micellar solution was carried out to investigate the adsorption of the sulfonate from the micellar solution.

Flasks containing a certain weight of crushed Berea sandstone were used for the experimental work. Micellar solutions (with or without polymer solution) with different concentrations were added to the flasks. All samples were shaken approximately twice a day to keep the micellar sample uniform throughout the flask. Periodically, a 15- to 20-cm³ sample was taken from each flask. These samples were filtered to remove any sandstone particles. An

*Minimum values obtained from the production data.

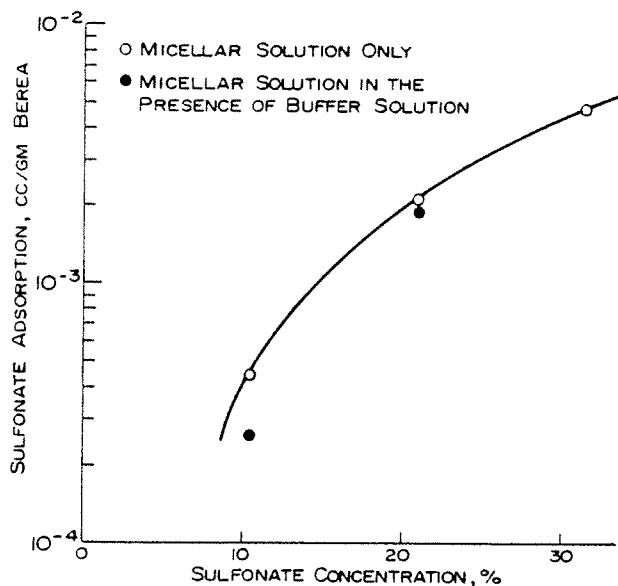


Fig. 13 - Effect of Kelzan buffer on sulfonate adsorption.

equal amount of a calcium chloride solution was added to each sample to separate the micellar into oleic phase and aqueous phase. The samples were undisturbed overnight to allow time for the two phases to separate. After separations, the oleic phase was analyzed with an infrared spectrophotometer to determine the percent sulfonate in the oleic phase. The percent sulfonate in the oleic phase then was converted to percent sulfonate in the complete micellar solution. This value then was compared with the percent sulfonate in the original micellar solution. The difference in the two values is the percent of the sulfonate adsorbed. Fig. 13 shows the effect of sulfonate concentration as a function of adsorption on the Berea sand, and it is seen that the amount adsorbed increases with concentration. This figure also shows the effect of the presence of the polymer solution on sulfonate adsorption. It should be mentioned that all points appearing in Fig. 13 are average values of 10 experiments carried out under the same conditions. As shown in this figure, less adsorption was obtained in the presence of polymer solution. In addition, this behavior is more significant at the lower sulfonate concentration. The behavior of sulfonate adsorption in the presence of buffer solution (all other factors being unchanged) indicates that some of the polymer was adsorbed on the rock surface. This is true, since polymer adsorption depends on the nature of the rock and the polymer solution. The reduced sulfonate adsorption in the presence of the polymer solution is a desirable phenomenon from the viewpoint of sulfonate conservation and integrity of the micellar slug.

Another series of experiments using crushed Berea sandstone and micellar solutions was carried out to find at what rate sulfonate adsorption occurs. Fig. 14 shows the amount of sulfonate adsorbed on crushed Berea as a function of number of days that the micellar fluid contacts the rock. The crossplot of

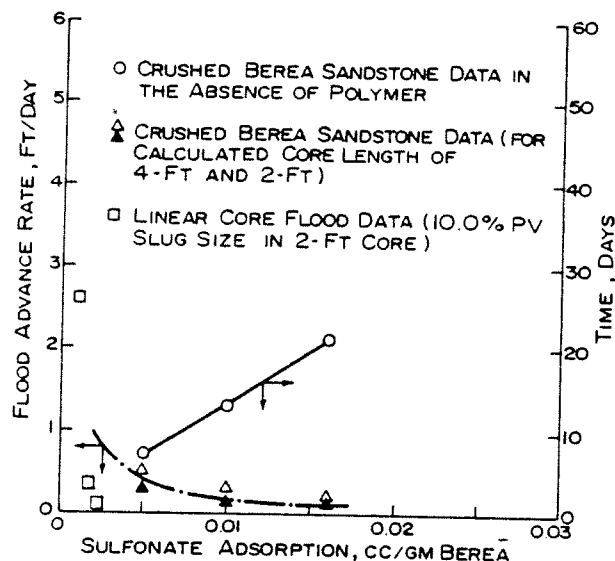


Fig. 14 - Effect of flood advance rate on sulfonate adsorption.

adsorption as a function of frontal advance rate in the same figure is based on the assumption that 1 PV of the micellar has been injected into the cores. Fig. 14 shows that sulfonate adsorption decreases markedly with frontal advance rate.

Three linear core tests were devoted to study sulfonate adsorption during the micellar flooding process at high and low rates. The data obtained from the core tests showed that the decrease in flow rate caused a small observable change in sulfonate adsorption as shown in Fig. 14. This behavior was due to the presence of the buffer solution used in the core test.

Phase Behavior, Micellar Slug Breakdown, and Mixing Mechanism

The pseudoternary diagram for the micellar slug/crude/brine system was obtained on the basis of phase properties of a large number of samples chosen on the ternary diagram.¹²

Fig. 15 is a ternary diagram of the Richburg-micellar/Bradford-crude/sodium-chloride-brine system. As shown in this diagram, Line XYZ passes from the immiscible region to the small miscible region, crossing the binodal curve at Point Y, when the micellar solution is added to a mixture of oil and water represented by Point X. The ternary diagram, however, indicates that the system used in the present investigation was almost immiscible.

Fig. 16 is a similar diagram for the Bradford-micellar/Bradford-crude/350-ppm-Kelzan-buffer system. In this case, the miscibility region is nearly the same as in the previous system.

The phase behavior of the system used in this study was shown in Figs. 15 and 16 discussed previously. These ternary diagrams indicate that the breakdown of the micellar slug occurs soon after its injection.

Additionally, it was found that tertiary oil recovery at 1 ft/D decreased if the micellar slug was

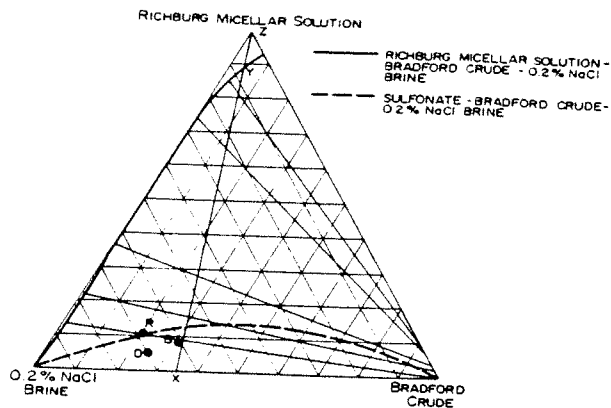


Fig. 15 - Phase diagram of Richburg-micellar/Bradford-crude/0.2%-NaCl-brine system.

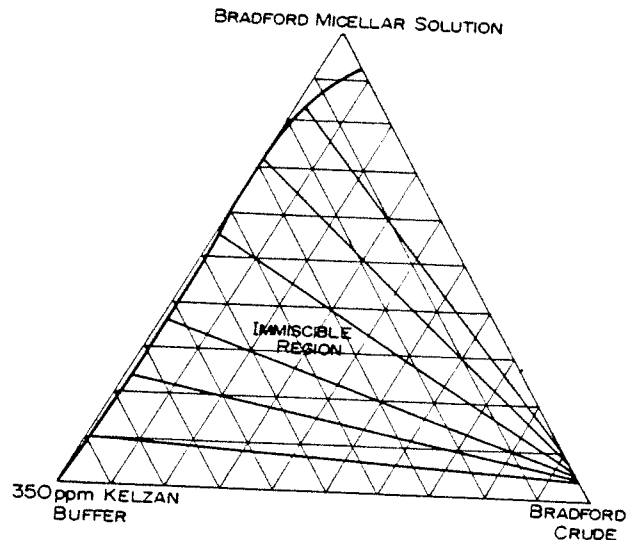


Fig. 16 - Phase diagram of Bradford-micellar-solution/Bradford-crude/350-ppm-Kelzan-buffer system.

decomposed, whereas at 0.5 ft/D the oil recovery showed a slight increase when using the decomposed slug. As mentioned before, this implies similar displacement behavior for both integral and decomposed slugs at 0.5 ft/D.

As mentioned earlier, viscous and capillary forces and mobility control play an important role in the mechanism of the displacement process. In addition to these factors, rate itself may be a factor in the decomposition of the slug. This can be confirmed by Fig. 4 where the tertiary recovery behavior with both integral and decomposed slugs at 1.0 and 0.5 ft/D is shown. Comparison of the two cases shows that the difference in oil recovery for the integral and decomposed slug is significant at 1.0 ft/D, whereas at 0.5 ft/D this difference is negligible. In other words, the micellar slug was affected by the mixing mechanism (decomposition) to an extent that depends on the flood advance rate. Phase behavior of ternary diagram shown in Fig. 15 ensures that the micellar slug in both cases remains in the immiscible region. However, in the case of the sulfonate/Bradford-crude/0.2%-NaCl-brine system, Points R and D (which represent the integral slug and the decomposed slug, respectively) indicate that the composition represented by Point D is in the immiscible region, whereas Point R is on the binodal curve.

Actually, when the slug breakdown theory was proposed, it was expected that the study of this effect will lead to significant conclusions related to the micellar behavior taking place in the core. This is because decomposition of the micellar slug always implies associated changes in sulfonate concentration, viscosity, and interfacial properties.

Since the final oil saturation was reduced by the breakdown of the slug at 1.0 ft/D and since this behavior was not observed at 0.5 ft/D, the slug breakdown took place as a result of changing flood advance rate. Phase behavior of the system used in

this study indicates that the breakdown of the micellar slug occurs soon after its injection. This means that the displacement behavior at both rates should be similar. However, the experimental results showed different behavior at 1.0 and 0.5 ft/D. This may be due to the longer contact time at low flood advance rates which permits greater mass transfer between the aqueous and oleic phases. This may have resulted in the regeneration of the slug at lower rates.

Interpretation of Rate Effect in Light of Mechanisms Present

Two principal mechanisms are responsible for high oil recoveries at both high and low rates, thus leading to a minimum in the recovery-rate curve. At high rates, the recovery increase is due to the predominance of viscous forces (high capillary numbers were obtained at these rates), leading to the high values of the pressure gradient observed during the flood. At low rates, recovery tends to decrease with decreasing rate due to the very low pressure gradients (Fig. 6). However, mobility control starts to make itself felt more strongly as the rate decreases. The minimum total mobility of the oil/water bank was found to be 0.083 cp^{-1} on the basis of relative permeability measurements. To obtain a favorable mobility ratio, the mobility of the buffer solution should be less than this minimum value, which can be obtained at very low rates as Fig. 8 shows. At the same time, the variation of the total mobility of the stabilized bank was found to be rate independent, which indicates that the mobility of the buffer solution is the controlling parameter in improving the displacement efficiency at very low flood advance rates. This was verified by carrying out an experimental run at the reciprocal of the minimum mobility (12 cp).

The results of this run (using 470-ppm Kelzan buffer) indicated that the displacement efficiency was