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The Influence of Temperature on Surface and Microscopic Properties of Surfactant Solutions in Relation to Fluid Displacement Efficiency in Porous Media

The surface properties, microscopic structure of foam, and flow through porous media behavior of mixed surfactant solutions (sodium lauryl sulfate plus lauryl alcohol) have been studied at various temperatures in relation to enhanced heavy oil recovery processes. The studies reported here suggest that temperature has a remarkable influence on the microscopic structure of foam and the flow through porous media behavior of the surfactant solutions. The surface tension and bubble size decreased as the temperature increased. The foam volume increased, whereas foam half-life (or foam stability) decreased with increasing temperature. A linear increase in bubble size with time was observed at different temperatures. The rate of change in bubble size increased with temperature. A significant reduction in effective air mobility and an improvement in fluid displacement efficiency were observed with increasing temperature. All measured parameters changed strikingly in the temperature range of 20–40°C, whereas they exhibited small changes between 40 and 80°C for the surfactant system investigated. The effect of temperature on half-life of foam and on the effective air mobility was most pronounced as compared to that on other parameters. An attempt is made to correlate quantitatively the foam volume of surfactant solution with fluid displacement efficiency in porous media.

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SCOPE

Steam flooding and other thermal processes are employed for enhanced oil recovery from heavy oil reservoirs. Steam flooding is expected to reduce the steam/oil ratio and to improve oil recovery. Various problems occur with steam or gas driven processes in petroleum reservoirs. Because of the density difference between gas and liquid phases, the lighter gas phase tends to ride over the liquid phase. This preferential movement of the gas phase through the upper part of the reservoir is called gravity override. The gas phase also channels through the high permeability zones of the reservoir. As a consequence of channeling and gravity override, the heat distribution through the reservoir is not uniform. These problems lead to early gas breakthrough in production wells and reduced oil recovery. One mechanism for decreasing gas mobility is to produce *in situ* foam by the gas phase. Reduced gas mobility would result in higher oil recovery. In practice, the injection of an aqueous surfactant solution prior to gas injection forms *in situ* foam as the gas fingers through the surfactant solution.

The specific objectives of the present study were to determine: (1) the effects of temperature and brine on the surface tension and foaminess of surfactant solutions, (2) the effects of temperature and brine on bubble size, (3) the stability of foam at various temperatures, (4) the effect of temperature on effective air mobility, and (5) the effects of temperature and brine on fluid displacement efficiency in a porous medium. These factors control the efficiency of foam displacement, which in turn reduces the tendency of the gas to finger through the liquid phase and thereby improves the fluid displacement efficiency in a porous medium.

CONCLUSIONS AND SIGNIFICANCE

The laboratory displacement experiments have shown that the formation of an *in situ* foam bank between the displacing gas and the liquid significantly reduces gas mobility in a porous medium and thereby increases the fluid displacement efficiency. The ability of surfactant solutions to produce *in situ* foam is one of the important factors for displacing fluid in a porous medium. Moreover, foam stability is not required for effective air mobility reduction and for the enhancement of fluid displacement efficiency in a porous medium. Results of the present studies of the surface properties of surfactant solutions, microscopic structure, and flow through porous media

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behavior of foam at various temperatures lead to the following major conclusions.

1. Surface tension of the mixed surfactants increased with the addition of brine, whereas a decrease in surface tension was observed with increasing temperature.

2. A quantitative correlation among bubble size, temperature, and time has been established. Average bubble size decreased with increasing temperature. In addition, upon increasing the temperature, the bubble size increased sharply with elapsed time.

3. The ability of the surfactant solutions to generate foam increased with increasing temperature, while the foam stability decreased with increasing temperature. It was observed that the foaminess of surfactant solutions is favorable for fluid displacement efficiency as well as for air mobility reduction.

4. The effective air mobility in the porous media decreased with increasing pressure gradient and temperature.

5. A quantitative correlation has been established between the foaminess of surfactant solution (static foaminess test) and fluid displacement efficiency in porous media (dynamic foaminess test).

6. Among all parameters measured, the effect of temperature was most pronounced on foam stability and effective air mobility.

INTRODUCTION

Considerable research has been carried out on the displacement of light oils using surfactant-polymer flooding (Shah and Schechter, 1976; Shah, 1981). However, for heavy oils, the injection of steam or gas in a petroleum reservoir has been employed for reducing the steam/oil or gas/oil ratio and thereby improving oil recovery (Ramey and Brigham, 1976; Stokes et al., 1977; Prats, 1978; Peterson, 1978). A number of significant problems (Farouq Ali and Meldau, 1978; Sharma et al., 1982a; Dilgren et al., 1982) exist with steam or gas driven processes in a porous medium due to the density difference between the gas and liquid phases. The gravity override, hydrodynamic fingering, and rapid flow of gas in high permeability zones result in early breakthrough of the gas phase while bypassing a large fraction of the reservoir. It is well understood (Holm, 1968) that when two immiscible phases (e.g., gas and liquid) 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. The presence of foam considerably reduces the effective permeability of the porous medium to each phase (Fried, 1961; Bernard and Holm, 1964).

A number of research papers have been published regarding the rheological and physicochemical properties of foams (Marsden and Khan, 1966; Shah et al., 1979; Holcomb, et al., 1981), the use of foam as a displacing fluid (Goktekin, 1968; Slattery, 1974, 1979), and the use of foam as a blocking agent (O'Brien, 1967; Albrecht and Marsden, 1970). Holm (1968) reported the mechanism of gas and liquid flow through porous media in the presence of foam. Most of these studies were carried out at atmospheric pressure and ambient temperature. Our previous communication (Sharma et al., 1982b) presented a correlation of the surface and microscopic properties of foaming solutions with the flow through porous media behavior of foam at ambient temperature. These studies show that the surface properties of surfactant solutions and the microscopic characteristics of the foam considerably influence the breakthrough time and fluid displacement efficiency in a porous medium.

The formation of a foam bank between the displacing air and the displaced aqueous surfactant solution strikingly improved the fluid recovery in a porous medium as compared to the recovery without surfactant solutions. For mixed surfactant systems at normal temperature, a minimum in 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 components of the surfactant had the same chain length (Sharma et al., 1982b). The flow through porous media results were also compared with the data obtained using water, brine, and sodium dodecyl sulfate alone. Increase in the length of the porous medium improved both breakthrough time and fluid displacement efficiency in sandpacks as well as in Berea cores. Elson and Marsden (1978) studied the ability of various commercial surfactants to function at elevated temperatures and over extended periods of time. Beyers et al. (1972) reported that the bulk foam has measurable flow properties up to 100°F (37.8°C) and 860 psi (5.9 MPa). But to our knowledge no one has studied the influence of temperature on the surface and microscopic properties of surfactant solutions in relation to reservoir applications of foams. Therefore, the present paper reports the effects of temperature on the surface properties of surfactant solutions in relation to fluid displacement efficiency and effective mobility of gas in a porous medium.

EXPERIMENTAL

Materials

Sodium dodecyl sulfate (purity > 99%) was supplied by Aldrich Chemical Co., Milwaukee, WI. Alkyl alcohols were purchased from Chemical Samples Co., Columbus, OH. Sodium chloride was obtained either from Fisher Scientific Co., Orlando, FL., or from Mallinckrodt Inc., St. Louis, MO. Double distilled water was used throughout the measurements. Sand, used as a porous medium, was supplied by AGSCO Corp., Paterson, NJ. The size distribution for the sand used was 45–142 micron with average particle size of 90 micron. The transducer used for the measurements of pressure across the porous medium was purchased from Validyne Engineering Corp., Northridge, CA. The recorder was a Heath/Schlumberger Model 225, Heath Co., Benton Harbor, MI. The water was pumped using Cheminert metering pump Model EMP-2, Laboratory Data Control, Riviera Beach, FL.

Selection of Surfactants

Mixed surfactant solutions of sodium dodecyl sulfate and dodecanol at 5 mM/l and 0.5 mM/l concentration respectively were employed in the present study. These molecules are tightly packed at the air-liquid interface and this packing can significantly alter the properties of foams (i.e., surface viscosity, bubble size and foam stability, etc.). A detailed discussion of this is given elsewhere (Sharma et al., 1982b). Foams prepared from mixed surfactants were studied at various temperatures exterior to porous media. The purpose of these experiments was to correlate the effects of the surface properties of surfactant solutions and the average bubble size on the behavior of a foam in a porous medium by measuring the breakthrough time and fluid displacement efficiency at breakthrough as a function of temperature.

Methods

Surface Tension. The surface tension of the freshly prepared solutions was measured with a Wilhelmy plate (Osipow, 1977) at various temperatures. The platinum plate was always cleaned and was exposed to the flame of a Bunsen burner before use.

Foaminess of the Surfactant Solutions. Surfactant solutions (50 ml) were placed in a glass cylinder [dia. 2 in. (51 mm) and height 18 in. (457 mm)] containing a sieve of 25–50 micron size at the bottom. The foams were produced by the injection of air at a constant pressure of 2 psig (13.8 kPa) for one minute from a compressed air cylinder. The volume of the foam generated was recorded at different temperatures.

Bubble Size. A rectangular plexiglass cell [2 in. × 2 in. × 1 in. (51 mm × 51 mm × 25 mm)] was used for measurement of bubble size. Surfactant solutions (10 ml) were placed in the cell. The foam was prepared by shaking the plexiglass cell for 2 minutes. Photomicrographs of the foams were taken with the help of a camera attached to a microscope. The average size of foam bubbles was determined from a size distribution analysis of the photomicrographs.

Fluid Displacement in Porous Media. The sandpacks used as porous media were flushed vertically with carbon dioxide for an hour to displace interstitial air. Distilled water was pumped into the porous medium to determine the pore volume (PV). Trapped gas bubbles in pores are easily eliminated because carbon dioxide is soluble in water. About five pore volumes of water were pumped through at various flow rates to wash out carbon dioxide as well as to determine the absolute permeability. After the porous medium was characterized, surfactant solutions of known surface properties were injected at constant flow rate. This injection of surfactant was followed by air flow. The pressure difference across the porous medium was measured using a pressure transducer and recorder. The transducer was calibrated before use with the help of a sensitive pressure gauge. The breakthrough time and fluid displacement efficiency were recorded at various temperatures.

RESULTS AND DISCUSSION

Surface Tension of Surfactant Solutions

Sodium dodecyl sulfate and dodecanol in a molar ratio of 10:1 were used as mixed surfactants. Figure 1 illustrates the variation in surface tension of the mixed surfactant solutions as a function of temperature. A decrease in surface tension was observed with increasing temperature. As the temperature is raised, the kinetic energy of the molecules increases, resulting in a decrease in attractive forces between the molecules which in turn reduces the surface tension of the surfactant solutions. A similar trend in variation of surface tension with temperature was observed in the presence of NaCl.

The behavior of mixed surfactant system ($C_{12}H_{25}SO_4Na$ + $C_{12}H_{25}OH$) is more complicated in the presence of brine. The addition of brine to the surfactant solutions results in an increase in surface tension as shown in Figure 1. This increase in surface tension is probably caused by the decrease in solubility of dodecanol in sodium dodecyl sulfate solution in the presence of brine. Klevens (1950) reported a marked decrease in the amount on n-octanol solubilized in potassium tetradecanoate solutions containing increasing amounts of potassium chloride. The concentration of the mixed surfactant solutions for these observations is well above the critical micelle concentration (CMC). It is recognized (Corrin and Harkins, 1947) that the addition of electrolytes or long chain alcohols lowers the CMC of ionic surfactants. If the effect of temperature is considered, the situation becomes much more complicated. In the absence of additives, the CMC of ionic surfactants generally increases with an increase in temperature (Ginn et al., 1960). In order to solubilize dodecanol in surfactant solutions, the concentration of surfactant used for foam generation was always above the CMC at all temperatures.

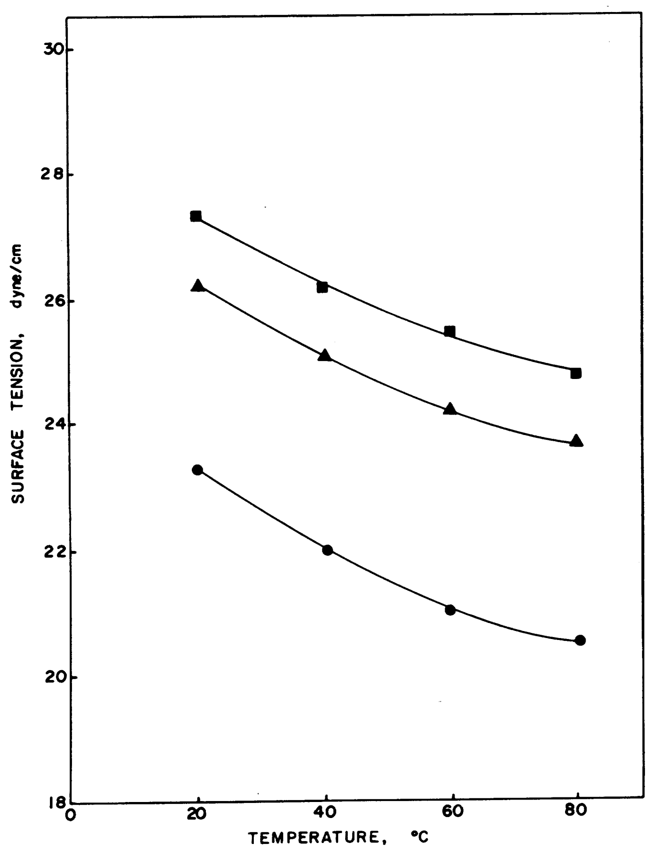

Figure 1. Effect of temperature on surface tension of surfactant solutions containing sodium dodecyl sulfate and dodecanol (5 mM:0.5 mM). (●) 0.0% NaCl (▲) 0.5% NaCl (■) 1.0% NaCl.

Foaminess of the Surfactant Solutions and Foam Stability

The ability of mixed surfactants to generate foam as a function of temperature was studied in the presence and in the absence of NaCl. The results obtained are shown in Figure 2. The foam-producing capacity of the surfactant solutions increased with increasing temperature. A steep increase in the maximum foam volume generated was observed up to 40°C. The maximum foam volume increased more gradually with further increases in temperature from 40 to 80°C.

The addition of brine to the mixed surfactant solution results in a slight decrease of the foam volume. The trend in the variation of the maximum foam volume with temperature was found to be the same in the presence or the absence of brine.

The foaminess of the surfactant solutions as a function of temperature can be correlated by the equation:

$$F = F_{20}e^{A(T-20)} \tag{1}$$

where A is a constant 1.6×10^{-3}), F is the foaminess of surfactant

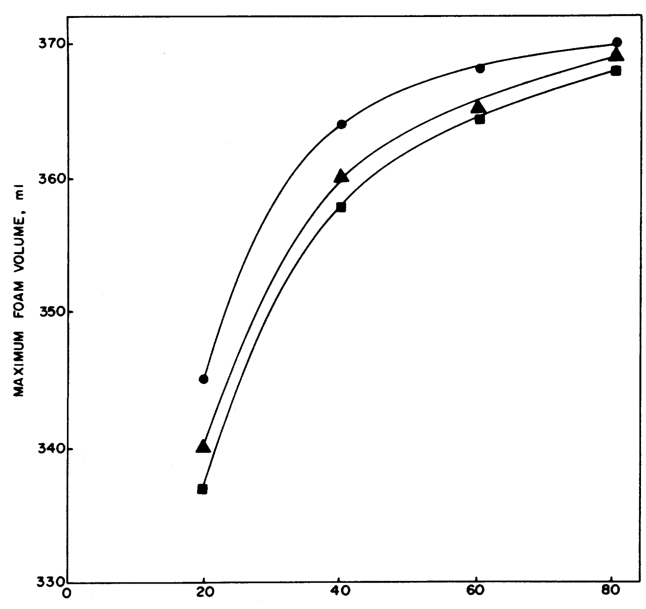

Figure 2. Effect of temperature on foaminess of solutions containing sodium dodecyl sulfate and dodecanol (5 mM:0.5 mM). (●) 0.0% NaCl (▲) 0.5% NaCl (■) 1.0% NaCl.

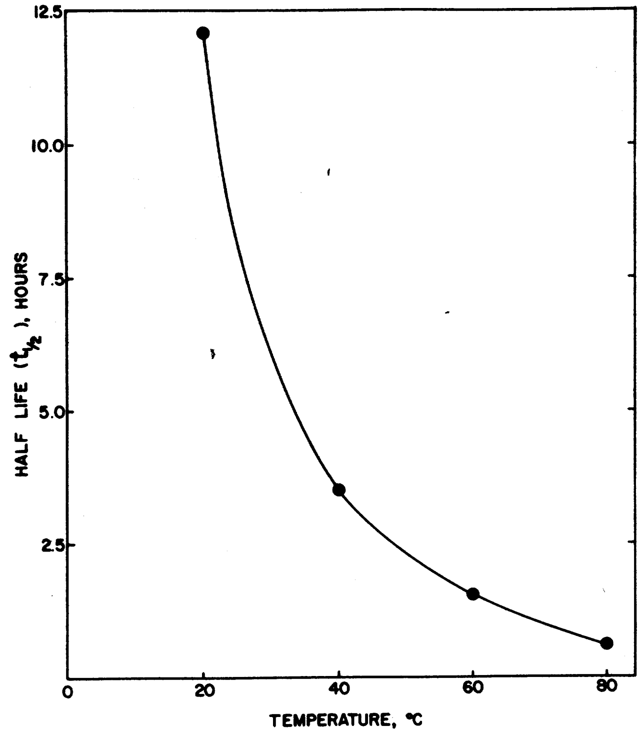

Figure 3. Effect of temperature on half life of foams containing sodium dodecyl sulfate and dodecanol (5 mM:0.5 mM).

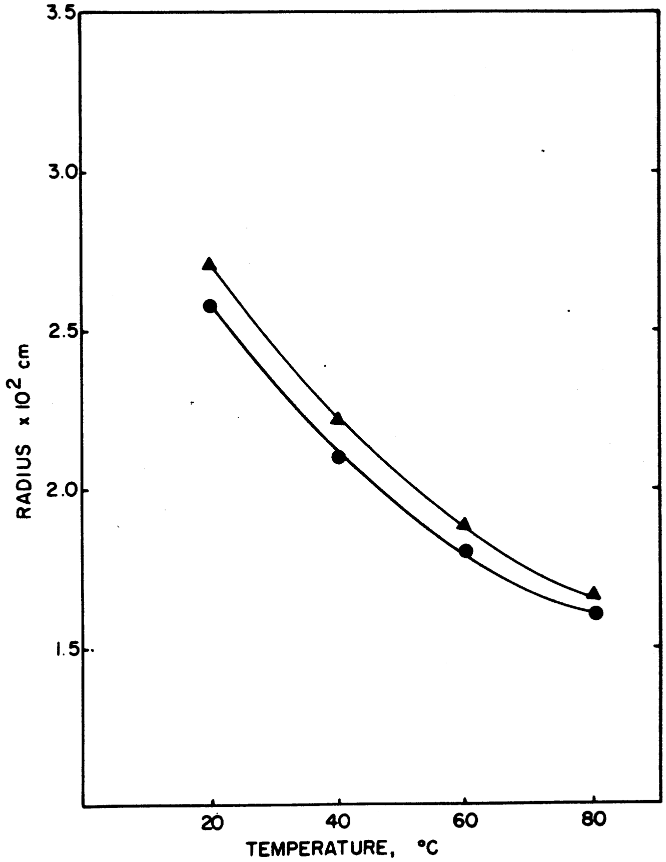

Figure 5. Effect of temperature on bubble size in foams containing sodium dodecyl sulfate and dodecanol (5 mM:0.5 mM). (●) 0.0% NaCl (▲) 0.5% NaCl.

solution at temperature T°C, and F_{20} is the foaminess at 20°C. The reproducibility of the data was within ±4.0%. Using Eq. 1, the foaminess of surfactant solutions can be evaluated at any desired temperature.

In order to delineate the effect of temperature on foam stability, the half-life ($t_{1/2}$) of foams was measured at various temperatures. Half-life is the time required to reduce foam volume to half of its initial value. Figure 3 illustrates the variation in half-life of foams as a function of temperature. In general, the half-life of foam decreased with increasing temperatures. A sharp decrease in foam half-life was observed in the temperature range of 20–40°C. With further increases in temperature, the half-life decreased gradually.

Average Size of Bubbles

Figure 4 presents the photomicrographs of foams at various temperatures. The bubble size decreases with increasing temperature. The change in radius of the bubbles as a function of temperature in the presence of 0.5% NaCl is illustrated in Figure 5. At a particular temperature, the bubble size increased slightly in the presence of brine.

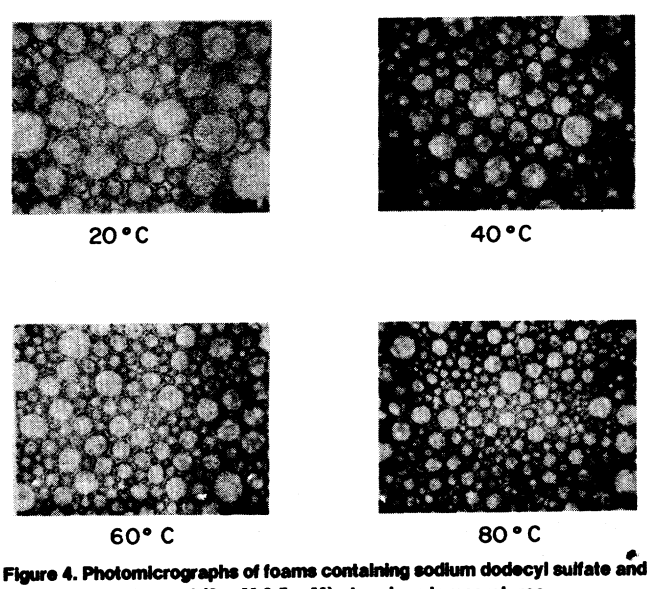

Figure 4. Photomicrographs of foams containing sodium dodecyl sulfate and dodecanol (5 mM:0.5 mM) at various temperatures.

The variation in bubble size as a function of time at various temperatures is shown in Figure 6. The standard deviations for the experimental data for bubble size at 20, 40, and 80°C are ±0.172, ±0.558, and ±2.425, respectively. The bubble size increases with elapsed time due to coalescence. It increases rapidly with time at higher temperatures. The surfactant solutions produced smaller bubbles initially at higher temperatures. In Figure 6, curves intersect each other at a particular elapsed time, which indicates that a specific time the surfactant solutions produce same size foam at various temperatures. In order to evaluate the size of foam bubbles, a quantitative correlation among bubble size, temperature, and time has been established:

$$r = (aT + b)t + (cT + d) \tag{2}$$

where r is the radius of foam bubbles; T is the temperature; t is the elapsed time and a, b, c, and d are the constants. The values of these constants are as follows:

$$a = 2.96 \times 10^{-5} \text{ cm/min °C}$$

$$b = -5.70 \times 10^{-4} \text{ cm/min}$$

$$c = -1.82 \times 10^{-4} \text{ cm/°C}$$

$$d = 3.14 \times 10^{-2} \text{ cm}$$

With these constants, the bubble size can be evaluated at any time at a particular temperature. The calculated data are in good agreement (within ±4%) with the experimental values of bubble size.

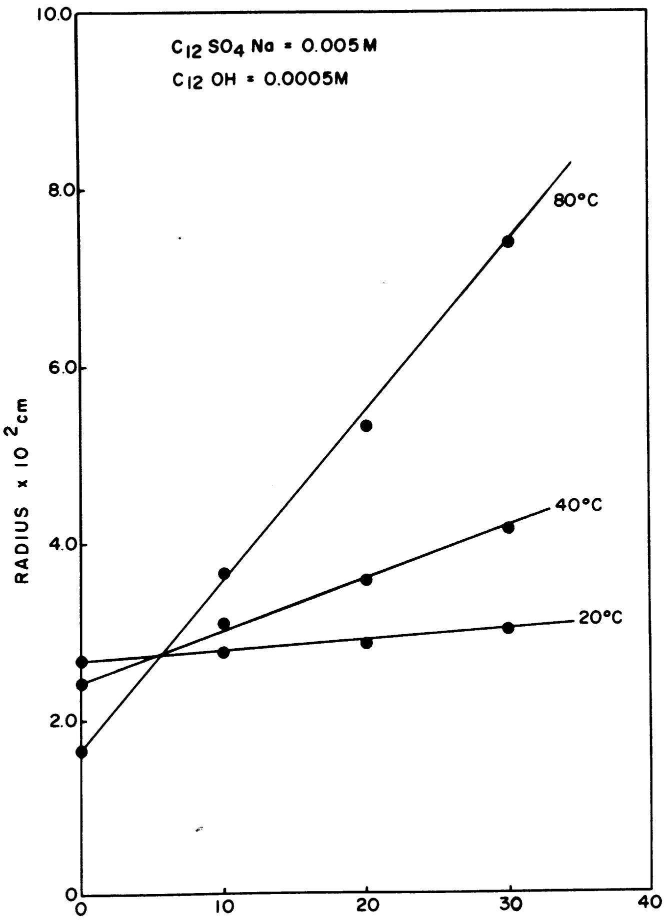

Figure 6. Bubble size as a function of time at different temperatures.

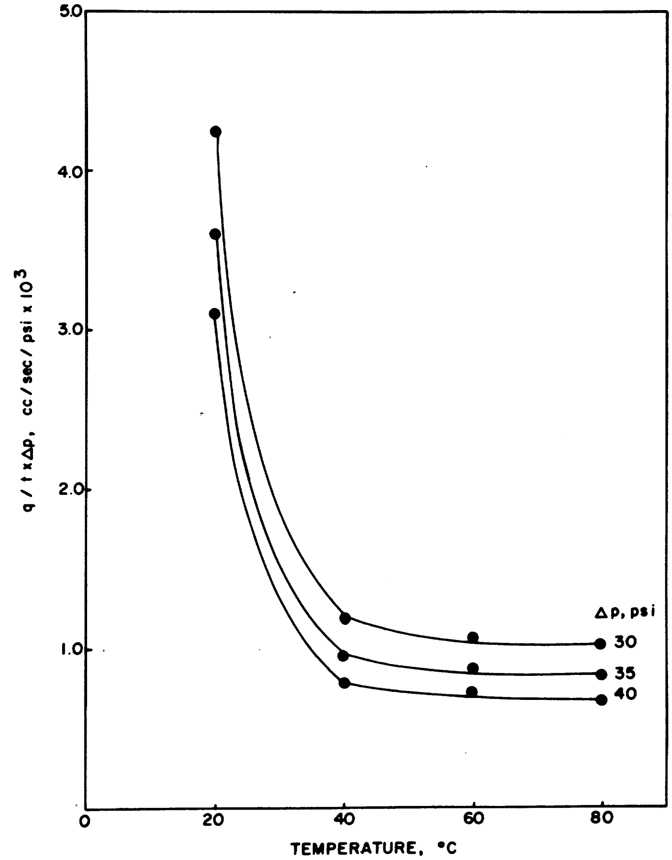

Figure 7. Effect of temperature on effective air mobility at various pressure drops (Δp).

Fluid Displacement In Porous Media

To correlate gas flow through porous media in the presence of surfactant solutions with the surface properties and microscopic characteristics of foams, the breakthrough time and fluid displacement efficiency at breakthrough were measured. In order to be consistent in the interpretation of the results, the flow of injected air in the porous media has been treated according to Darcy's law. Darcy's law for a gas phase flowing in a linear system gives (Craft and Hawkins; 1959):

$$q_{sc} = \frac{T_{sc} \times A_c \times K_g \times (p_1^2 - p_2^2)}{2\,P_{sc} \times T \times Z \times \mu_g \times \Delta L} \tag{3}$$

where q_{sc} is the constant gas flow rate measured at some standard absolute pressure (p_{sc}) and temperature (T_{sc}), K_g is the effective gas permeability, μ_g is the gas viscosity, T is the temperature, A_c 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 displacement experiments were conducted at constant temperature and downstream pressure (p_2) was atmospheric pressure. The pressure drops across the porous media were always less than 50 psi (344.5 kPa), so the gas deviation factor (Z) was neglected. Cumulative volume (q) of the fluid collected at gas breakthrough time (t_b) was measured at room temperature and atmospheric pressure. Therefore, the flow rate term q_{sc} (Eq. 3) can be replaced by the term q/t_b, which represents an average flow rate during an experiment until injected gas breakthrough. Equation 3 can be rewritten as follows:

$$q/t_b = \frac{K_g \times A_c \times \Delta(p^2)}{\mu_g \times \Delta L} \tag{4}$$

where

$$\Delta(p^2) = \left[\frac{p_1^2 - p_2^2}{2\,p_{sc}}\right]$$

Equation 4 can be rearranged for analysis and interpretation of results in terms of effective gas mobility in a porous medium:

$$\text{Effective Gas Mobility } (K_g/\mu_g) = \frac{q \times \Delta L}{t_b \times A_c \times \Delta(p^2)} \tag{5}$$

The flow cross-sectional area (A_c) and length of the porous media (ΔL) were kept constant in all displacement experiments. In order to correlate surface and microscopic properties of surfactants with flow through porous media behavior, surfactant solutions of known surface properties were used. Figure 7 illustrates the effective air mobility as a function of temperature at various pressure drops (Δp). The effective air mobility in the presence of surfactant solutions decreased with increasing temperature. However, a sharp reduction in effective air mobility was observed in the temperature range 20–40°C, whereas the effective mobility decreased gradually beyond 40°C. The trend in the variation of effective mobility versus temperature was same for different pressure drops (Δp).

The effect of pressure gradient ($\Delta p/\Delta L$) on effective air mobility at various temperatures is shown in Figure 8. The effective air mobility, in general, decreased with increasing pressure gradient ($\Delta p/\Delta L$). With an increase in pressure drop, the amount as well as structure of the foam generated *in situ* probably changes, which in turn reduces effective air mobility. A large reduction in effective air mobility was observed with an increase in pressure gradient at 20°C. Moreover, effective air mobility decreased only gradually with pressure gradient beyond 40°C. At a particular pressure gradient [45 psi/ft (1 MPa/m)] effective air mobility reduced nearly fourfold in the temperature range 20–40°C, while only a slight decrease in effective mobility was observed beyond 40°C. These results are in agreement with previous findings (Sharma et al., 1983c). Elson and Marsden (1978) measured the flow rate of gas in the presence of various commercial surfactants. At temperatures of 100°C and higher, injection of surfactant solution into

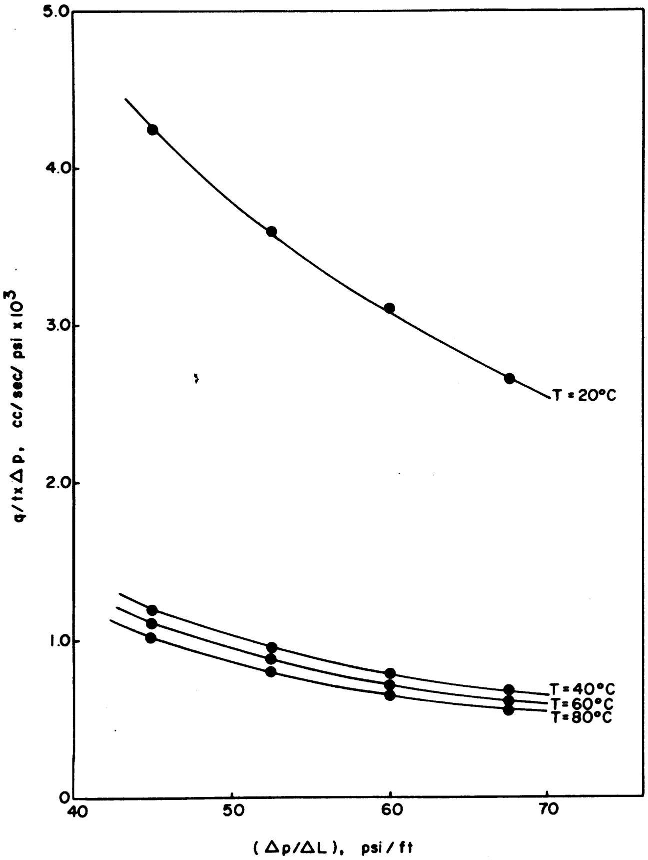

Figure 8. Effect of pressure gradient ($\Delta p/\Delta L$) on effective air mobility at various temperatures.

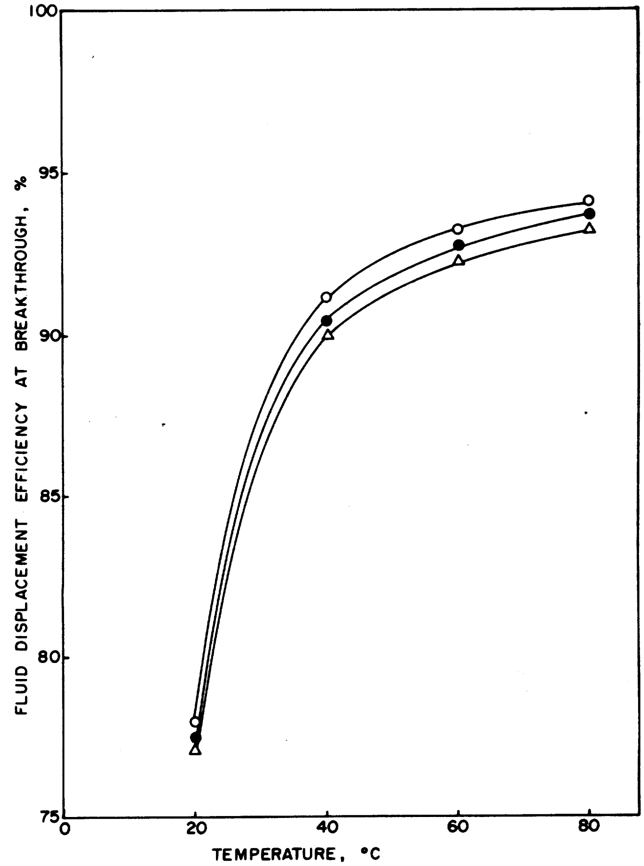

Figure 9. Effect of temperature on fluid displacement efficiency in sandpacks containing sodium dodecyl sulfate plus dodecanol (5 mM:0.5 mM) solution. (○) 0.0% NaCl (●) 0.5% NaCl (△) 1.0% NaCl.

unconsolidated porous media decreased gas flow much more than simply injection of water. The effectiveness of surfactant solutions to reduce gas flow rate decreased with elapsed time but can be renewed by injection of more surfactant solution. These observations are consistent with our results on effective air mobility in porous media.

Figure 9 delineates the effect of temperature on fluid displacement efficiency at breakthrough in the presence and in the absence of brine. A pressure drop of 45 psi (310 kPa) was used for the fluid recovery measurements. The fluid displacement efficiency at breakthrough increased with temperature. A steep increase in fluid recovery was observed in the temperature range 20–40°C. The fluid displacement efficiency at breakthrough increased gradually beyond 40°C. The presence of 0.5 and 1.0 NaCl slightly reduced fluid recovery at breakthrough at various temperatures.

A quantitative correlation (Eq. 6) between the fluid displacement efficiency and temperature can be expressed as:

$$E = E_{20} - e^{B(T-20)} \tag{6}$$

where B is a constant equal to 4.0×10^{-3}, E is the fluid displacement efficiency at temperature T°C, and E_{20} is the displacement efficiency at 20°C. In order to correlate the foaminess of surfactant solutions with the fluid displacement efficiency in porous media, Eqs. 1 and 6 can be expressed as follows:

$$\ln E = 2.5 \ln F + C \tag{7}$$

where

$$C = \ln E_{20} - 2.5 \ln F_{20} \tag{8}$$

The value of C decreases with increasing concentration of sodium chloride in the system. The variation in C as a function of sodium chloride concentration is given in Table 1. The results are reproducible within ±4%.

The comparison of these results with the foaminess of surfactant solutions (Eq. 7 and Figure 2) shows that the ability of the surfactants to produce *in situ* foam is one of the important factors in the displacement of fluid in a porous medium. Moreover, the stability of a foam is not required for efficient fluid displacement or for a decrease in the effective air mobility in a porous medium. It is concluded that the effectiveness of foam in displacing fluid in porous media and reducing air mobility increases with increasing temperature.

TABLE 1. VALUES OF CONSTANT C AT VARIOUS CONCENTRATIONS OF NaCl

NaCl *Concentration*, %	C
0.0	−10.252
0.5	−10.222
1.0	−10.218

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NOTATION

a,b,c,d = constants
A,B,C = constants
A_c = cross-sectional area of porous medium
E = fluid displacement efficiency at T°C
E_{20} = fluid displacement efficiency at 20°C

F = foaminess of surfactant solutions at $T°C$
F_{20} = foaminess of surfactant solutions at 20°C
K_g = effective gas permeability
ΔL = length of porous media
p_1 = upstream pressure
p_2 = downstream pressure
p_{sc} = standard absolute pressure
q = cumulative volume of fluid collected at gas breakthrough time
q_{sc} = gas flow rate
r = bubble radius
t = time
t_b = breakthrough time
T = temperature
T_{sc} = standard absolute temperature
Z = gas deviation factor
μ_g = gas viscosity

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