Correlation of Chain Length Compatibility and Surface Properties of Mixed Foaming Agents with Fluid Displacement Efficiency and Effective Air Mobility in Porous Media

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The effects of chain length compatibility and surface properties of mixed foaming agents on fluid displacement efficiency and effective air mobility in porous media were investigated. Sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$) and various alkyl alcohols (e.g., $C_8OH, C_{10}OH, C_{12}OH, C_{14}OH$, and $C_{16}OH$) were used as mixed foaming agents. It was observed that the surface properties of surfactant solutions and flow behavior of foams through porous media were influenced by the chain length compatibility of the surfactant molecules. The increase in the length of porous media improved fluid displacement efficiency while breakthrough time per unit length decreased slightly with increase in the length of porous media. For mixed surfactant systems, a minimum in surface tension, a maximum in surface viscosity, a minimum in bubble size, a maximum in breakthrough time, a maximum in fluid displacement efficiency, and a minimum in effective air mobility were observed when the two components of the surfactant system had the same chain length. These results indicate that the surface properties of foaming solutions and molecular packing at interfaces exhibit a striking correlation with breakthrough time, fluid displacement efficiency, and effective air mobility in porous media.

Introduction

Considerable research has been carried out on formation, rheological, and physicochemical properties of foams by various investigators (Raza and Marsden, 1967; Lord, 1981; Marsden and Khan, 1966; Grove et al., 1951; Sibree, 1943; King, 1944; Burcik, 1953; Shih and Lemlish, 1971; Holcomb et al., 1980,1981). It has been reported that the formation of foam and various physicochemical properties of the system are influenced by the alkyl chain length of mixed foaming agents (Shah, 1971; Shah and Schulman, 1967; Shah et al., 1978). For example, the surface viscosity and foam stability are influenced by the alkyl chain length of the mixed surfactants. Moreover, it has also been shown previously (Schick and Fowkes, 1957; Shah and Shiao, 1975; Lawrence, 1960; Ries and Gabor, 1967; Meakins, 1968; Cameron and Crouch, 1963; Fort, 1962) that the critical micelle concentration (cmc), the average area per molecule in mixed monolayers, emulsion stability, rust prevention, dielectric absorption, and lubrication properties are strongly influenced by the alkyl chain length compatibility of the mixed surfactants.

The use of foams has been developed in recent years in the field of oil and gas production. Because of their specific properties, foam has been used in the petroleum industry for various operations such as drilling, fracturing, completion, acidizing, and mobility control during oil recovery processes. Gas or steam can be injected in a petroleum reservior for oil recovery. Channeling and gravity override problems are common during gas or steam flooding processes. Channeling is due to the high mobility of displacing gas and low mobility of displaced oil. The gravity override effect occurs due to the density difference between the gas and the reservoir fluids. Therefore, gas emerges early at the production wells and also bypasses a considerable volume of the petroleum reservoir.

Surfactants can be used as additives to reduce gas mobility, which in turn reduces channeling and gravity override due to formation of in situ foam. Foam is a material with properties that are considerably different from those of its components (Sibree, 1943); for example, the viscosity of a foam is greater than either of its components (e.g., gas or surfactant solution). In addition to this, foam can easily overcome gravitational effects and can pass through most regions of a heterogeneous reservoir. A number of research papers have been published on foam behavior in porous media (Batra and Holm, 1970; Shelton and Yarborough, 1977; Slattery, 1979; Raza, 1970; Albrecht and Marsden, 1970; Bernard and Holm, 1964; Kanda and Schechter, 1976; Minssieux, 1974; Holm, 1970; Dilgren et al., 1982).

The formation of a foam bank between the displacing gas and aqueous surfactant solution can cause three possible effects on flow through porous media as shown in Figure 1. First, it can act as a gravity override reducing agent in steam or gas drive processes due to generation of foam within porous media (Figure 1A). Gravity override of injected gas 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 (Figure 1B). Finally, 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 (Figure 1C). Moreover, the interrelationship of molecular properties of foaming agents with EOR efficiency of steam or gas drive processes is represented in Figure 2. It is evident that the 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.

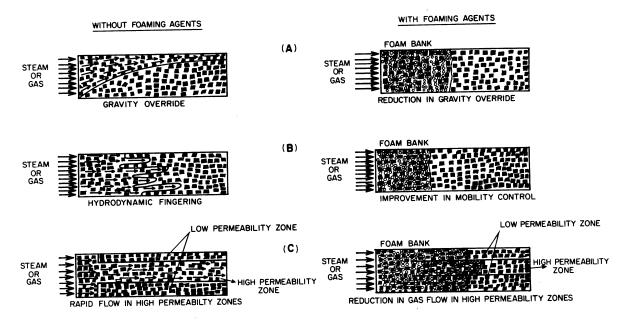


Figure 1. Possible effects of foam on transport of steam or gas in porous media.

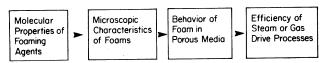


Figure 2. Interrelationship of molecular properties of foaming agents with the efficiency of steam or gas drive processes.

Materials and Methods

(a) Materials. Sodium dodecyl sulfate was supplied by Aldrich Chemical Co., Milwaukee, WI. Alkyl alcohols (98% pure) were obtained by Chemical Samples Co., Columbus, OH. All surfactants were used as received. Sodium chloride was purchased either from Mallinckrodt Inc., St. Louis, MO, or from Fisher Scientific Co., Orlando, FL. Deionized, distilled water was used in all experiments.

The Berea core slab was purchased from Cleveland Quarry, Cleveland, OH. The slab was cut into the desired length of cores in our laboratory so that consistent and uniform permeabilities could be obtained. The sandstone cores were cast in Hysol Tooling compound (Hi-Co Associates, Orlando, FL) inside PVC pipes. The sand, used as a porous medium, was obtained from AGSCO Corp., Paterson, NJ. The sandpacks had permeabilities of about 2.4 darcy and porosity of 40%, whereas Berea sandstones had permeabilities of about 275 millidarcy and porosity of 18%. The transducer (Model DP-15) used for the measurements of pressure across the porous medium was purchased from Validyne Engineering Corp., Northridge, CA. The recorder was obtained from Heath/Schlumberger (Model 225), Heath Company, Monton Harbor, MI. The water was pumped using Cheminert metering pump Model EMP-2, Laboratory Data Control, Riviera Beach, FL.

- (b) Methods. (I) Surface Tension. The surface tension of the freshly prepared foaming solutions was measured by the Wilhelmy plate method (Wilhelmy, 1863). The platinum plate was always cleaned and heated to a red color with a Bunsen burner before use. All measurements were carried at 20 °C.
- (II) Surface Viscosity. A single knife-edge rotational viscometer was used for the measurement of surface viscosity of the foaming solutions (Brown et al., 1953). Surfactant solution (20 mL) was poured in the cup. About 10 min was allowed for the surfactant molecules to diffuse into the surface layer. The bob was then lowered onto the

surface by observing the meniscus at the edge of the bob. The angular deflection was measured at various speeds. The rotational speed was adjusted continuously and smoothly to the desired speed from 0 to 10 rpm. The bob with 4 cm diameter and the cup with 5 cm diameter were used for most of the measurements. The bob and the cup were cleaned first by dipping in the soap solution then they were rinsed with distilled water for about 5 min. At least three readings were taken for each solution. The results were reported as the average values.

(III) Bubble Size. A special type of rectangular plexiglass cell was used for measurements of bubble size (Sharma et al., 1982). Surfactant solution (10 mL) was placed in the cell. The foams were generated by shaking the plexiglass cell for 2 min. The photomicrographs of foams were taken with a camera attached to a microscope. An average size of the bubbles was determined from the size frequency analysis of the photomicrographs.

(IV) Fluid Displacement in Porous Media. Sandpacks or the Berea cores, used as porous media, were flushed vertically with carbon dioxide for about an hour to displace interstitial air. Several pore volumes of distilled water were pumped and the pore volume (PV) of the porous medium was determined. By this procedure, the trapped gas bubbles in porous media were easily eliminated due to the solubility of carbon dioxide in water. Five pore volumes of water were pumped through at different flow rates to wash out carbon dioxide as well as to determine the absolute permeability of the porous media using the Darcy equation (Darcy, 1856). The permeability of the porous medium in horizontal position was determined. The surfactant solution of known surface properties was injected in a porous medium at constant flow rate. This was followed by a constant air flow for generation of in situ foam. 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 at breakthrough were recorded for a constant applied pressure.

Results and Discussion

(A) Surface Properties of Foaming Solutions. In order to correlate the effect of chain length compatibility with surface properties of the foaming solutions, sodium

Table I. The Effect of Chain Length Compatibility of Foaming Agents on Surface Tension, Surface Viscosity, Bubble Breakthrough Time, Fluid Displacement Efficiency, and Effective Air Mobility

system	C ₁₂ H ₂₅ SO ₄ Na + C ₈ OH	$C_{12}H_{25}SO_4Na + C_{10}OH$	$C_{12}H_{25}SO_4Na + C_{12}OH$	C ₁₂ H ₂₅ SO ₄ Na + C ₁₄ OH	C ₁₂ H ₂₅ SO ₄ Na - C ₁₆ OH
surface tension, dyn/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	18.5	23.5	29.5	18.0	17.0
psi					
fluid displacement					
efficiency in %				na aanna laar dii kalee ahaa kalee kal Maria kalee ka	Figure per services of
in sandpacks	77.8	78.1	83.0	69.6	68.9
at 5 psi				rescul e di Sulvo	n ang ont Ananie
in Berea cores	54.3	58.6	62.9	47.1	45.7
at 40 psi					
effective air mobility,					
cm ² /(s psi)		14		2P_92a_0E	0.00 10-2
in sandpacks	11.91×10^{-3}	7.27×10^{-3}	6.86×10^{-3}	8.76×10^{-3}	9.63×10^{-3}
at 5 psi		95	menaured at son	star well-san tun	1 00 10-1
in Berea cores	1.81×10^{-4}	1.54×10^{-4}	1.32×10^{-4}	1.62×10^{-4}	1.66×10^{-4}
at 40 psi					
C _{I2}	SO ₄ Na +C ₈ OH		C _{I2} SO ₄ Na+C _{IC}	OH	
$C_{12}SO_4N_0 + C_{12}OH$	C.,	SO4Na + C14O	H	C12SO4Na +	CICOH
0 2004140 10 2011		24	theoret Ruid da	12 4	10

Figure 3. Photomicrographs of foams containing sodium dodecyl sulfatte (0.005 M) and various alkyl alcohols (0.0005 M) at 15 min after foams were produced.

dodecyl sulfate ($C_{12}H_{25}SO_4Na$) and various alkyl alcohols of different chain lengths (i.e., C₈OH, C₁₀OH, C₁₂OH, C₁₄OH, and C₁₆OH) in a molar ratio 10:1 were used as mixed surfactant systems. Surface tension (γ) and surface viscosity (η_s) of various mixed surfactant systems are shown in Table I. It was observed that the surface tension was the lowest when both of the components of the foaming agents had the same chain length (i.e., C₁₂H₂₅SO₄Na + C₁₂OH). On the other hand, a maximum in surface viscosity was observed when the foaming agents possessed similar chain length. These results show that the chain length compatibility of the surfactant molecules strikingly affects the surface tension and surface viscosity of the surfactant solutions. The surfactant molecules having the same chain length are tightly packed at the air-liquid interface, as compared to the molecules of the dissimilar chain length (Shah et al., 1978; Shah and Shiao, 1975). The high surface viscosity is known (Brown et al., 1953) to reduce the rate of thinning of the liquid films which in turn increase the foam stability. Shah and co-workers (1969, 1975) have shown 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 a 1:3 mixture of decanoic acid-decanol had maximum stability (Shah, 1970, 1971).

(B) Microscopic Characteristics of Foams. Figure 3 shows the photomicrographs of various foams at 15 min after the foams were generated. It is observed that the mixed surfactant having the same chain length (C₁₂H₂₅SO₄Na + C₁₂OH) produce smaller size bubbles as compared to a surfactant having dissimilar chain length. The average size of bubbles was determined from the size frequency analysis of the photomicrographs.

Table I shows the radii of the bubbles produced by various mixed surfactant systems. The average bubble size was a minimum for the mixed foaming agents of similar chain length and increased with increasing difference in the chain length. Upon using mixed monolayers (Shah and Shiao, 1975), it has been shown that the molecules pack tightly at the air-liquid interface when the chain length of both of the components is equal. It was proposed that as the difference in the chain length increases, the thermal disturbances (e.g., rotational, vibrational, and oscillational

(C) Fluid Displacement in Porous Media. The breakthrough time and fluid displacement efficiency at breakthrough were measured to correlate gas mobility in a porous medium in the presence of surfactant solutions with chain length compatibility and surface properties of mixed surfactant systems. The effective air mobility in porous media in the presence of surfactant solution was calculated by use of Darcy's law for linear displacement. Accordingly, the gas flowing in a linear system can be given as follows (Craft and Hawkins, 1959)

$$q_{\rm sc} = \frac{T_{\rm sc} A K (p_1^2 - P_2^2)}{2 P_{\rm sc} T Z \mu_{\rm g} \Delta L} \tag{1}$$

where $q_{\rm sc}$ is the constant gas flow rate measured at some standard absolute pressure $(p_{\rm sc})$ and temperature, $(T_{\rm sc})$, $\mu_{\rm g}$ is the gas viscosity, $k_{\rm g}$ is the effective gas permeability, T is the temperature of the fluid, A is the flow cross-sectional area, Z is the gas deviation factor at flow conditions, and p_1 and p_2 are the upstream and downstream absolute pressures.

The flow through porous media experiments were performed at constant temperature and the downstream pressure (p_2) was atmospheric pressure. The pressure drops across the porous medium were always less than 50 psi and thus the gas deviation factor (Z) can be neglected. Cumulative volume (q) of the fluid collected at gas breakthrough time (t) was measured at room temperature and atmospheric pressure. Therefore, the flow rate term $q_{\rm sc}$ (eq 1) can be replaced by the term q/t, which represents an average flow rate of the gas in the porous medium until gas breakthrough. Equation 1 can be rewritten as

$$q/t = \frac{K_{\rm g}A(\Delta p^2)}{\mu_{\rm g}\Delta L} \tag{2}$$

where

$$(\Delta p^2) = \frac{{p_1}^2 - {p_2}^2}{2p_{\rm sc}}$$

Equation 2 can be rearranged for analysis and interpretation of the results in terms of an effective gas mobility in a porous medium.

effective gas mobility =
$$\frac{K_{\rm g}}{\mu_{\rm g}} = \frac{q\Delta L}{At(\Delta p^2)}$$
 (3)

The flow cross-sectional area (A) and length of the porous medium (ΔL) were kept constant. In order to correlate surface properties of the foaming solutions with effective air mobility, the displacement experiments were performed both in sandpacks and Berea cores.

(I) The Breakthrough Time, Fluid Displacement Efficiency, and Effective Air Mobility in Sandpacks with and without Surfactants. Figure 4 shows the variation in breakthrough time and fluid recovery at air breakthrough as a function of pressure drops (Δp) in sandpacks without foaming agents, whereas the breakthrough time and fluid displacement efficiency at air breakthrough in sandpacks with surfactants are illustrated in Figure 5. To keep breakthrough time within the measurable limits, the fluid displacement experiments were performed between 1.5 and 18 psi. In the absence of the surfactants, the fluid recovery was about 5–7%, whereas in the presence of surfactants it was 70 to 80%. The

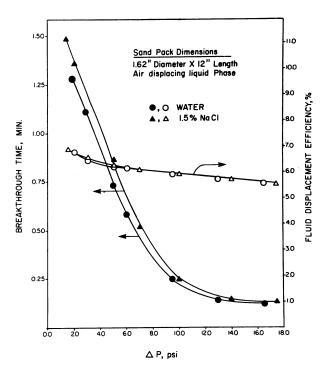


Figure 4. Effect of pressure drop (ΔP) on breakthrough time and fluid displacement efficiency at breakthrough in sandpacks without surfactant.

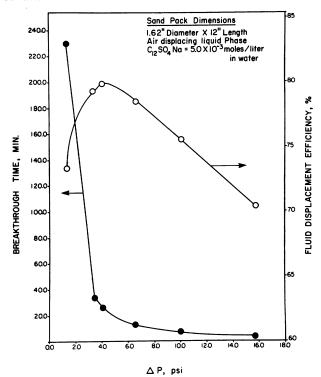


Figure 5. Effect of pressure drop (ΔP) on breakthrough time and fluid displacement efficiency at breakthrough in sandpacks with surfactant.

maximum breakthrough time increased from 1.5 to 230 min in the presence of the surfactant. Replacing water with 1.5% brine gave the same fluid displacement efficiency in sandpacks. The trend in variation of the breakthrough time was found to be the same for water and 1.5% brine.

In order to measure the fluid displacement efficiency in sandpacks in the presence of the foaming agent, sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$) was used at 0.005 M concentration. In the presence of the surfactant, the fluid displacement efficiency at air breakthrough increased at

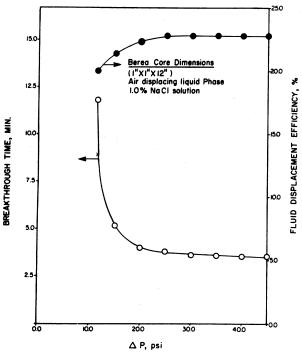


Figure 6. Effect of pressure drop (ΔP) on breakthrough time and fluid displacement efficiency at breakthrough in Berea cores without surfactant.

low Δp values, and a maximum occurred at 4 psi. The breakthrough time decreased sharply up to 4 psi, and a slight decrease in the breakthrough time was observed with further increase in Δp .

The effective air mobility in sandpacks in the presence and the absence of surfactants was calculated with eq 3. In the absence of surfactants, the effective air mobility remained constant with increasing pressure drops (Δp) , while effective air mobility increased to 5 psi and remained constant with further increase in pressure drop (Δp) in the presence of surfactants. The effective air mobility decreased by 50% in the presence of the surfactant, as compared to that without the surfactant.

(II) The Breakthrough Time, Fluid Displacement Efficiency, and Effective Air Mobility in Berea Cores with and without Surfactants. Figures 6 and 7 represent the variation in the breakthrough time and fluid displacement efficiency at breakthrough in Berea cores in the absence and the presence of surfactants, respectively. To keep the breakthrough time within measurable limits, the fluid displacement efficiency in sandstones was measured between 10 and 50 psi. In the absence of the surfactant, a continuous increase in fluid displacement efficiency was observed to 25 psi and remained constant with further increase in pressure drops (Figure 6). The total volume of the fluid recovered was 20-22%. A sharp decrease in the breakthrough time was observed to 20 psi, whereas the breakthrough time remained constant with further increase in pressure drop.

In the presence of surfactants, a linear decrease in fluid displacement efficiency was observed in Berea cores in contrast to the maximum observed for the sandpacks (Figures 5 and 7). A sharp decrease in breakthrough time was observed in Berea cores at low values of pressure drop (<35 psi) and with further increase in Δp , the breakthrough time decreased gradually. A comparison of fluid displacement efficiency and breakthrough time at 30 psi indicates that the presence of the surfactant increased the fluid displacement efficiency by 34% and breakthrough time by 16-fold.

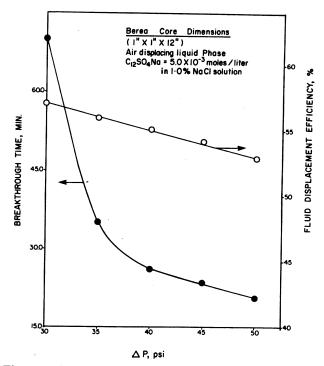


Figure 7. Effect of pressure drop (ΔP) on breakthrough time and fluid displacement efficiency at breakthrough in Berea cores with surfactant.

The results indicate that both breakthrough time and fluid displacement efficiency at foam breakthrough increase considerably with the presence of surfactants, and the effective air mobility decreases significantly in sandpacks as well as in Berea cores. The effective air mobility in Berea cores is smaller by two orders of magnitude as compared to that in sandpacks. The low values of effective mobility in Berea cores were observed to be due to the low permeability of porous media. It is evident that the formation of in situ foam bank between displacing air and displaced fluid decreased the gravity override of air considerably, as well as the permeability of porous media to air, which in turn improved both breakthrough time and fluid recovery. The presence of foam bank in sandpacks improved fluid displacement efficiency to a much greater extent as compared to Berea cores. The conclusions drawn from this study are consistent with those reported by previous investigators (Bernard and Holm, 1964) using different parameters. Moreover, the trend in the variation of breakthrough time vs. pressure drop was found to be the same in the presence or the absence of foam for both sandpacks and Berea cores (Figures 4-7).

(III) Effect of the Length of Porous Media on Breakthrough Time, Fluid Displacement Efficiency, and Effective Air Mobility. A series of experiments were performed varying the length of porous media, while holding sandpacks diameter and injected air pressure gradient (5 psi/ft) constant. The values of breakthrough time and fluid displacement efficiency, as a function of the length of porous media in the presence of sodium dodecyl sulfate (C₁₂H₂₅SO₄Na) and mixed anionic and nonionic surfactants (i.e., $C_{12}H_{25}SO_4Na + C_{12}H_{25}OH$)*, are summarized in Table II. It is obvious from Table II that the fluid displacement efficiency increased with increase in the length of porous media with or without surfactants, whereas the breakthrough time/ft decreases slightly with the length of porous media. The order of increase in the breakthrough time and fluid displacement efficiency, with respect to different surfactants, was found to be: water < sodium dodecyl sulfate < mixed sodium dodecyl sulfate

Table II. Effect of the Length of Porous Media on Breakthrough Time and Fluid Displacement Efficiency

no. system		breakthrough time/ft, min length of sandpack			fluid displacement efficiency, % length of sandpack		
	system	1 ft	2 ft	4 ft	1 ft	2 ft	4 ft
1	H ₂ O	0.73	0.67	0.45	6.51	7.35	8.20
2	C ₁₂ H ₂₅ SO ₄ Na	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

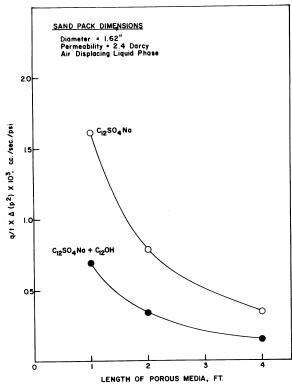


Figure 8. Effect of the length of porous media on effective air mobility.

and dodecyl alcohol. The breakthrough time and fluid displacement efficiency in the presence of surfactants increased manifold as compared to that without the surfactants. This suggests that the generation of in situ foam decreases gravity override, as well as gas flow in porous media, and hence injected air passes through a larger number of pores, which in turn increases both the breakthrough time and fluid displacement efficiency in porous media.

Figure 8 shows the variation in effective air mobility as a function of the length of porous media in the presence of surfactants. The effective mobility decreased with increasing length of the porous media. A sharp decrease in the air mobility was noticed up to 3 ft. Moreover, the mixed anionic and nonionic ($C_{12}H_{25}SO_4Na + C_{12}H_{25}OH$) surfactants decreased effective air mobility to a greater extent as compared to sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$) alone. It appears that the breakthrough time, fluid displacement efficiency, and effective air mobility depend on the surface properties of the surfactants as well as the length of porous media.

(IV) The Breakthrough Time, Fluid Displacement Efficiency, and Effective Air Mobility in the Presence of Mixed Surfactants. In order to delineate the effect of chain length compatibility and surface properties of surfactant solutions on breakthrough time, fluid displacement efficiency, and effective air mobility in a porous medium, sodium dodecyl sulfate $(C_{12}H_{25}SO_4Na)$ and various alkyl alcohols $(C_nH_{2n+1}OH)$ were used as mixed surfactants. Table I summarizes the results of the displace-

ment studies performed in sandpacks as well as in Berea cores. The breakthrough time, fluid displacement efficiency, and air mobility were influenced by the chain length compatibility of the surfactant molecules. It was observed that the breakthrough time and fluid displacement efficiency were found to be at a maximum when both components of the mixed surfactant system had the same chain length.

The mixed anionic and nonionic surfactants of similar chain length (e.g., $C_{12}H_{25}SO_4Na + C_{12}H_{25}OH$) improved fluid recovery by approximately 15% as compared to that by mixed surfactants of dissimilar chain length (e.g., $C_{12}H_{25}SO_4Na + C_{16}H_{33}OH$) in sandpacks as well as in Berea cores. In sandpacks, the breakthrough time in the presence of mixed surfactants of equal 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 surfactant 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 surfactant was found to be the same in Berea cores. A considerable reduction in effective air mobility was observed with mixed surfactants of similar chain length.

Figure 9 illustrates a correlation of the breakthrough time, fluid displacement efficiency, and effective air mobility with the chain length compatibility and surface properties of surfactants. From these studies it can be concluded that a minimum in surface tension, a maximum in surface viscosity, a minimum in bubble size, a minimum in effective air mobility, a maximum in breakthrough time, and a maximum in fluid displacement efficiency occurs when both components of the surfactant system have the same chain length. Our explanation for these chain length compatibility effects is shown schematically in Figure 10, based upon the concept of thermal motion of hydrocarbon chains at the air-liquid interface proposed by Adam (1938). The mixed surfactant molecules of equal chain length form a tighly packed mixed monolayer at the air-liquid interface. When the chain length of surfactants is not equal, the portion of the hydrocarbon chain above the height of the adjacent hydrocarbon chain will exhibit thermal motion (vibrational, rotational, and oscillational). If thermal motions were limited to the portion above the height of the adjacent hydrocarbon chain, it would not change the packing of the molecules or the average area/molecule. However, the thermal disturbances probably extend along the alkyl chain toward the polar part of the surfactant molecule which, in turn, exhibit a greater area/molecule in mixed monolayers at the air-liquid interface (Shah and Shiao, 1975). Moreover, as the difference in hydrocarbon chains of foaming agents increases, the expansion of a mixed monolayer also increases because the length of the segment undergoing rotation, vibration, and oscillation increases. The cones with the dashed lines (Figure 10) show the time-average space occupied by the segment of hydrocarbon chain of surfactants. A similar concept was also used by previous investigators (Shah and Shiao, 1975; Phillips et al., 1970) to explain results on mixed monolayers of various ionic and nonionic surface-

active agents. Shah and Shiao (1975) reported that in the

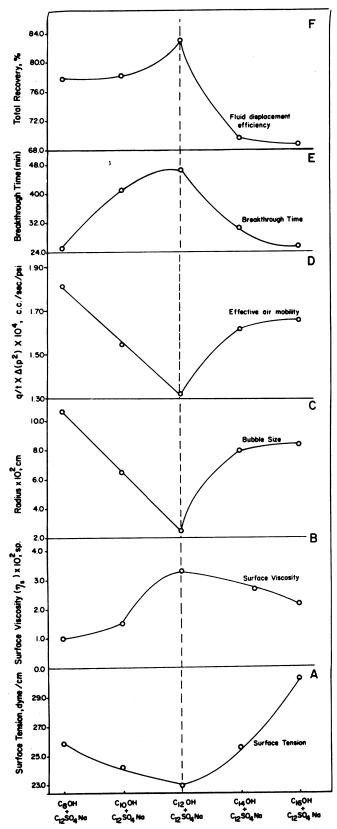


Figure 9. A correlation of surface properties of surfactant solutions with their porous media behavior.

mixed monolayers of various alcohols, the average area per molecule is at a minimum when both components possess the same chain length. The results indicate that the chain length compatibility also influences the bubble size and stability (Shiao, 1976). These results suggest that the molecular packing at the air-liquid interface and surface properties of surfactant solutions exhibit a striking cor-

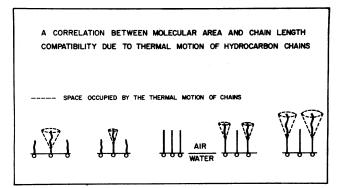


Figure 10. Schematic of the thermal motion of the upper segments of hydrocarbon chains of foaming agents at air-liquid interface. The cones shown by dashed lines represent the space occupied by the thermal disturbance of the segments.

relation with bubble size, breakthrough time, fluid displacement efficiency, and effective air mobility in porous media.

Acknowledgment

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Nomenclature

A =flow cross-sectional area

 K_{σ} = effective gas permeability

 $\Delta L = \text{length of porous medium}$

 p_1 = absolute upstream pressure

 p_2 = absolute downstream pressure

 $p_{\rm sc}$ = standard absolute pressure

 $\Delta p = \text{pressure drop}$

q =water flow rate

 $q_{\rm sc}$ = gas flow rate at standard $P_{\rm sc}$ and $T_{\rm sc}$ T = flow temperature

 $T_{\rm sc}$ = standard absolute temperature

t = gas breakthrough time

= gas viscosity

 $\mu_g = \text{gas viscosity}$ Z = gas deviation factor

 $\gamma = surface tension$

 $\eta_{\rm s} = {\rm surface \ viscosity}$

Registry No. C₈OH, 111-87-5; C₁₀OH, 112-30-1; C₁₂OH, 112-53-8; $C_{14}OH$, 112-72-1; $C_{16}OH$, 36653-82-4; $C_{12}H_{25}SO_4Na$, 151-21-3.

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