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The Chain Length Compatibility and Surface Properties of Foaming Solutions in Relation to Fluid Displacement Efficiency in Porous Media

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ABSTRACT

Laboratory experiments were conducted to determine the effect of chain length compatibility on surface properties of foaming solutions, breakthrough time and fluid displacement efficiency in porous media. Sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$) and alkyl alcohols (e.g. C_8OH, $C_{10}OH$, $C_{12}OH$, $C_{14}OH$ and $C_{16}OH$) in a molar ratio 10:1 were used as mixed foaming agents. It was observed that both breakthrough time and fluid recovery were influenced by the chain length compatibility of the surfactant molecules. The maximum breakthrough time and fluid displacement efficiency were observed when both components of the foaming system possessed the same chain length. The observed results were compared with data obtained using water, brine and sodium dodecyl sulfate alone.

Mixed anionic and non-ionic foaming agents of similar chain length ($C_{12}H_{25}SO_4$ Na + $C_{12}H_{25}OH$) improved fluid displacement efficiency by approximately 15% as compared to that by mixed foaming agents of dissimilar chain length ($C_{12}H_{25}SO_4Na$ + $C_{16}H_{33}OH$) in both sand packs (Permeability 2.445 D) as well as Berea cores (Permeability 275 mD). In sand packs, the breakthrough time in the presence of mixed foaming system of the similar chain length ($C_{12}H_{25}SO_4Na$ + $C_{12}H_{25}OH$) increased by 72.3% as compared to that by the dissimilar chain length system ($C_{12}H_{25}SO_4Na$ + $C_{16}H_{33}OH$). Similar results were obtained in Berea cores.

The effects of applied air pressure (ΔP) and length of the porous media on ultimate fluid recovery and breakthrough time were studied in the presence and the absence of foam. The trend in variation of the breakthrough time with ΔP was found to be the same in the presence or the absence of the foaming agents for both sand packs and Berea cores. A sharp decrease in breakthrough time was observed at low pressures. Further increase in the pressure, the breakthrough time decreased slightly. For sand packs, the fluid displacement efficiency in the absence of foam continuously decreased with increase in ΔP, whereas in the presence of foam, a maximum occurred at 4 psi/ft. However, in case of Berea cores, a continuous increase in fluid displacement efficiency was observed at low ΔP values and remained constant with further increase in ΔP. The increase in the length of porous media improved both breakthrough time and fluid displacement efficiency in sand packs as well as in Berea cores.

We correlated the breakthrough time and fluid displacement efficiency with the surface properties of the foaming solutions. For mixed surfactant systems (e.g. $C_{12}H_{25}SO_4Na$ + $C_nH_{2n+1}OH$), the surface tension and surface viscosity of the foaming solutions were measured. The size of the foam bubbles was determined by microphotographs of the foam. From the studies on mixed surfactant systems it was observed that a minimum in surface tension, a maximum in surface viscosity, a minimum in bubble size, a maximum in bubble stability, a maximum in fluid displacement efficiency and a maximum in breakthrough time were observed when the two components have the same chain length. These studies suggest that the surface properties and molecular packing at interfaces have a striking correlation with breakthrough time and fluid displacement efficiency in porous media.

INTRODUCTION

In 1958, Bond and Holbrook[1] 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 known[14] 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 media to each phase is considerably reduced as compared to the permeability measured in the absence of foam.[11,12]

References and Illustrations at end of paper

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 to this, foam is a relatively low density material which can easily overcome gravitational effects and can pass through most regions of a heterogeneous petroleum reservoir. Deming[13] has reported that the high foaming ability and an increase in plasticity of foam favor high fluid displacement efficiency in porous media.

Fried[11] stated that foam moves as a body when a stable foam is present in porous media, while Holm[14] suggested that in the presence of foam, gas and liquid flow separately through porous media and that foam does not flow through porous medias as a body, even when the liquid and gas are combined outside the system and injected as foam. Holm[14] proposed that liquid moves through the porous media via film network of the 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.[15-28]

The formation of a foam bank between the displacing air and the displaced aqueous foaming solution has three possible effects on flow through porous media (Fig. 1). Firstly, it can act as a gravity override reducing agent in steam or gas drive processes due to generation of foam within porous media (Fig. 1A). Gravity override of injected gases can be reduced manifold which may result in improved oil recovery. Secondly, 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). Lastly, foam can also be used as a selective permeability reducing agent (i.e. blocking agent) since it is effective in reducing the gas permeability of porous media in high permeability zones (Fig. 1C). Figure 2 presents the interrelationship of molecular properties of foaming agents with EOR efficiency of steam or gas drive processes. It's evident that molecular properties of foaming agents can influence the microscopic characteristics of foam which in turn can influence its flow behavior in porous media and ultimately the oil recovery efficiency.

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

MATERIALS AND METHODS

(A) Materials

Sodium dodecyl sulfate was obtained from Aldrich Chemical Company, Milwaukee, WI. Alkyl alcohols (98% pure) were supplied by Chemical Samples Company, Columbus, OH. All foaming agents were used as such without further treatment. Sodium chloride was obtained either from Mallinckrodt Inc., St. Louis, MO or from Fisher Scientific Company, Orlando, FL. Deionized, distilled water was used in all experiments.

The Berea sandstones were supplied by Cleveland Quarry, Cleveland, OH. The sandstone cores were cast in Hysol Tooling Compound (Hi-Co Associates, Orlando, FL) Inside PVC pipes. The sand used as porous media was purchased from AGSCO Corp., Paterson, NJ. The sand packs had permeability of about 2.4 darcy and porosity of 40%, whereas Berea sandstones had permeability of about 275 millidarcy and porosity of 18%.

(B) Methods

(i) Surface Tension

The surface tension of the freshly prepared foaming solutions was measured using the Wilhelmy plate method.[29] All measurements were carried out at 20°C.

(ii) Surface Viscosity

A single knife-edge rotational surface viscometer was used for the measurement of surface viscosity of the foaming solutions.[30] At least three readings were taken for each solution. The results were reported as the average values.

(iii) Bubble Size

The microphotographs of the foam were taken using a camera attached to the microscope. The average size of the foam bubbles was determined from the size frequency analysis of a microphotograph.

(iv) Fluid Displacement in Porous Media

The sandpacks (diameter 1.62" x length 12") or the Berea Cores (1" x 1" x 12") used as porous media were flushed vertically with carbon dioxide about an hour to displace interstitial air. Deionized, distilled water was pumped through using a Cheminert metering pump (Model CMP-2, Laboratory Data Control, Riviera Beach, FL), and the pore volume (PV) was determined. By this procedure, the trapped gas bubbles in porous were easily eliminated due to the solubility of carbon dioxide in water. Five pore volume water was pumped through at different flow rates to wash out carbon dioxide as well as to determine the absolute permeability of the porous media using Darcy equation.[31] After the permeability was determined, several pore volumes of the foaming solution of known surface properties were injected in 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 (Validyne DP-15, Validyne Engineering Corporation, Northridge, CA) and recorder (Heath/Schlumberger 255, Heath Company, Benton Harbor, MI). 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.

RESULTS AND DISCUSSION

(A) Surface Properties of Foaming Solutions

Sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$) and alkyl alcohols (e.g., C_8OH, $C_{10}OH$, $C_{12}OH$, $C_{14}OH$ and $C_{16}OH$) in a molar ratio 10:1 were used as foaming agents in all experiments. The following surface properties of the foaming solutions were measured.

(i) Surface Tension

Table 1 shows the surface tension of various foaming solutions which contain foaming agents of various chain length. It was observed that the surface tension was the lowest when both the components of the foaming solution had the same chain length. The surface tension increased as the difference in the chain length of the foaming agents increased.

(ii) Surface Viscosity

Surface viscosity of various mixed foaming systems is shown in Table 1. The maximum surface viscosity was observed when the foaming agents possessed the similar chain length, whereas surface viscosity decreased as the difference in the chain length of the foaming agents increased. This shows that the chain length compatibility strikingly affects the surface viscosity of the foaming solutions. The surfactant molecules of the similar chain length are tightly packed at the air/liquid interface, as compared to the molecules of the dissimilar chain length.[32,33] The high surface viscosity is known[30] to reduce the rate of thinning of liquid films resulting in high foam stability. Shah and coworkers[33,34] have reported that the increase in foam stability of decanoic acid solution in the presence of decanol is due to the increase in surface viscosity caused by the alcohol. At pH 9.0, foams of decanoic acid and 1:3 mixture of decanoic acid-decanol had maximum stability.[35,36]

(B) Microscopic Characteristics of Foams

Figure 3 shows the microphotographs of various foams at 15 minutes interval after the foams were generated. It is evident that the mixed foaming agents of similar chain length ($C_{12}H_{25}SO_4Na + C_{12}H_{25}OH$) produced smaller foam bubbles as compared to that by the mixed foaming agents of dissimilar chain length. The average size of foam bubbles was determined from size frequency analysis of the microphotographs.

Table 1 includes the radii of the bubbles of various mixed foaming systems. The average size of the foam bubbles was a minimum for the foaming agents of similar chain length and increased with increasing difference in the chain length of foaming agents. Using monolayers, it has been shown[32] that the molecules pack tightly in the mixed film when the chain length of both components is equal. Moreover, it is likely that as the difference in the chain length increases, the thermal disturbances (e.g. rotational, vibrational and oscillational motions) and the area/molecule increase.

(C) Foam Behavior in Porous Media

(i) The Breakthrough Time and Fluid Displacement Efficiency in the Absence of Foaming Agents

Figures 4 and 5 represent the variation in breakthrough time and fluid displacement efficiency as a function of applied air pressure (ΔP) in sandpacks and Berea cores, respectively without any foaming agent. To keep the breakthrough time within the measurable limits, the fluid displacement efficiency in sandpacks was measured between 1.5-18 psi, whereas, 10-50 psi air pressures were used for fluid displacement efficiency in Berea cores. For sandpacks, a slight decrease in fluid displacement efficiency with increasing ΔP was observed and about 5-7% fluid was recovered. Replacing water with brine gave the same fluid displacement efficiency in sand packs. The breakthrough time decreased sharply at low ΔP values and remained constant at high ΔP values.

For Berea cores, however, a continuous increase in fluid displacement efficiency was observed up to 25 psi and remained constant with further increase in ΔP (Fig. 5). The total volume of fluid recovered was 20-22%. A sharp decrease in the breakthrough time was observed up to 20 psi, whereas further increase in pressure, the breakthrough time remained the same. At a pressure of 15 psi, the breakthrough time increased by approximately thirty-fold in Berea cores, as compared to sandpacks, where the fluid displacement efficiency increased nearly 4.5 times.

(ii) The Breakthrough Time and Fluid Displacement Efficiency in the Presence of Foaming Agents

Figures 6 and 7 show the variation in the breakthrough time and fluid displacement efficiency in the presence of foam in sandpacks and Berea cores, respectively. The concentration of the foaming agent ($C_{12}H_{25}SO_4Na$) used was 5.0×10^{-3} M. The foaming solution also contained 1.0% brine for the measurement of fluid recovery in Berea cores. In sandpacks, the fluid displacement efficiency increased at low ΔP values and a maximum occurred at 4 psi. Further increase in ΔP, a continuous decrease in fluid displacement efficiency was observed. The breakthrough time decreased sharply up to 4 psi and a slight decrease in the breakthrough time was observed with further increase in ΔP. At 4 psi, the fluid displacement efficiency improved about 73.6% in the presence of foam, as compared to that without the foam. The breakthrough time was measured to be 1 minute in the absence of foam and 27 minutes in the presence of foam at 4 psi in sandpacks.

For Berea cores, the fluid displacement experiments in the presence of foam were performed between 30-50 psi. A linear decrease in fluid displacement efficiency was observed in contrast to the maximum observed for the sandpacks, in the measured range of ΔP. A sharp decrease in breakthrough time was observed for low values of ΔP (<35 psi) and with further increase in ΔP, the breakthrough time decreased gradually. At 30 psi, the fluid displacement efficiency improved about 34.3% in the presence of foam as compared to that without the foam. The breakthrough time was 3 minutes 40 seconds in the absence of foam and 70 minutes in presence of foam at 30 psi.

The results show that both the breakthrough time and fluid displacement efficiency are improved considerably in the presence of foam in sandpacks as well as in Berea cores. It is evident that the formation of in situ foam bank between displacing air and displaced liquid reduced considerably the gravity override of air, as well as the permeability of porous media to air, which improved both the breakthrough time and fluid displacement efficiency. However, the presence of a foam bank in sandpacks improved fluid displacement efficiency to a much greater extent as compared to Berea cores. Moreover, the trend in the variation of breakthrough time with ΔP was found to be the same in the presence or the absence of foam for both sandpacks and Berea cores.

(iii) The Breakthrough Time and Fluid Displacement Efficiency in the Presence of Mixed Foaming Agents

In order to delineate the effect of chain length compatibility 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 10:1. Table 1 represents the variation in breakthrough time and fluid displacement efficiency in sandpacks as well as in Berea cores. The volume of fluid recovered was found to be greater in sandpacks as compared to Berea cores. It was observed that the breakthrough time and fluid displacement efficiency were influenced by the chain length compatibility of the surfactant molecules. The breakthrough time and fluid displacement efficiency were found to be maximum when both components of the mixed foaming system had the same chain length.

The mixed anionic and nonionic foaming agents of similar chain length (e.g. $C_{12}H_{25}SO_4Na + C_{12}H_{25}OH$) improved fluid recovery by approximately 15 percent as compared to that by mixed foaming agents of dissimilar chain length (e.g. $C_{12}H_{25}SO_4Na + C_{16}H_{33}OH$) in sandpacks and Berea cores. It appears that the chain length compatibility influences the molecular packing at the air/liquid interfaces and changes surfaces properties of foaming solutions as well as fluid displacement efficiency in porous media. In sandpacks, the breakthrough time in the presence of mixed foaming agents of similar chain length (e.g. $C_{12}H_{25}SO_4Na + C_{12}H_{25}OH$) increased by 72.3% as compared to that by the dissimilar chain length foaming system (e.g. $C_{12}H_{25}SO_4Na + C_{16}H_{33}OH$). The trend in variation of the breakthrough time as a function of the chain length compatibility of mixed foaming agents was found to be the same in Berea cores.

Figure 8 illustrates a correlation of the breakthrough time and fluid displacement efficiency with the chain length compatibility and surface properties of foaming agents. From these studies it can be suggested that a maximum in surface viscosity, a minimum in surface tension, a minimum in bubble size correlate with a maximum in fluid displacement efficiency and a maximum in 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.

(iv) Effect of The Length of Porous Media on Break-Through 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 sodium dodecyl sulfate and 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 represented in Table II. Three sandpacks of the same diameter but of different lengths (e.g., 1, 2 and 4 feet) were selected and a constant air pressure (ΔP) of 5 psi/ft was used.

It is obvious from Table II that the fluid displacement efficiency increases with increasing length of the porous media in the absence and in the presence of foaming agents whereas the breakthrough time/ft decreases. 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 time and fluid displacement efficiency in the presence of foaming agents increased manifold as compared to that 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 foaming solutions depend on the chain length compatibility of the mixed surfactants. For mixed foaming systems, a minimum in surface tension and a maximum in surface viscosity were observed when both components of the system had the same chain length ($C_{12}H_{25}SO_4Na + C_{12}H_{25}OH$). The increase in surface tension or decrease in surface viscosity was measured with increasing difference in the chain length of the surfactants.

2. The average size of bubbles changes with the chain length compatibility of foaming agents. 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 chain length of surfactants increases.

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, as compared that by an anionic ($C_{12}H_{25}SO_4Na$) foaming agent alone, or 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 media in the absence or in the presence of foaming agents.

5. The breakthrough time/ft was found to decrease with the length of the porous media in the absence or in the presence of foaming agents.

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

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TABLE - I

The Effect of Chain Length Compatibility of Foaming Agents on Surface Tension, Surface Viscosity, Bubble Size, Breakthrough Time, and Fluid Displacement Efficiency.

System	$C_{12}H_{25}SO_4Na$ + C_8OH	$C_{12}H_{25}SO_4Na$ + $C_{10}OH$	$C_{12}H_{25}SO_4Na$ + $C_{12}OH$	$C_{12}H_{25}SO_4Na$ + $C_{14}OH$	$C_{12}H_{25}SO_4Na$ + $C_{16}OH$
Surface Tension, (dynes/cm.)	25.88	24.26	22.97	25.61	30.32
Surface Viscosity, (s.p.)	0.98×10^{-2}	1.45×10^{-2}	3.20×10^{-2}	2.62×10^{-2}	2.10×10^{-2}
Bubble Size, Radius (cm.)	10.60×10^{-2}	6.50×10^{-2}	2.50×10^{-2}	8.00×10^{-2}	8.70×10^{-2}
Breakthrough Time, (min.)					
In Sandpacks 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 %					
In Sandpacks 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

TABLE - II

Effect of the length of porous media on breakthrough time and fluid displacement efficiency

S.No.	System	Breakthrough Time/Ft, Min. Length of Sandpack			Fluid Displacement Efficiency, % Length of Sandpack		
		1 ft	2 ft	4 ft	1 ft	2 ft	4 ft
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

WITHOUT FOAMING AGENTS

WITH FOAMING AGENTS

(A)

STEAM OR GAS

GRAVITY OVERRIDE

FOAM BANK

STEAM OR GAS

REDUCTION IN GRAVITY OVERRIDE

(B)

STEAM OR GAS

HYDRODYNAMIC FINGERING

FOAM BANK

STEAM OR GAS

IMPROVEMENT IN MOBILITY CONTROL

LOW PERMEABILITY ZONE

(C)

STEAM OR GAS

RAPID FLOW IN HIGH PERMEABILTY ZONES

HIGH PERMEABILITY ZONE

LOW PERMEABILITY ZONE

FOAM BANK

STEAM OR GAS

HIGH PERMEABILITY ZONE

REDUCTION IN GAS FLOW IN HIGH PERMEABILITY ZONES

Fig. 1—Possible effects of foam on transport of steam or gas in porous media.

| Molecular Properties of Foaming Agents | ▶ | Microscopic Characteristics of Foams | ▶ | Behavior of Foam in Porous Media | ▶ | Efficiency of Steam or Gas Drive Processes |
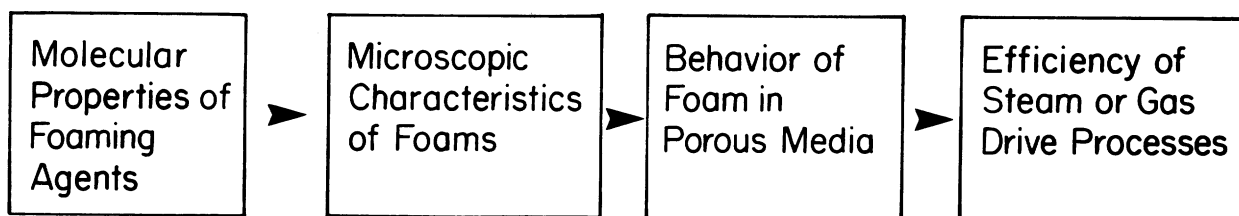
Fig. 2—Interrelationship of molecular properties of foaming agents with the efficiency of steam or gas drive processes.
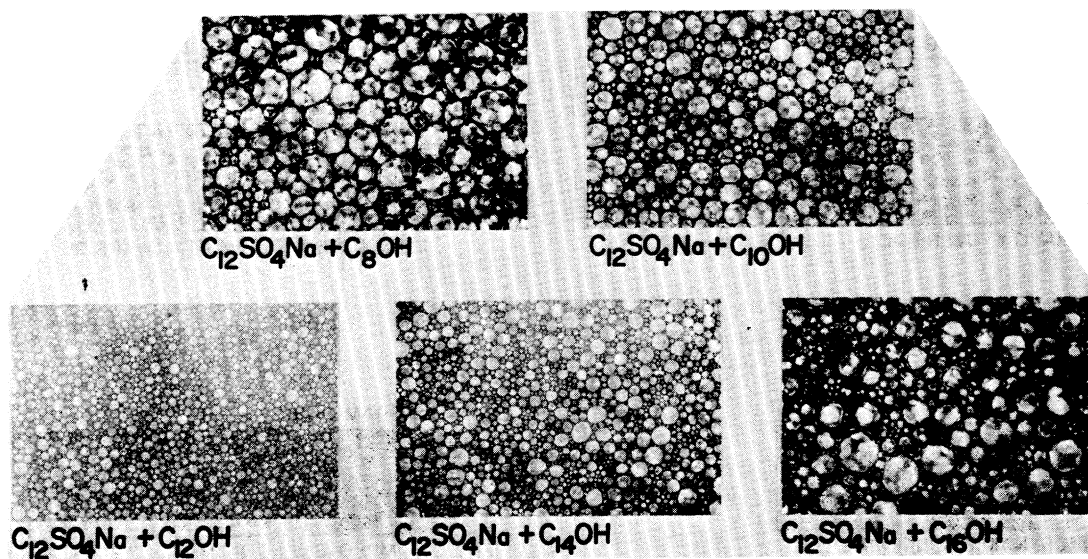
Fig. 3—Microphotographs of foams containing $C_{12}SO_4Na$ (0.0005M) and various alkyl alcohols (0.0005M) at 15 minutes after the foams were produced.
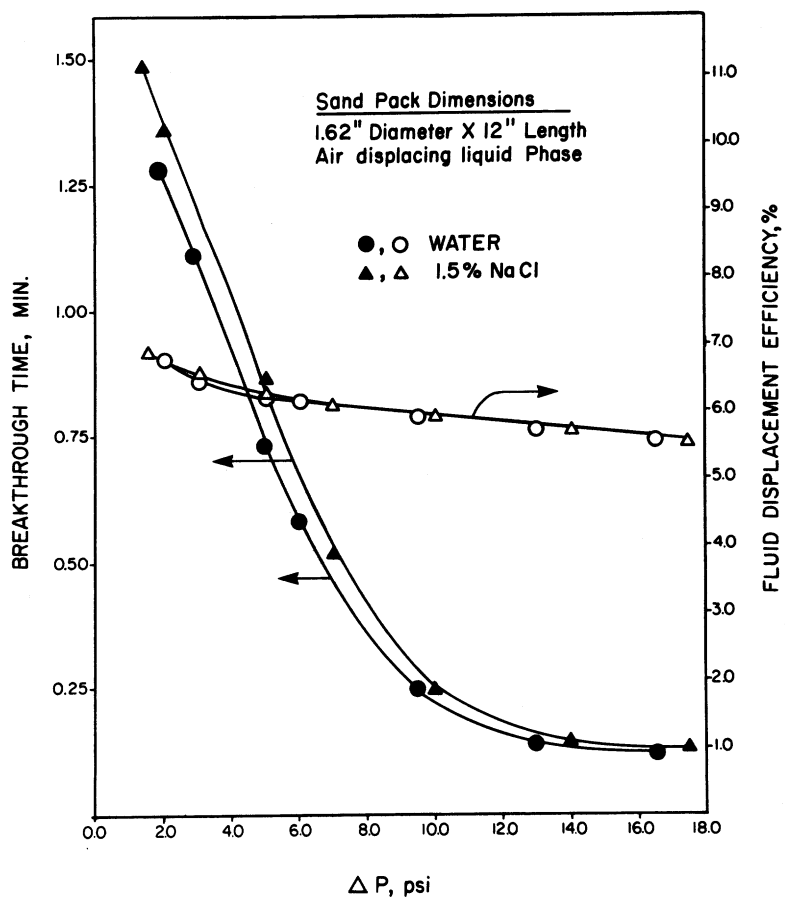

Fig. 4—Effect of ΔP on breakthrough time and fluid displacement efficiency in sandpacks without foaming agent.
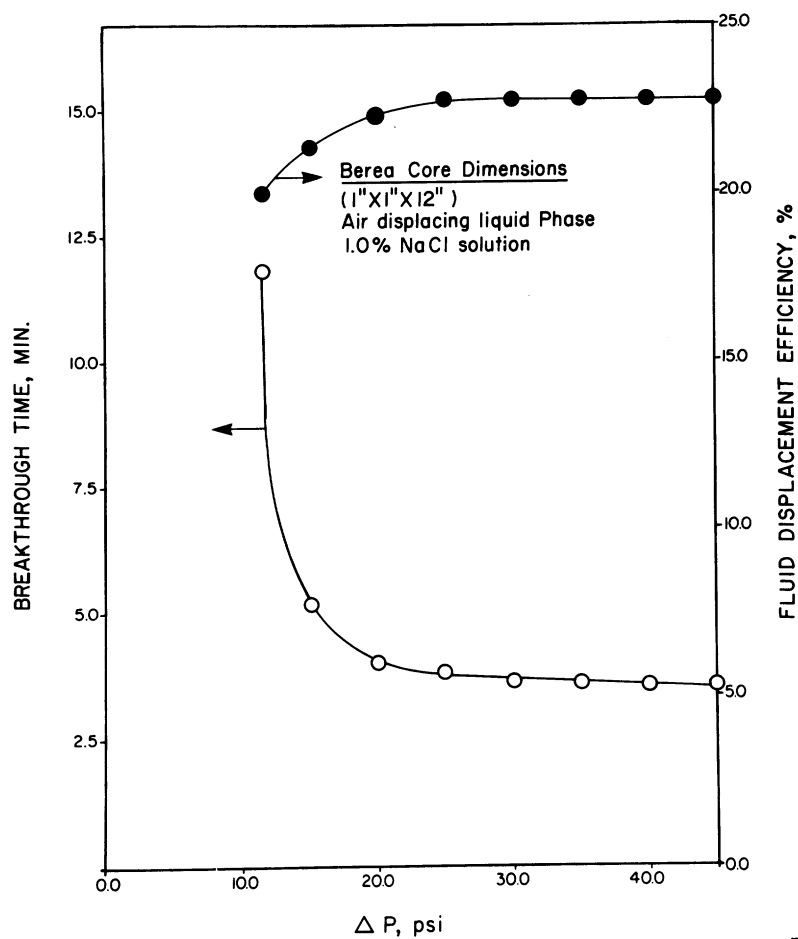
Fig. 5—Effect of ΔP on breakthrough time and fluid displacement efficiency in Berea cores without foaming agent.
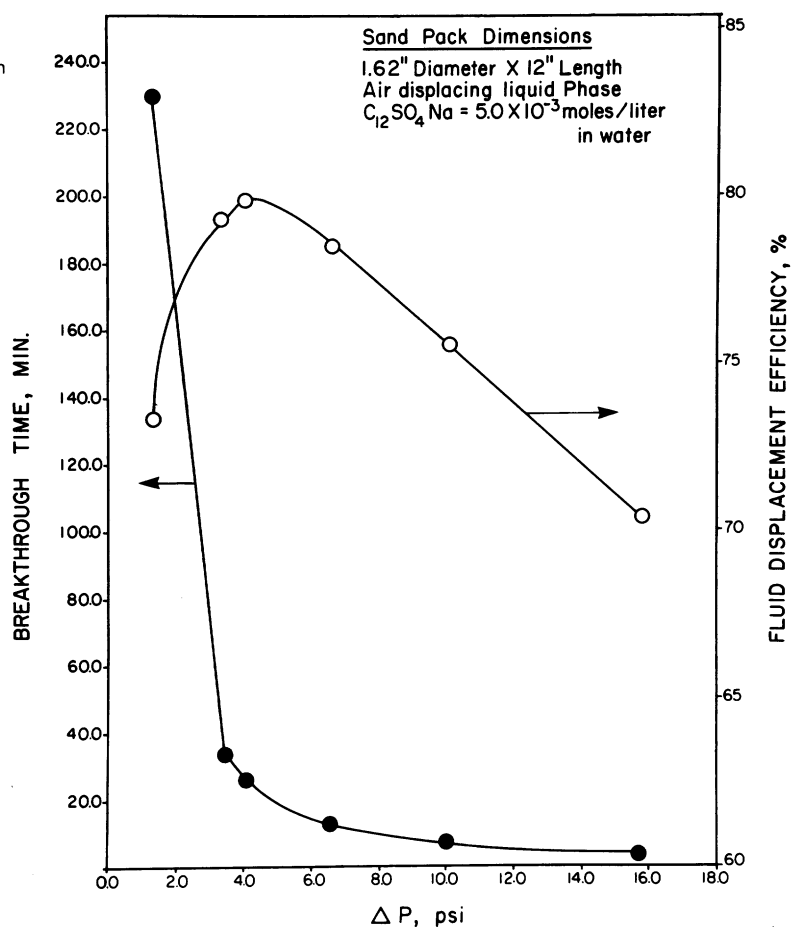

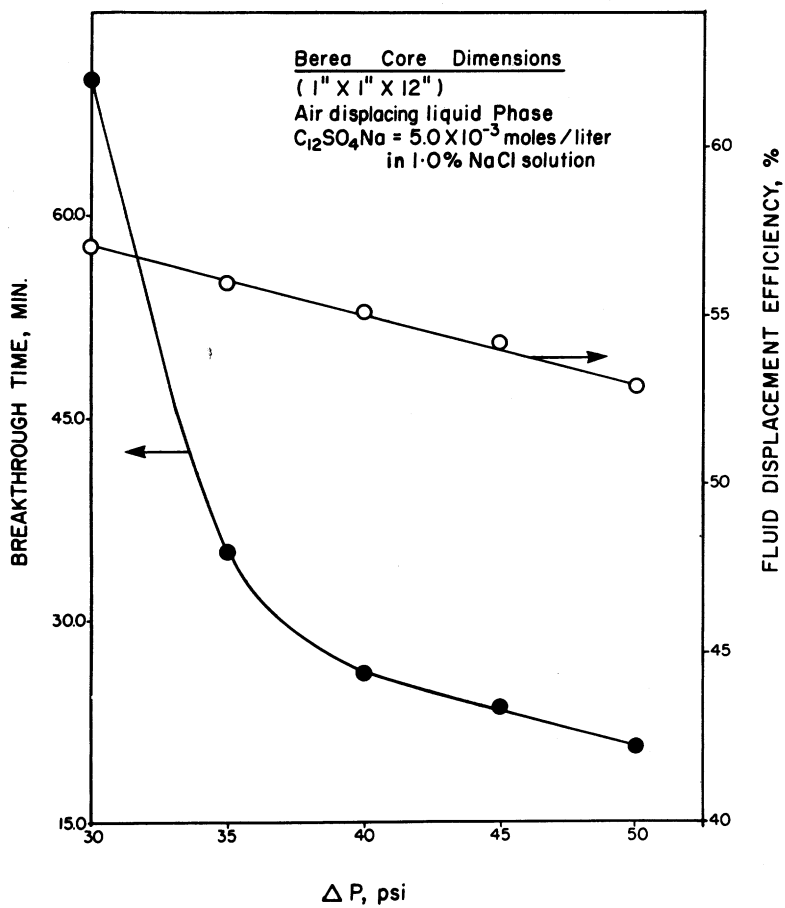**Fig. 6**—Effect of ΔP on breakthrough time and fluid displacement in sandpacks with foaming agent.

Fig. 7—Effect of ΔP on breakthrough time and fluid displacement efficiency in Berea cores with foaming agent.
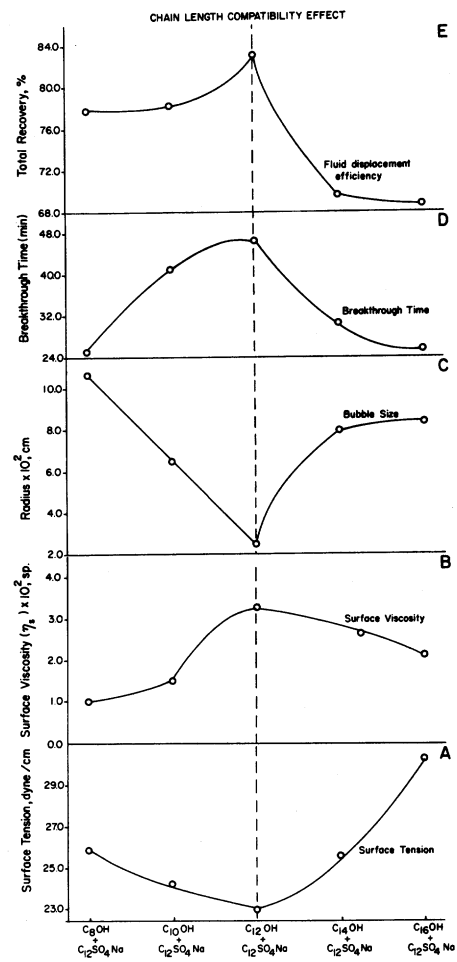

Fig. 8—A correlation of surface properties of foaming solutions with their porous media behavior.