

Effect of Mixed-Chain-Length Surfactants on Fluid Displacement in Porous Media by In-Situ Foaming Process

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Summary. A laboratory study was designed to improve fluid displacement efficiency in porous media by an in-situ foaming process and to determine the effect of mixed surfactant chain length on surface properties of foaming solutions, bubble size, breakthrough time, and fluid displacement in porous media. We screened various mixed surfactant systems, such as sodium dodecyl sulfate and alkyl alcohols. Maximum breakthrough time and fluid displacement efficiency were observed when both components of the mixed foaming system possessed the same chain length. Results were compared with data obtained using water, brine, and sodium dodecyl sulfate alone.

The microscopic studies revealed that the order of bubble size measured outside the porous medium for various mixed surfactants was indeed maintained in a micromodel. The increase in the porous medium length improved breakthrough time and fluid displacement efficiency in sandpacks and in Berea cores. Mixed surfactant systems showed a correlation among surface properties of foaming solutions, bubble size, breakthrough time, and fluid displacement efficiency in a porous medium. Maximum foaminess, minimum bubble size, minimum surface tension, maximum surface viscosity, maximum breakthrough time, and maximum fluid displacement efficiency were observed when the two components of the surfactant system had the same chain length.

Introduction

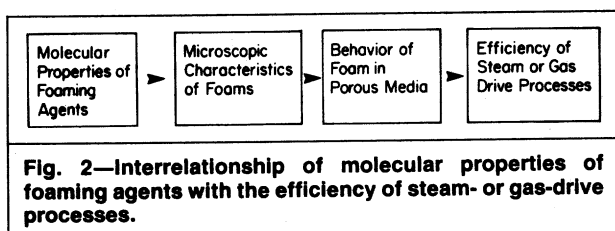
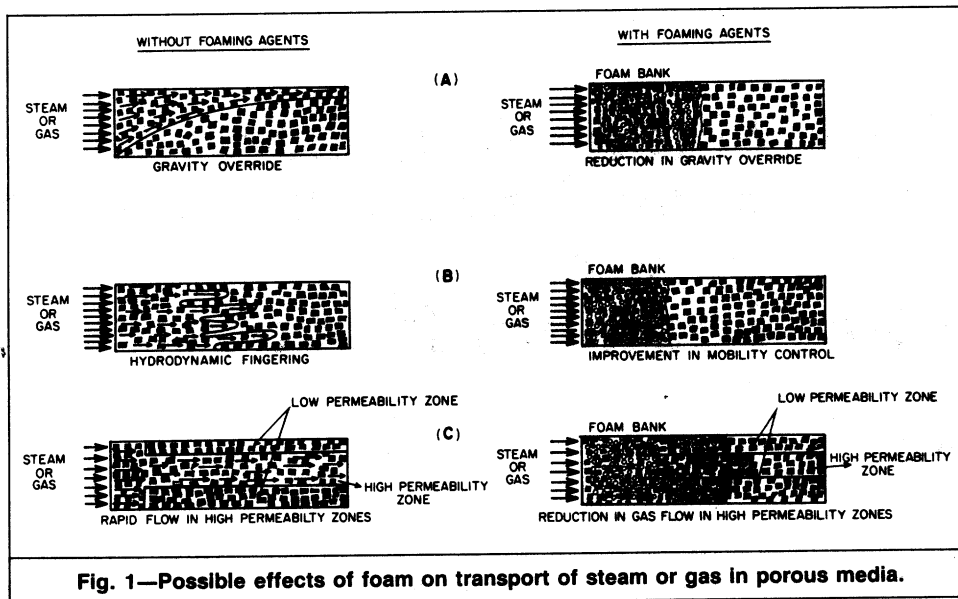
In 1958, Bond and Holbrook¹ proposed that the oil-recovery agent may be a mixture of gas and an aqueous solution of a surface-active agent (e.g., foam instead of surfactant solution). The foam process to improve oil recovery has since been studied by various investigators.²⁻¹⁰ In their experiments, a water-soluble surfactant with foam-producing characteristics was injected into an underground formation as an aqueous slug. This slug was followed by gas to produce in-situ foam.

It is well known¹¹ that when two immiscible phases (e.g., liquid and gas) flow through a porous medium, each phase may be considered to follow separate paths or channels. As the saturation of the immiscible phases changes, the number of channels available to each phase also changes. The effective permeability of each phase is influenced by the percent saturation of that phase. In the presence of foam, the effective permeability of the porous medium to each phase is considerably reduced as compared to the permeability measured in the absence of foam.^{12,13}

Foam is a material with properties that are considerably different from those of its components; for example, the viscosity of a foam is greater than either of its components (i.e., gas or surfactant solution). In addition, foam is a relatively low-density material that can easily over-

come gravitational effects and can pass through most regions of a heterogeneous petroleum reservoir. Deming¹⁴ has reported that the high foaming ability and decrease in plasticity of foam favor high fluid displacement efficiency in porous media. Surface plasticity is manifested when the surface viscosity is non-Newtonian, but the bulk viscosity of the solution is Newtonian. An ideal solution has a shearing stress that is directly proportional to the rate of shear. A plastic substance, however, will not flow at all at low rates of shear until a certain critical value of shear (true yield) has been reached. Thereafter, the plastic flows at a rate proportional to the total stress minus the yield stress. Surface plasticity in some surface-active solutions was proposed to explain the foam stability by Wilson and Ries.¹⁵ They found that the plastic solutions gave erroneously high surface tension because the yield value of the plastic film was added to the true surface tension.

Fried¹² stated that foam moves as a body when a stable foam is present in porous media, while Holm¹¹ suggested that gas and liquid flow separately through porous media in the presence of foam and that foam does not flow through porous media as a body, even when the liquid and gas are combined outside the system and injected as foam. Holm¹¹ proposed that liquid moves through the porous medium by way of a film network of bubbles, and gas moves progressively through the system by breaking



and reforming bubbles throughout the length of the flow path. During the last few years, several research papers have appeared on behavior of foam in porous media.¹⁶⁻²⁹

The formation of a foam bank between the displacing air and the displaced aqueous surfactant solution has three possible effects on flow through porous media (Fig. 1). First, it can act as a gravity-override reducing agent in steam- or gas-drive processes as a result of the generation of foam within porous media (Fig. 1A). Gravity override of injected gases can be reduced many times, which may result in improved oil recovery. Second, foam can be used as a mobility control agent. The mobility of an injected steam or gas can be controlled by the generation of in-situ foam (Fig. 1B). Third, foam can be used as a selective permeability-reducing agent (i.e., blocking agent) because it is effective in reducing the gas permeability of porous media in high-permeability zones (Fig. 1C). Fig. 2 presents the interrelationship of molecular properties of foaming agents with EOR efficiency of steam- or gas-drive processes. We propose that molecular properties of foaming agents can influence the microscopic characteristics of foam that in turn can influence its flow behavior in porous media and ultimately the oil-recovery efficiency.

A survey of the literature reveals that most of the research has been done in connection with foam flow behavior in porous media. This paper correlates the surface properties of foaming solutions and foam microscopic characteristics with foam behavior in porous media (e.g., breakthrough time and fluid displacement efficiency).

Materials and Methods

Materials. Sodium dodecyl sulfate and alkyl alcohols (98% pure) were used. All foaming agents were used as

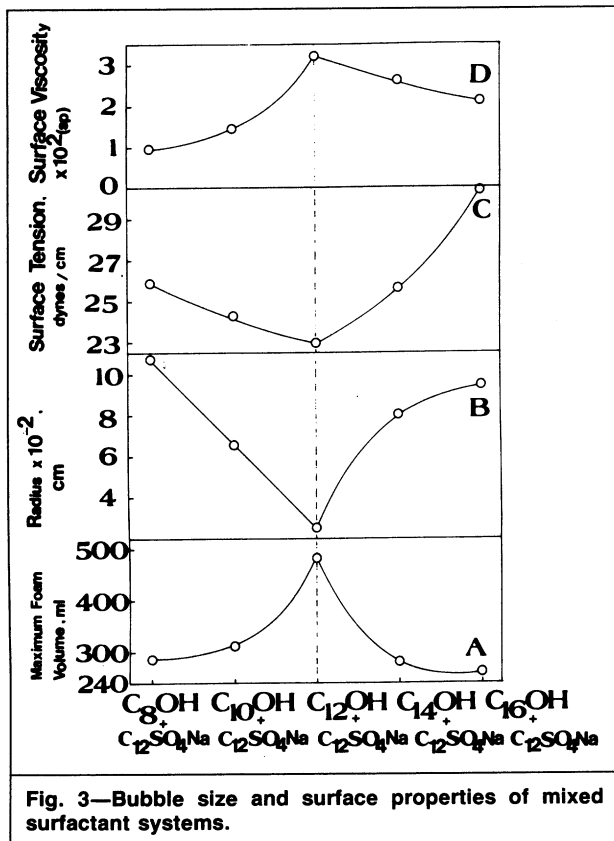
received without further treatment. Deionized, distilled water was used in all experiments.

The Berea sandstone cores were cast in Hysol™ tooling compound inside PVC pipes. The sandpacks had a permeability of about 2.4 darcies and a porosity of 40%, whereas Berea sandstones had a permeability of about 275 md and a porosity of 18%.

Methods. Foaminess. A glass cylinder with 0.79-in. [2-cm] diameter and 46.5-in. [118-cm] length was used for the measurement of foaminess. The cylinder contained a sieve of 20 to 50 μm at the bottom and an outer jacket for water circulation to keep the temperature constant. Foaming solution (20 mL) was poured into the cylinder. The foams were produced by the injection of gas from a compressed air cylinder. The time (5 minutes) and pressure (1 psi [6.9 kPa]) for air injection were kept constant for all experiments. The volume of foam generated during a constant time was recorded. The results were reproducible within $\pm 5\%$.

Bubble Size. To determine the bubble size, two sets of experiments were conducted. In the first series of experiments, the photomicrographs of foams produced in a micromodel were taken with a video camera attached to the microscope. A micromodel with a pore neck of 50 μm and a pore diameter of 100 μm was used for this study. The micromodel was saturated with surfactant solution. This was followed by air flow to generate in-situ foam. In the second series of experiments, the photomicrographs of foams were taken outside the porous media. A special type of rectangular plexiglass cell was used for foam generation. Surfactant solution (10 mL) was taken into the cell, and the foams were generated by shaking the plexiglass cell for 2 minutes. An average bubble size outside the micromodel was determined from the size frequency analysis of the photomicrographs and results obtained are shown in Fig. 3.

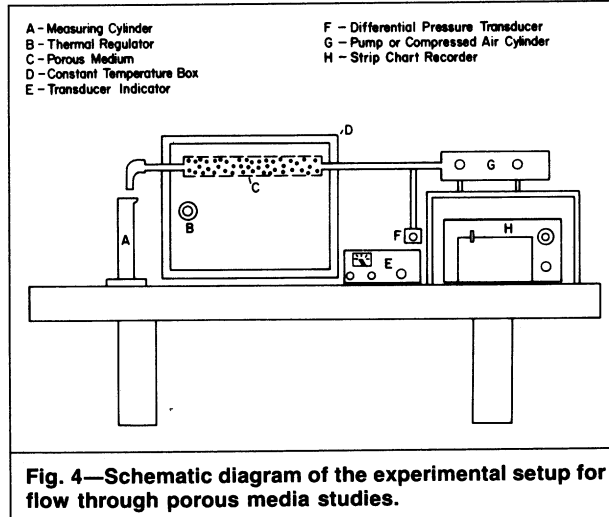
Surface Tension. The surface tension of the freshly prepared foaming solutions was measured by the Wilhelmy plate method.³⁰ The platinum blade was always cleansed and heated to a red color with a Bunsen burner before use. All measurements were carried out at 68°F [20°C].



Surface Viscosity. A single knife-edge rotational surface viscometer was used for the measurement of surface viscosity of the foaming solutions.³¹ At least three readings were taken for each solution. The results were reported as the average values.

Fluid Displacement in Porous Media. The apparatus used for flow-through-porous-media studies is shown in Fig. 4. The sandpacks (diameter 1.62 in. [4.11 cm] × length 12 in. [30.5 cm]) or the Berea cores (1 × 1 × 12 in. [2.5 × 2.5 × 30.5 cm]) used as porous media were flushed vertically with CO₂ for about 1 hour to displace interstitial air.

Deionized, distilled water was pumped through with a Cheminert™ metering pump and the PV was determined. By this procedure, the trapped gas bubbles in the porous medium were easily eliminated because of the solubility of CO₂ in water. In Berea cores, 1% NaCl was used in all experiments, whereas the displacement experiments in sandpacks and micromodels were conducted without NaCl. Five PV's of water were pumped through at different flow rates to determine the absolute permeability of the porous media using the Darcy equation.³² After the permeability was determined, several PV's of the surfactant solution were injected into the porous medium at constant flow rate. This was followed by air flow. The pressure difference across the porous medium was measured with a pressure transducer and recorder. The pressure transducer was calibrated before use with a sensitive pressure gauge. The breakthrough time and fluid displacement efficiency were determined for a constant pressure difference across the porous medium. All experiments were carried out at 68°F [20°C]. The data were reproducible within ±6%.



Results and Discussion

Bubble Size and Surface Properties of Foaming Solutions. Sodium dodecyl sulfate (C₁₂H₂₅SO₄Na) and alkyl alcohols (e.g., C₈OH, C₁₀OH, C₁₂OH, C₁₄OH, and C₁₆OH) in a molar ratio of 10:1 were used as foaming agents in all experiments. The following surface properties of the solutions and bubble size were measured.

Foaminess of Mixed Surfactant Solutions. Table 1 shows the foaminess of various mixed surfactant solutions. The maximum volume of the foam produced in a given time (5 minutes with air pressure of 1 psi [6.9 kPa]) was recorded. It was observed that the foaminess was maximum when both the components of the surfactant system had the same chain length. The foaminess decreased as the difference in the alkyl chain length increased. From monolayer studies, it has been shown³³ that the surfactant molecules pack tightly in the mixed film when the chain length of both components is equal. It is likely that the molecular packing affects the foaminess of the surfactant solutions.

Bubble Size in Micromodel. To demonstrate the existence of foam in the pores of porous media, the experiments were performed in the micromodels to generate in-situ foam as described in the experimental section. The photomicrographs of foams produced in the micromodel are shown in Fig. 5. These photomicrographs indicate that the injection of a gas in the micromodel filled with surfactant solution can generate foam in situ. It is evident that the mixed surfactants of similar chain length (C₁₂H₂₅SO₄Na + C₁₂H₂₅OH) produced smaller foam bubbles than the surfactant system with dissimilar chain length.

In separate experiments, the average size of bubbles outside the micromodel was determined. The foams were prepared by shaking a plexiglass cell by hand for 2 minutes. The average radii of the bubbles of various mixed surfactant systems, determined by the size frequency analysis of photomicrographs, are shown in Table 1. These results indicate that the average size of the bubbles was minimum for the mixed surfactants of similar chain length. Thus it is evident that the foams produced by mixed surfactant systems exhibit the same trend in the micromodel as that observed outside the micromodel. For a given surfactant system, the specific shape and size of the bubbles

TABLE 1—THE EFFECT OF MIXED CHAIN LENGTH SYSTEMS ON FOAMINESS, SURFACE TENSION, SURFACE VISCOSITY, BUBBLE SIZE, BREAKTHROUGH TIME, AND FLUID DISPLACEMENT EFFICIENCY

System	$C_{12}H_{25}SO_4Na$ + C_8OH	$C_{12}H_{25}SO_4Na$ + $C_{10}OH$	$C_{12}H_{25}SO_4Na$ + $C_{12}OH$	$C_{12}H_{25}SO_4Na$ + $C_{14}OH$	$C_{12}H_{25}SO_4Na$ + $C_{16}OH$
Foaminess, mL	285	310	480	298	260
Bubble size, radius, cm	10.60×10^{-2}	6.50×10^{-2}	2.50×10^{-2}	8.00×10^{-2}	8.70×10^{-2}
Surface tension, dynes/cm	25.88	24.26	22.97	25.61	30.32
Surface viscosity, sp	0.98×10^{-2}	1.45×10^{-2}	3.20×10^{-2}	2.62×10^{-2}	2.10×10^{-2}
Breakthrough time, minutes					
In sandpicks at 5 psi	25.1	41.3	46.8	30.6	27.2
In Berea cores at 40 psi	18.5	23.5	29.5	18.0	17.0
Fluid displacement efficiency, %					
In sandpicks at 5 psi	77.8	78.1	83.0	69.6	68.9
In Berea cores at 40 psi	54.3	58.6	62.9	47.1	45.7

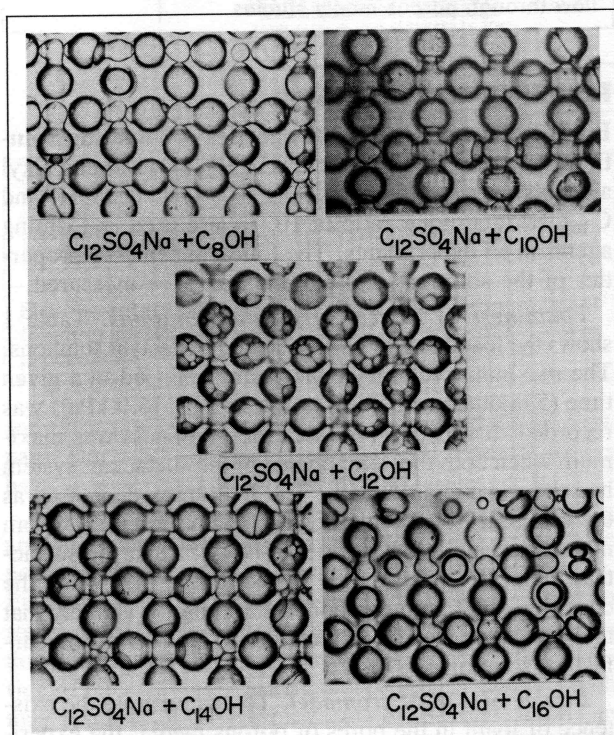


Fig. 5—Photomicrographs of foams in micromodel (pore neck $50 \mu m$ \times pore diameter $100 \mu m$).

outside porous media may differ from that present in the porous medium because of the pore size.

Surface Tension of the Mixed Surfactant Systems. Table 1 includes the surface tension of various mixed surfactant solutions. The data of surface tension were consistent with the foaminess of surfactant solutions and bubble size in foams as one would expect from the literature.³⁰ For the mixed surfactant system of equal chain length, a minimum in surface tension was observed. As the difference in the chain length of the foaming agents is increased, the surface tension also increased. It has been proposed that as the difference in the chain length increases, the thermal disturbances such as oscillational, vibrational, and rotational motions of the alkyl chains increase, which in turn results in the increase in area per molecule in the mixed films.³³

Surface Viscosity of the Mixed Surfactant Systems. The data of surface viscosity for various mixed foaming systems are reported in Table 1. The maximum surface

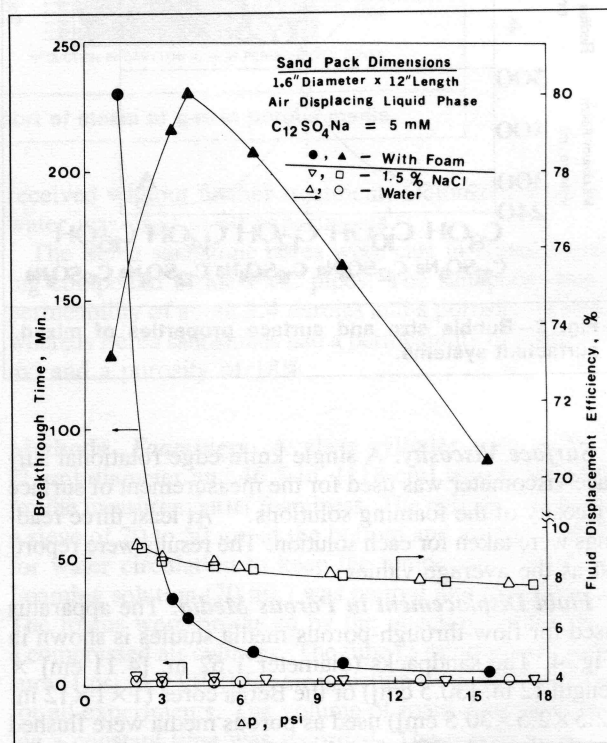


Fig. 6—Effect of Δp on breakthrough time and fluid displacement efficiency in sandpicks with and without foaming agent.

viscosity was observed for the mixed surfactant system that contains equal alkyl chain length. This shows that the chain length of the mixed surfactant systems strikingly affects the surface properties of the solutions. The high surface viscosity is known³¹ to reduce the rate of thinning of liquid films resulting in the high foam stability observed for these systems. Previous investigators^{34,35} have reported that the increase in foam stability of decanoic acid solution in the presence of decanol is a result of the increase in surface viscosity caused by the alcohol. It was observed that the surfactant molecules of similar chain length are tightly packed at the air/water interface compared with the molecules of dissimilar chain length.^{33,34} At pH 9.0, foams of decanoic acid and 1:3 mixture of decanoic acid/decanol had maximum stability.^{36,37}

Foam Behavior in Porous Media. To determine the behavior of foam in porous media, breakthrough time and

fluid displacement efficiency were measured in sandpacks as well as in Berea cores. The breakthrough time is the time required by gas to travel from injection site to production site, and the fluid displacement efficiency is the total fluid recovered from a porous medium until the breakthrough of the gas phase at the production site. The effect of pressure drop, length of the porous medium, and mixed surfactant systems on these parameters were studied to correlate the foam behavior in porous media with the surface properties of the foaming solutions and bubble size.

Breakthrough Time and Fluid Displacement Efficiency in Sandpacks With and Without Foam. Fig. 6 represents the variation in breakthrough time and fluid displacement efficiency as a function of applied air pressure (Δp) with and without foaming agent. To keep the breakthrough time within measurable limits, the fluid displacement efficiency and breakthrough time were measured between 1.5 and 18 psi [10.3 and 124.1 kPa]. A small decrease in fluid displacement efficiency with increasing Δp was observed and about 5 to 7% fluid was recovered in the absence of foam. When water was replaced with brine, the same fluid displacement efficiency was recovered without foaming agents.

The displacement experiments were also performed in the presence of 5 mmol foaming agent ($C_{12}H_{25}SO_4Na$) to measure the breakthrough time and fluid displacement efficiency in a porous medium. An increase in fluid displacement efficiency was observed at low Δp values and a maximum occurred at 4 psi [27.6 kPa] in the sandpack. With a further increase in Δp , the fluid displacement efficiency decreased continuously. The breakthrough time decreased sharply up to 4 psi [27.6 kPa], and a slight decrease in the breakthrough time was observed with further increase in Δp . At 4 psi [27.6 kPa], the fluid displacement efficiency increased by about 72% in the presence of foam compared with that without foam. The breakthrough time was about 1 minute in the absence of foam and 27 minutes in the presence of foam in sandpacks at 4 psi [27.6 kPa].

Breakthrough Time and Fluid Displacement Efficiency in Berea Cores With and Without Foam. Fig. 7 shows the variation in the breakthrough time and fluid displacement efficiency in Berea cores with and without foaming agents. To keep the breakthrough time within measurable limits, the displacement experiments in Berea cores were performed by injection of gas phase between 10 and 50 psi [68.9 and 345 kPa]. In contrast to sandpacks, a small increase in fluid displacement efficiency was observed up to 25 psi [172 kPa] and remained constant beyond this pressure in the absence of surfactants. The total fluid recovered without foam was 20 to 22%. The breakthrough time decreased sharply up to 20 psi [138 kPa] and remained constant beyond this pressure.

The fluid displacement efficiency decreased linearly as a function of pressure drop in the presence of foaming agents in Berea cores in contrast to the maximum observed in sandpacks. At 30 psi [207 kPa], an additional 34.3% of fluid was recovered in the presence of foam compared with that without the foam. A sharp decrease in breakthrough time was observed for low values of pressure drop (< 35 psi [241 kPa]), whereas the breakthrough time decreased gradually beyond this. The breakthrough time at $\Delta p = 30$ psi [207 kPa] increased nearly 19 times in the

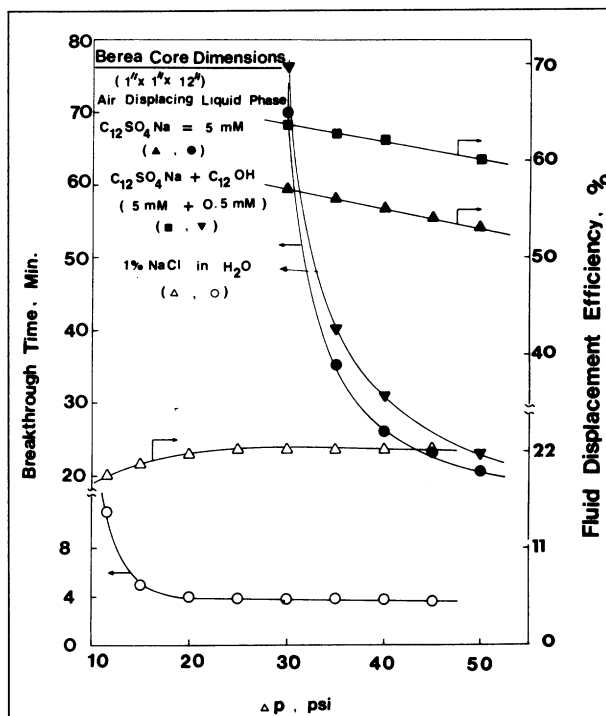


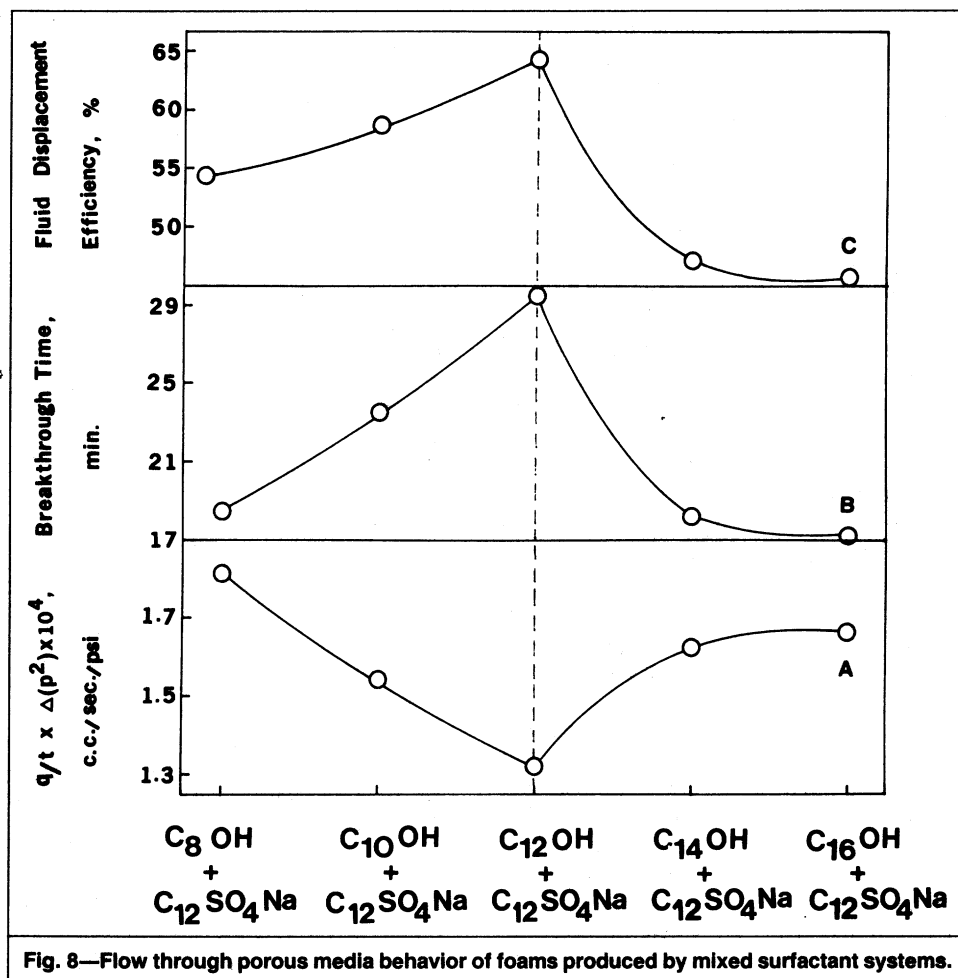
Fig. 7—Effect of Δp on breakthrough time and fluid displacement efficiency in Berea cores with and without foaming agent.

presence of foam compared with breakthrough time without foam. The mixed surfactant system of equal chain length significantly improved fluid displacement efficiency and breakthrough time as compared with sodium dodecyl sulfate alone (Fig. 7).

The results show that both the breakthrough time and fluid displacement efficiency are improved in the presence of foam in sandpacks as well as in Berea cores. The formation of an in-situ foam bank between displacing gas and displaced liquid reduced significantly the gravity override of gas, as well as the permeability of porous media to gas, which improved both the breakthrough time and fluid displacement efficiency. The presence of a foam bank, however, improved fluid displacement efficiency in sandpacks to a much greater extent than in Berea cores.

Breakthrough Time and Fluid Displacement Efficiency in the Presence of Mixed Foaming Agents. To delineate the effect of mixed chain length and surface properties of foaming solutions on breakthrough time and fluid displacement efficiency in porous media, sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$) and various alkyl alcohols ($C_nH_{2n+1}OH$) were used as mixed foaming agents in a molar ratio of 10:1. Table 1 represents the variation in breakthrough time and fluid displacement efficiency in sandpacks and in Berea cores. The volume of fluid recovered was found to be greater in sandpacks than in Berea cores. Maximum breakthrough time and fluid displacement efficiency were found when both components of the mixed foaming system had the same chain length.

Mixed chain length appears to influence the molecular packing at the air/liquid interface and changes surface properties of foaming solutions as well as fluid displacement efficiency in porous media. The trend in variation of breakthrough time as a function of the mixed chain



length of foaming agents was found to be the same in Berea cores and sandpacks.

Figs. 3 and 8 illustrate a correlation of the breakthrough time and fluid displacement efficiency with the microscopic and surface properties of foaming agents. These studies suggest that maximum foaminess, maximum surface viscosity, minimum surface tension, and minimum bubble size correlate with minimum effective air mobility, maximum fluid displacement efficiency, and maximum breakthrough time. These results suggest that the molecular packing at the air/liquid interface and surface properties of the foaming agents have a striking correlation with breakthrough time and fluid displacement efficiency in porous media.

Effect of Length of Porous Media on Breakthrough Time and Fluid Displacement Efficiency. The variation in breakthrough time and fluid displacement efficiency

as a function of the length of porous media in the presence of mixed anionic and nonionic foaming agents (e.g., $C_{12}H_{25}SO_4Na + C_{12}H_{25}OH$), as well as in the absence of foaming agent, is given in Table 2. Three sandpacks of the same diameter but of different lengths (e.g., 1, 2, and 4 ft [0.3, 0.6, and 1.2 m]) were selected and a constant air pressure (Δp) of 5 psi/ft [113 kPa/m] was used.

It is obvious from Table 2 that the fluid displacement efficiency increases as the length of the porous medium increases, with or without the presence of foaming agents. The breakthrough time per foot decreases with the length of sandpack without surfactants but remained almost constant in the presence of surfactants. The order of increase in the breakthrough time and fluid displacement efficiency with respect to different foaming agents was found to be: water < sodium dodecyl sulfate < mixed sodium dodecyl sulfate plus dodecyl alcohol. The breakthrough

TABLE 2—EFFECT OF THE LENGTH OF POROUS MEDIA ON BREAKTHROUGH TIME AND FLUID DISPLACEMENT EFFICIENCY

Sample Number	System	Breakthrough Time (min/ft)			Fluid Displacement Efficiency (%)		
		1-ft sandpack	2-ft sandpack	4-ft sandpack	1-ft sandpack	2-ft sandpack	4-ft sandpack
1	H_2O	0.73	0.67	0.45	6.51	7.35	8.20
2	$C_{12}H_{25}SO_4Na$	19.00	18.50	18.22	79.70	82.00	83.50
3	$C_{12}H_{25}SO_4Na$ + $C_{12}OH$	46.50	46.25	45.00	83.00	86.40	88.30

time and fluid displacement efficiency in the presence of foaming agents increased many times more than without the foaming agents. This suggests that the generation of in-situ foam reduces gravity override as well as flow rate of air in porous media, and hence, increases both the breakthrough time and the fluid displacement efficiency in porous media.

Conclusions

1. The surface properties of the surfactant solutions depend on the mixed chain length of the surfactants. For mixed foaming systems, maximum foaminess, minimum surface tension, and maximum surface viscosity were observed when both components of the system had the same chain length ($C_{12}H_{25}SO_4Na + C_{12}H_{25}OH$).

2. For mixed foaming systems, the foaming agents of equal chain length produced the smallest bubbles. The size of the bubbles increases as the difference in surfactant chain length increases. A similar trend in the variation of bubble size was observed in the micromodel.

3. Mixed anionic and nonionic foaming agents ($C_{12}H_{25}SO_4Na + C_{12}H_{25}OH$) of similar chain length improved fluid displacement efficiency as well as breakthrough time compared with that by an anionic ($C_{12}H_{25}SO_4Na$) foaming agent alone, by mixed foaming agents of dissimilar chain lengths, or without any foaming agent.

4. An increase in the fluid displacement efficiency was observed with the length of the porous medium in the presence of foaming agents.

5. The breakthrough time per foot was found to remain constant with the length of the porous medium in the presence of foaming agents.

6. The surface properties of foaming solutions and the bubble size of foam showed a strong correlation with the flow behavior of foam in porous media. For mixed foaming systems (e.g., $C_{12}H_{25}SO_4Na + C_nH_{2n+1}OH$), maximum foaminess, minimum surface tension, maximum surface viscosity, minimum bubble size, minimum effective air mobility, maximum breakthrough time, and maximum fluid displacement efficiency were observed when both the components had the same chain length.

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SI Metric Conversion Factors

cp	× 1.0*	E-03	= Pa·s
cu in.	× 1.638 706	E+01	= cm ³
dynes/cm	× 1.0*	E+00	= mN/m
ft	× 3.048*	E-01	= m
in.	× 2.54*	E+00	= cm
psi	× 6.894 757	E+00	= kPa

*Conversion factor is exact.

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