Mobility Control in the Displacement of Residual Oil by an Unstable Foam

A qualitative analysis is developed for the displacement of an unstable foam in a porous structure. The effects of the magnitude of the London-van der Waals forces, of the surface tension, of the surface viscosities, of the quality (volume fraction of the gas), of the bubble size, and of the viscosity of the foaming agent solution are investigated. A number of qualitative conclusions are drawn regarding three aspects of mobility control: distribution of bypassed oil, speed of displacement, and displacement efficiency.

Ideally, any change in formulation should increase both the speed of displacement and the displacement efficiency. This is possible only by decreasing the surface viscosities. With all of the other variables, whenever either the speed of displacement or the displacement efficiency is increased, the other is decreased. Whether both the speed of displacement and the displacement efficiency actually increase on reducing the surface viscosities depends on whether the effects of the surface viscosities are dominant.

PIL-SOO HAHN,
T. R. RAMAMOHAN,
and J. C. SLATTERY
Department of Chemical Engineering
Northwestern University
Evanston, IL 60201

SCOPE

The displacement of crude oil by carbon dioxide or steam is unstable. The gas will finger ahead through the oil, bypassing larger portions of it, which means that the mobility (ratio of permeability to viscosity) of the gas is much larger than that of the liquid. It may be possible to control the mobility of the gas by introducing it as a foam.

The void volume in a permeable rock, such as that in which oil is found, is composed of many intersecting irregular pores, the mean diameter of which may be on the order of 20 μ (Batra and Dullien, 1973). It is unlikely that, within such a small-scale pore network, a foam has the same ordered structure of thin films intersecting in plateau borders that we observe when the same liquid and gas are shaken together in a graduate cylinder. Within the pore network, the aqueous surfactant solution from which the foam is formed is likely to be dispersed in the form of thin films separating bubbles of gas. This conception of the foam structure is supported by Mast's (1972) observations.

Consider two neighboring pore networks having different mean pore radii that offer parallel paths for displacement. If the oil is displaced by the foam more rapidly in the network having the smaller mean pore radius, a portion of the oil in the network having the larger mean pore radius will be bypassed and lost. We can improve the displacement efficiency of a foam to the extent that we can cause the foam to move through all portions of the network with the same rate of displacement.

It is easier to discuss this mechanism on a smaller scale. Figure 1 shows a pore that bifurcates to form two pores of unequal diameters that rejoin downstream. For an efficient process, we must be able to displace the foam through both the large and the small pores. If the foam moves through the large pore more rapidly, residual oil will tend to be trapped in the small pore; if the foam moves through the small pore more rapidly, oil will be bypassed in the large pore. We can improve both the local and the sweep efficiencies of a foam displacement to the extent that we can cause the foam to move through large and small pores at nearly the same rate.

We must distinguish between stable and unstable foams. Mast (1972) observed that, in an unstable foam, liquid and gas are transported through the progressive rupture and regeneration of the foam structure. In a stable foam, the liquid and gas are displaced as a body.

Holm (1968) suggested that foams capable of displacement in porous media are unstable in the sense defined here. This was supported by Slattery's (1979) analysis of displacement of stable forms, which showed that there is a critical surface tension above which the foam cannot move. For most foams, the surface tension is considerably larger than this critical value.

Our objective is to develop a qualitative analysis for the displacement of an unstable foam in a porous structure. This will form the basis for a discussion of two aspects of mobility control using unstable foams: speed of displacement and displacement efficiency. Although the assumptions are quite different, this qualitative analysis takes the same form as those used previously in discussing interfacial effects during the entrapment and displacement of residual oil (Slattery, 1974) and during the displacement of residual oil by stable foams (Slattery, 1979). The effects of the surface viscosities on displacement first suggested by Slattery (1974) have now been confirmed both by a quantitative analysis (Giordano and Slattery, 1983) and by an experimental study (Stoodt and Slattery, 1984), which may lend some further confidence to the results that follow.

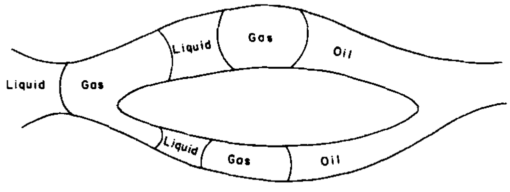

Figure 1. Foam displacing oil from bifurcated pore.

CONCLUSIONS AND SIGNIFICANCE

An unstable foam will preferentially displace through an intermediate range of pore sizes, bypassing any residual oil present both in the larger pores and in those pores whose diameter is less than the critical diameter required for foam formation.

The speed of displacement of an unstable foam will be enhanced by making it less stable (increasing the magnitude of the negative disjoining pressure attributable to London-van der Waals forces), increasing the surface tension, decreasing the surface viscosities, increasing its quality (volume fraction of gas), increasing the bubble size, and decreasing the viscosity of the foaming agent solution. Naturally, there is a maximum quality consistent with the existence of a foam.

The displacement efficiency of an unstable foam will be enhanced by making it more stable (reducing the magnitude of the negative disjoining pressure attributable to the London-van der Waals forces), decreasing the surface tension, decreasing the surface viscosities, decreasing its quality, decreasing the bubble size, and increasing the viscosity of the foaming agent solution. But note that there are both a minimum quality and a minimum bubble size below which unstable foams are not formed.

The ideal objective would be to increase both the speed of displacement of an unstable foam as well as its displacement efficiency. This is possible only by decreasing the surface viscosities. With all of the other variables, whenever either the speed of displacement or the displacement efficiency is increased, the other is decreased. This means that a more efficient recovery will in general be slower.

Whether one alters the concentration of the existing surfactant or introduces a new surfactant, it is nearly impossible to reduce the surface viscosities without also changing other physical properties such as the surface tension. For example, if the surface tension is increased, the displacement efficiency will tend to decrease; if the surface tension is decreased, the speed of displacement will tend to decrease. If both the speed of displacement and the displacement efficiency are to increase as the surface viscosities are reduced, the effects of the surface viscosities must be dominant. The question as to whether they will be dominant in any given situation is beyond the scope of this discussion. It can be answered only by a quantitative analysis.

STATEMENT OF PROBLEM

Mast (1972) observed that, in an unstable foam, liquid and gas are transported through the progressive rupture and regeneration of the foam structure. In a stable foam, the liquid and gas are displaced as a body. Holm (1968) suggested that foams capable of displacement in porous media are unstable.

Motivated by Mast's (1972) observations and Holm's (1968) suggestion, we make the following assumptions about the manner in which an unstable foam is driven by a pressure gradient through the single pore shown in Figure 2.

The gas segments shown in Figure 2 do not wet the pore walls; they are separated from the pore walls by a continuous coating of the aqueous surfactant solution that completely wets the pore wall. Most of the aqueous surfactant solution from which the foam is formed is found in a series of thin films stretching across the pore; only a small amount is retained in the continuous coating on the pore wall. As a result of the pressure drop across the pore, each gas segment in the pore is at a different pressure, although the pressure within each segment is nearly uniform.

Once a thin film is formed, it drains under the influence of the pressure drop across it as well as London-van der Waals forces, until it becomes unstable and ruptures. When a film ruptures, the pressure drop across the pore is no longer balanced, which forces the remaining structure of thin liquid films and gas segments to advance, until a new film is formed and the pressure drop is once again balanced. This process of films rupturing and reforming is continually repeated as the foam is displaced through the pore. We assume in the analyses to follow that the rate-controlling step in this process is the time for an individual film to drain and rupture.

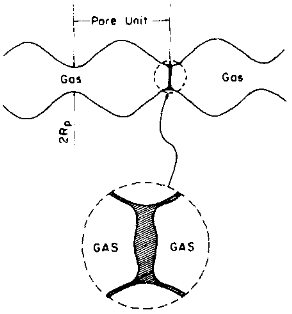

Figure 2. Segment of pore containing bubbles of gas separated by a liquid film.

We wish to emphasize that the phase interfaces which separate the liquid films from the gas segments in Figure 2 do not intersect the pore wall to form three-phase lines of contact. If they did, the liquid films would not be able to drain under the influence of the pressure drop across them and the London-van der Waals forces. In contrast, we do believe that the gas segments in stable foams wet the pore walls and that in these cases the phase interfaces that separate the liquid films from the gas segments do intersect the pore wall to form three-phase lines of contact (Slattery, 1979).

Our objective is to develop three qualitative analyses for the displacement of an unstable foam in a single pore. These will form the basis for a discussion of three aspects of mobility control in porous media using unstable foams: distribution of bypassed oil, speed of displacement, and displacement efficiency. The first analysis is relatively simple to use and it is sufficient for understanding the effects of the London-van der Waals forces, of interfacial tension, of bubble size, and of the viscosity of the foaming agent solution. Analysis II will be employed to enhance our understanding of the distribution of bypassed oil and to examine the effects of foam quality; analysis III, to consider the effects of the surface viscosities.

ANALYSIS I

Within these thin, draining, liquid films, the mutual force per unit mass $\boldsymbol{b}_m$ known as the London-van der Waals force, is representable in terms of a scalar potential φ:

$$\boldsymbol{b}_m = -\nabla\varphi \tag{1}$$

At a planar fluid-fluid interface (Ruckenstein and Jain, 1974)

$$\rho\varphi \doteq \rho\varphi_0 = \Phi_B + B/h^m \tag{2}$$

where ρ is the mass density of the liquid film and Φ_B is the interaction potential per unit volume of a semifinite film liquid in the limit as the fluid-fluid interface is approached. We speak of

$$\Pi \equiv -\frac{B}{h^m} \tag{3}$$

as the disjoining pressure of a flat film of thickness h. When B is positive, the interaction potential per unit volume of the film liquid at the interface is larger than it would be if this phase were semi-infinite. This corresponds to a negative disjoining pressure that acts to attract the two fluid-fluid interfaces. When the film thickness is less than 120 Å, $m = 3$ and $|B| \sim 10^{-21}$ J; when the film thickness is larger than 400 Å, $m = 4$ and $|B| \sim 10^{-28}$ J·m (Churaev, 1974a,b).

When a small gas bubble is driven through a continuous liquid phase to a liquid-gas interface, a thin liquid film is created between them and drains until an instability forms and coalescence occurs. Lin and Slattery (1982) developed a hydrodynamic theory for the first portion of this coalescence process: the drainage of the thin film while it is still sufficiently thick that the effects of London-van der Waals forces and electrostatic forces can be ignored. In developing this theory, they assumed that the phase interfaces bounding the film were immobile. An immobile interface is one in which either the surface tension gradient or the surface viscosities are sufficiently large that the tangential component of velocity is zero and lateral motion is precluded. A mobile interface is one in which surface tension is independent of position and the surface viscosities are identically zero.

Chen et al. (1984) and Hahn et al. (1985) have extended this theory for small bubbles or drops to include the effects of the London-van der Waals forces corresponding to a negative disjoining pressure, although they neglect the influence of any electrostatic forces. In aqueous films that are thinner than the electrostatic double layer, the disjoining pressure will have a positive component that acts to repel the two interfaces bounding the film. Depending on its strength relative to the London-van der Waals forces, it may play an important role in determining the stability of the film. Because the dependence of film thickness on radial position within the film is weak, they assumed that the local value of the interaction energy per unit volume of the film liquid at the liquid-gas interfaces is given by Eq. 2.

Since the critical film thicknesses measured or predicted by Allan et al. (1961), MacKay and Mason (1963), Vrij (1966), Ivanov et al. (1970), Burrill and Woods (1973), and Chen et al. (1984) are normally larger than 120 Å, Hahn et al. (1985) recommend $m = 4$ in Eq. 2. Because the results of Hahn et al. (1985) and of Chen et al. (1984) for $m = 4$ are qualitatively similar, we will adopt the latter whose form is more convenient for our present purposes.

For the case corresponding to $m = 4$ in Eq. 2, Chen et al. (1984) found that the coalescence time t_c (the elapsed time between the formation of a film and its rupture) can be expressed as

$$t_c = 0.446\,\tau_{(4)} \tag{4}$$

where

$$\tau_{(4)} = 2.02\mu R_b B^{-2/5}(R^2/\gamma)^{3/5} \tag{5}$$

μ is the viscosity of the film liquid, γ the surface tension, R_b the radius of the bubble, and R the radius of the dimpled film. In deriving Eq. 4, Chen et al. (1984) have neglected the short time required for the formation of the film (Marrucci, 1969).

The rupture of a thin film and coalescence of two gas bubbles in Figure 2 is not the same as the coalescence of a gas bubble at an extended gas-liquid interface. But we will assume here that these problems are qualitatively similar. This will be sufficient, since our intention is to develop a qualitative rather than quantitative analysis of displacement in a single capillary.

In general, we can expect the rim radius R to be proportional to the force driving the coalescence process (Lin and Slattery, 1982). In this case, the driving force is proportional to the macroscopic pressure gradient. We will assume that this pressure gradient and the individual bubble volumes are sufficiently large that

$$R \sim R_p \tag{6}$$

$$R_b \sim R_p \tag{7}$$

where R_p is the pore throat radius. Note that, when Eq. 4 is applied to the confined film shown in Figure 2, R_b should be interpreted as an effective bubble radius.

Our conception is that, every time a liquid film in Figure 2 ruptures, all remaining films advance a distance proportional to the distance between neighboring films, nL^*R_p. Here n is the total number of pore units divided by the number of liquid films and L^* is the ratio of the length of the pore unit shown in Figure 2 to R_p. This implies that the speed of displacement v of an unstable foam within a single pore is proportional to this distance divided by the lifetime of a single film:

$$v \sim nL^*R_p/t_c \tag{8}$$

In view of Eqs. 4 through 7, this becomes

$$v = \frac{k_1 n \gamma^{3/5} B^{2/5}}{\mu R_p^{6/5}} \tag{9}$$

where k_1 is a proportionality factor that depends primarily on the geometry.

ANALYSIS II

The above analysis can be revised to include the effects of foam quality, the volume fraction of gas in the foam.

Let us assume that the volume fraction f of liquid in the foam is proportional to the volume of liquid in an individual film divided by the total volume of liquid and gas in the pore associated with a single draining liquid film:

$$f \sim \frac{\pi R_p^2 h_0}{nV} = \frac{\pi h_0}{nR_pV^*} \tag{10}$$

With reference to Figure 2, V is the volume of a pore unit and

$$V^* \equiv V/R_p^3 \tag{11}$$

is a function only of pore geometry. We will identify this average film thickness h_0 as the initial thickness of a draining liquid film at the rim.

Equation 4 does not recognize the initial thickness of the draining liquid film. Experimentally we know that, as a bubble approaches an interface, a thin dimpled film is formed very rapidly (Marrucci, 1969). In deriving Eq. 4, it was assumed that the thin film began forming when the bubble was very far away from the liquid-gas interface. Equivalently, Eq. 4 can be said to include the negligible time required to form a thin dimpled film.

It is possible, but awkward, to modify Eq. 4 to take into account the initial film thickness. It is more convenient to use the qualitatively similar results that Chen et al. (1984) have derived for the case $m = 3$ in Eq. 2.

For the case corresponding to $m = 3$, Chen et al. (1984) found that the film thickness h at the rim can be expressed as a function of time t by

$$t = t_f - \frac{\tau_{(3)}}{2}\tan^{-1}[(h/a)^2] \tag{12}$$

in which

$$\tau_{(3)} \equiv 2.22\mu R_b R(\gamma B)^{-1/2} \tag{13}$$

$$a \equiv 1.055(BR^2/\gamma)^{1/4} \tag{14}$$

and t_f is the time for h to approach zero in the absence of any instabilities. Allowing for the development of an instability, they concluded

$$\begin{aligned} t_c &= t_f - \frac{\tau_{(3)}}{2}\tan^{-1}(3^{-1/2}) \\ &= \left[\frac{\pi}{4} - \frac{1}{2}\tan^{-1}(3^{-1/2})\right]\tau_{(3)} \\ &= 0.523\tau_{(3)} \end{aligned} \tag{15}$$

Referring to Eq. 12, we can identify

$$t_0 = t_f - \frac{\tau_{(3)}}{2}\tan^{-1}[(h_0/a)^2] \tag{16}$$

as the time at which the draining liquid film is first formed. It follows from Eqs. 15 and 16 that

$$t_c - t_0 = \frac{\mathcal{T}(3)}{2}\{\tan^{-1}[(h_0/a)^2] - \tan^{-1}(3^{-1/2})\}$$

$$= \frac{\mathcal{T}(3)}{2}\{\tan^{-1}[(h_0/a)^2] - 0.523\} \tag{17}$$

is the elapsed time between film formation and rupture.

In place of Eq. 8, we now have

$$v \sim \frac{nL^* R_p}{t_c - t_0} \tag{18}$$

We see from Eqs. 6, 7, and 17 that

$$v = \frac{k_2 n}{\mu R_p}(\gamma B)^{1/2}\{\tan^{-1}[(h_0/a)^2] - 0.523\}^{-1} \tag{19}$$

in which h_0 should be interpreted in terms of the volume fraction f of liquid in the foam or the foam quality $(1 - f)$ and k_2 is a proportionality factor that will be a function primarily of the geometry.

Notice, in order that v be positive and finite, we must require

$$\frac{h_0}{a} = k_3 n R_p^{1/2} f \left(\frac{\gamma}{B}\right)^{1/4} > 3^{-1/4} \tag{20}$$

in which k_3 is another proportionality factor. As we consider the implications of this relationship, it will be helpful to keep in mind that n, the total number of pore units divided by the number of liquid films, is proportional to the average volume of a single bubble.

ANALYSIS III

The theories of Lin and Slattery (1982), of Chen et al. (1984), and of Hahn et al. (1985) assumed that the interfaces bounding the draining film were immobile. Hahn and Slattery (1985) extended these theories for small bubbles or drops to include the effects of the surface viscosities and to consider the case of partially mobile interfaces, but they continued to neglect the influence of any electrostatic forces. They argued that the rate of thinning of the liquid film is sufficiently small that the surfactant concentration in each of the dividing surfaces bounding the film may be considered to be nearly independent of position. For this reason, they neglected the effect of the surface tension gradient with respect to the effect of the surface viscosities in the jump momentum balance or the force balance at each of the interfaces bounding the film. Employing a modification of the development by Barber and Hartland (1976; Flumerfelt et al., 1982) for a draining film bounded by parallel planes, they concluded that

$$t_c = 0.784 \mu R^2 t_c^* \left(\frac{R_b}{\gamma B}\right)^{1/2} \tag{21}$$

Here

$$t_c^* = \left\{\frac{1}{2}\left[\tanh(\log_{10}\alpha^{1/4} + 0.8902) + 1\right]\right\}^{1.045} \tag{22}$$

$$\alpha^{1/4} = \frac{(\kappa + \epsilon)}{6\mu R^2}\left(\frac{B R_b}{\gamma}\right)^{1/4} \tag{23}$$

κ is the surface dilatational viscosity and ϵ the surface shear viscosity. [In writing Eqs. 21 and 23, we have used Eq. 26 of Hahn and Slattery (1985) to eliminate $\Delta\rho g$ from their Eqs. 28 and 30.]

Equation 21 predicts that $t_c \rightarrow 0$ as $\alpha^{1/4} \rightarrow 0$ or as $(\kappa + \epsilon) \rightarrow 0$. This is a physically incorrect result, outside the range of validity for the computation of Hahn and Slattery (1985) for several reasons. As $t_c \rightarrow 0$, inertial effects become important, but these were neglected in their computation. Their argument assumes that the motion is sufficiently slow that the surface concentration of surfactant is nearly independent of position in the phase interfaces. This would certainly not be true as $t_c \rightarrow 0$. Finally, as $(\kappa + \epsilon) \rightarrow 0$, it would no longer be reasonable to neglect the effects of the surface tension gradient in the jump momentum balance.

Recognizing Eqs. 6 through 8 and 21, we can write still another alternative expression for the speed of displacement in a single pore:

$$v = \frac{k_4 n}{\mu R_p^{3/2} t_c^*}(\gamma B)^{1/2} \tag{24}$$

Here k_4 is a proportionality factor that can be expected to be a function primarily of the geometry, and Eq. 23 takes the revised form

$$\alpha^{1/4} = \frac{(\kappa + \epsilon)}{6\mu R_p^{7/4}}\left(\frac{B}{\gamma}\right)^{1/4} \tag{25}$$

DISTRIBUTION OF BYPASSED OIL

Inequality 20 says that the initial film thickness must be greater than the critical thickness at which the film becomes unstable and rupture occurs. It will always be satisfied, if a foam is formed. If the expected initial film thickness is smaller than the critical film thickness for a given pore, a foam will not be formed in this pore. This implies that

1. For a given physical system, foam quality $(1 - f)$, and bubble size, there is a minimum pore size, below which unstable foams are not formed and any residual oil present would be bypassed.

This is consistent with the observations of Mast (1972) that foam films are preferentially formed in the larger pores.

From Eq. 9 of Analysis I, we have

$$\frac{\partial v}{\partial R_p} = -\frac{6}{5}\frac{v}{R_p} \leqq 0 \tag{26}$$

Since this derivative is negative, the speed of displacement of a foam is smaller in larger pores than it is in smaller pores and

2. An unstable foam will preferentially displace through the smaller pores in which it can be formed, bypassing any residual oil present in the larger pores and in those pores whose diameter is less than the critical diameter required for foam formation.

Note Eq. 9 and this conclusion assume that the interfaces bounding a draining film are immobile.

Starting with Eq. 19, we reach the same conclusion.

If Eq. 24 is employed in order to take into account the effects of the surface viscosities, we find in apparent contrast with Eq. 26

$$\text{for } \log_{10}\alpha^{1/4} < -2.3\text{: } \frac{\partial v}{\partial R_p} > 0 \tag{27}$$

$$\text{for } \log_{10}\alpha^{1/4} \geqq -2.3\text{: } \frac{\partial v}{\partial R_p} \leqq 0 \tag{28}$$

But we believe that Eq. 27 can be ignored for two reasons. First, the restriction on $\alpha^{1/4}$ probably places it outside the range of validity for Eqs. 21 and 24 as explained in Analysis III. Second, we can estimate that, in order for Eq. 27 to apply, $(\kappa + \epsilon) < 10^{-3}$ mN s/m [assuming μ = 1 mN·s/m^2, R_P = 20 μm, γ = 60 mN/m, B = 10^{-28} J·m]. This would be in the lower range of what could be reasonably expected in a system containing one or more surfactants, since experience suggests that $\kappa \sim 10^2\epsilon$ (Stoodt and Slattery, 1984) and $\epsilon > 10^{-5}$ mN·s/m for such systems.

Conclusion 2 appears to be confirmed by Bernard and Holm (1964), who found that foam reduced the permeability of loose sand to a greater extent than that of tight sand. It appears to explain also why relatively stable foams have been recommended as blocking agents to seal leaks in gas storage reservoirs (Bernard and Holm, 1970; Albrecht and Marsden, 1970) and to reduce the flow through high permeability zones in heterogeneous reservoirs (Holm, 1970).

These observations are also consistent with the conclusions drawn by Slattery (1979) for the limiting case of stable foams. His analysis showed that there is a critical surface tension above which a stable foam cannot move. For most porous media, the surface tensions of commonly used, relatively stable foams will be above this critical value, which suggests that they be employed as blocking agents. If the surface tension of a stable foam were to be below this critical value, it would displace by a mechanism different than that described here, preferentially moving through the larger pores.

In order to improve the displacement efficiency of an unstable foam, we ust reduce $|\partial v/\partial R_p|$, forcing the foam to move through the large and small pores at more nearly the same speed. In what follows, we ask how various parameters affect $|\partial v/\partial R_p|$.

EFFECT OF LONDON-VAN DER WAALS FORCES

Differentiating Eq. 9, we find

$$\frac{\partial v}{\partial B} = \frac{2}{5}\frac{v}{B} \geqq 0 \tag{29}$$

Here we have recognized that we are considering the case of a negative disjoining pressure, which corresponds to a positive value of B in Eq. 2. Since this derivative is positive, we conclude:

3. The speed of displacement of an unstable foam will be enhanced by making it less stable or by increasing the magnitude of the negative disjoining pressure attributable to London-van der Waals forces.

Differentiating either Eq. 19 or Eq. 24 yields the same qualitative result.

In order to determine the effect upon displacement efficiency, consider in the context of Eq. 9

$$\frac{\partial}{\partial B}\left|\frac{\partial v}{\partial R_p}\right| = \frac{12}{25}\frac{v}{R_p B} \geqq 0 \tag{30}$$

Our goal should be to have the speed of displacement of an unstable foam be nearly the same in all pores or $|\partial v/\partial R_p|$ as small as possible. This implies

4. The displacement efficiency of an unstable foam will be enhanced by making it more stable or by reducing the magnitude of the negative disjoining pressure attributable to London-van der Waals forces.

Starting from Eq. 19, we reach the same conclusion. With Eq. 24, we find a narrow band ($-2.60 < \log_{10}\alpha^{1/4} < -2.30$) in which this trend is reversed. As explained in the previous section, this band probably has no practical significance.

There are no experimental data available with which to test these conclusions.

EFFECT OF SURFACE TENSION

We find by differentiating Eq. 9 that

$$\frac{\partial v}{\partial \gamma} = \frac{3}{5}\frac{v}{\gamma} \geqq 0 \tag{31}$$

which suggests

5. The speed of displacement of an unstable foam increases as the surface tension increases.

Starting with Eq. 24 yields the same result. Although there is a value of $h_0/a = 1.22$ below which Eq. 19 predicts that $\partial v/\partial \gamma$ will be negative, this initial film thickness is approaching the critical thickness $h_c = 0.760a$ at which the film becomes unstable and ruptures. While this does not violate Eq. 20, it is inconsistent with the more detailed computations of Hahn et al. (1985), which suggest $h_0 > 10h_c$. For this reason, we advise that this result be ignored and that conclusion 5 be assumed to apply in all cases.

Raza (1970) saw in his experimental studies with a mixed surfactant system that the breakthrough time increased with increasing concentration of surfactant up to the critical micelle concentration (CMC). Although he did not measure γ, the common experience is that γ decreases with increasing concentration of surfactant. Given that the breakthrough time is inversely proportional to the speed of displacement, Raza's (1970) observations below the CMC appear to be consistent with conclusion 5. [We have no definitive explanation for his observation that the breakthrough time decreased with increasing concentration above the CMC. It may be consistent with both conclusion 5 and conclusion 7. For at least some mixed surfactant systems, the surface tension reaches a minimum at the CMC and surface viscosities achieve maxima (Gupta and Wasan, 1974; Djabbarah and Wasan, 1982).]

In contrast with conclusion 5, Slattery (1979) predicts that the speed of displacement of a stable foam always decreases with increasing γ.

Since

$$\frac{\partial}{\partial \gamma}\left|\frac{\partial v}{\partial R_p}\right| = \frac{18}{25}\frac{v}{R_p \gamma} \geqq 0 \tag{32}$$

we are led to conclude

6. The displacement efficiency of an unstable foam increases with decreasing surface tension.

Starting with Eq. 19 again indicates that there is a value of $h_0/a = 1.54$ below which these trends are reversed. For the reason given above, we shall ignore this result. Beginning with Eq. 24, we find a narrow band ($-2.30 < \log_{10}\alpha^{1/4} < -2.12$) where the displacement efficiency of an unstable foam increases as the surface tension increases. As explained following Eq. 27, this band most likely has no practical significance.

There are no experimental data available with which to test conclusion 6.

For a stable foam, Slattery (1979) found that the displacement efficiency will always be enhanced by increasing the surface tension.

EFFECT OF SURFACE VISCOSITIES

Starting with Eq. 24, we see

$$\frac{\partial v}{\partial(\kappa + \epsilon)} = -0.227\,\frac{vM}{(\kappa + \epsilon)} \leqq 0 \tag{33}$$

where for convenience we have introduced

$$\begin{aligned} M &\equiv \frac{\operatorname{sech}^2(\log_{10}\alpha^{1/4} + 0.8902)}{t_c^{*0.957}} \\ &\equiv \frac{2\operatorname{sech}^2(\log_{10}\alpha^{1/4} + 0.8902)}{\tanh(\log_{10}\alpha^{1/4} + 0.8902) + 1} \end{aligned} \tag{34}$$

Equation 33 implies

7. The speed of displacement of an unstable foam will be enhanced by decreasing the surface viscosities.

Slattery (1979) came to a similar conclusion for stable foams.

Observe that for $\log_{10}\alpha^{1/4} < -2.3$:

$$\begin{aligned} \frac{\partial}{\partial(\kappa + \epsilon)}\left|\frac{\partial v}{\partial R_p}\right| &= 0.340\,\frac{vM}{R_p(\kappa + \epsilon)}[1 - 0.519M \\ &\quad - 1.014\tanh(\log_{10}\alpha^{1/4} + 0.8902)] < 0 \end{aligned} \tag{35}$$

and for $\log_{10}\alpha^{1/4} > -2.3$:

$$\begin{aligned} \frac{\partial}{\partial(\kappa + \epsilon)}\left|\frac{\partial v}{\partial R_p}\right| &= -0.340\,\frac{vM}{R_p(\kappa + \epsilon)}[1 - 0.519M \\ &\quad - 1.014\tanh(\log_{10}\alpha^{1/4} + 0.8902)] > 0 \end{aligned} \tag{36}$$

We will ignore Eq. 35 for the same reasons that we suggested ignoring Eq. 27. This permits us to conclude from Eq. 36 that

8. The displacement efficiency of an unstable foam increases with decreasing surface viscosities.

Slattery (1979) reached the opposite conclusion for stable foams.

Unfortunately, there are no data with which to test these conclusions. Kanda and Schechter (1976) measured breakthrough time and displacement efficiency for a variety of systems, but they examined the effect of varying the surfactant concentration in only one, the composition and properties of which were incompletely specified. [As discussed in the previous section, the observations of Raza (1970) may be consistent with conclusion 7, but he did not measure either of the surface viscosities.]

EFFECT OF FOAM QUALITY

The foam quality $(1 - f)$ is the volume fraction of gas in the foam.

Just as there is a minimum value that the quality can assume consistent with the existence of a foam, inequality 20 suggests that, for a given physical system, bubble size, and pore size distribution, there is an upper bound for $(1 - f)$ as well.

To determine the effect of foam quality upon its speed of displacement, consider as a result of Eq. 19

$$\frac{\partial v}{\partial(1 - f)} = 2vF/f \geqq 0 \tag{37}$$

where

$$F \equiv (h_0/a)^2 \{\tan^{-1}[(h_0/a)^2] - 0.523\}^{-1}\{1 + (h_0/a)^4\}^{-1} \tag{38}$$

Equation 37 indicates

9. The speed of displacement of an unstable foam will be enhanced by increasing its quality.

This agrees with the report by Holm (1968) that mobility increases with increasing foam quality. In contrast, Marsden and Khan (1966) found that mobility decreased with increasing foam quality. Holm (1968) suggests that the gas bubbles used by Marsden and Khan (1966) may have been smaller than the minimum required for displacement according to the mechanism assumed here (see conclusion 11).

Because

$$\frac{\partial}{\partial(1 - f)}\left|\frac{\partial v}{\partial R_p}\right| = \frac{2vF}{fR_p}\left[2F + \frac{2(h_0/a)^4}{1 + (h_0/a)^4}\right] \geqq 0 \tag{39}$$

we can state

10. The efficiency of an unstable foam will be enhanced by decreasing its quality.

This is consistent with the findings of Holm (1968) and of Minssieux (1974).

EFFECT OF BUBBLE SIZE

The average volume of a single bubble is proportional to n, the total number of pore units divided by the number of liquid films.

Inequality 20 says that the initial film thickness must be greater than the critical thickness at which the film becomes unstable and rupture occurs. It will always be satisfied, if a foam is formed. If the expected initial film thickness is smaller than the critical film thickness for a given pore, a foam will not be formed in this pore. In order that the expected initial film thickness not be smaller than the critical film thickness for a given pore, the available liquid cannot be divided among too many films. This implies that

11. For a given physical system, foam quality $(1 - f)$, and pore size, there is a minimum bubble size below which unstable foams are not formed.

As noted in the preceding section, Holm (1968) suggests that the gas bubbles used by Marsden and Khan (1966) may have been smaller than the minimum required for displacement according to the mechanism assumed here, which might explain why they found that mobility decreased with increasing foam quality in contrast with conclusion 9.

The effect of bubble size on speed of displacement follows from Eq. 9:

$$\frac{\partial v}{\partial n} = \frac{v}{n} > 0 \tag{40}$$

This tells us

12. The speed of displacement of an unstable foam increases with increasing bubble size.

Starting with Eq. 24 yields the same result. Although there is a value of $h_0/a = 1.6$ below which Eq. 19 predicts that $\partial v/\partial n$ will be negative, we suggest that this be ignored for the reason indicated following conclusion 5.

Conclusion 12 agrees with Holm's (1968) report that speed of displacement increased with increasing bubble size in the injected foam.

Observing that from Eq. 9

$$\frac{\partial}{\partial n}\left|\frac{\partial v}{\partial R_p}\right| = \frac{6}{5}\frac{v}{nR_p} > 0 \tag{41}$$

we can state

13. The displacement efficiency of an unstable foam increases with decreasing bubble size.

Although Eq. 19 predicts a value of $h_0 = 2.11$ below which $\partial/\partial n\,|\partial v/\partial R_p|$ will be negative, we suggest that this be ignored for the reason given following conclusion 5. Using Eq. 24, we find a narrow band $(-2.34 < \log_{10}\alpha^{1/4} < -2.30)$ in which the displacement efficiency of an unstable foam increases with increasing bubble size. For the reasons indicated following Eq. 27, we feel that this has no physical significance.

There are no experimental data with which to test this conclusion.

EFFECT OF VISCOSITY OF FOAMING AGENT SOLUTION

From Eq. 9, we have

$$\frac{\partial v}{\partial \mu} = -\frac{v}{\mu} \leqq 0 \tag{42}$$

and

14. The speed of displacement of an unstable foam will be enhanced by decreasing the viscosity of the foaming agent solution.

Equations 19 and 24 yield the same conclusion.

In a similar manner, we find from Eq. 9

$$\frac{\partial}{\partial \mu}\left|\frac{\partial v}{\partial R_p}\right| = -\frac{6}{5}\frac{v}{\mu R_p} \leqq 0 \tag{43}$$

which indicates

15. The displacement efficiency of an unstable foam will be enhanced by increasing the viscosity of the foaming agent solution.

Equation 19 leads to the same conclusion. Equation 24 says that there is a band $(-3.47 < \alpha^{1/4} < -2.30)$ in which the trend is reversed. For the reasons indicated following Eq. 27, we will ignore this result.

While there are no experimental data available with which to test either of these conclusions, both are identical with those proposed by Slattery (1979) for stable foams.

ACKNOWLEDGMENT

The authors are grateful for financial support received from Amoco Production Co., Exxon Education Foundation, Gulf Research and Development Co., and the Standard Oil Co. (Ohio).

NOTATION

a = defined by Eq. 14
b_m = mutual force per unit mass
B = parameter in Eq. 2 characterizing the strength of the London-van der Waals force of interaction
f = volume fraction of liquid in the foam
F = defined by Eq. 38
h = thickness of the liquid film at the rim
h_0 = initial thickness of the liquid film at the rim

k_1, k_2, k_3 = proportionality factors in Eqs. 9, 19, and 20
L^* = ratio of length of unit pore to R_p
m = parameter in Eq. 2
M = defined by Eq. 34
n = total number of pore units divided by the number of liquid films
R = radius of liquid film at rim
R_b = radius of gas bubble
R_p = pore throat radius
t = time
t_c = coalescence time
t_c^* = dimensionless coalescence time defined by Eq. 22
t_f = time for film thickness at rim to reduce to zero in absence of instabilities
t_0 = time when film is first formed
v = speed of displacement of foam
V = volume of unit pore
V^* = dimensionless volume of unit pore defined by Eq. 11

Greek Letters

α = defined by Eq. 23
γ = surface tension
ϵ = surface shear viscosity
κ = surface dilatational viscosity
μ = viscosity of liquid forming foam
Π = disjoining pressure defined by Eq. 3
ρ = liquid density
$\tau_{(4)}, \tau_{(3)}$ = defined by Eqs. 5 and 13
φ = potential for London-van der Waals force of interaction introduced in Eq. 1
φ_0 = potential for London-van der Waals force of interaction evaluated at fluid-fluid interface in Eq. 2
Φ_B = interaction potential per unit volume for semi-infinite liquid film introduced in Eq. 2
∇ = gradient operator

LITERATURE CITED

Albrecht, R. A., and S. S. Marsden, "Foams as Blocking Agents in Porous Media," *Soc. Petrol. Eng. J.*, **10**, 51 (1970).

Allan, R. S., G. E. Charles, and S. G. Mason, "The Approach of Gas Bubbles to a Gas/Liquid Interface," *J. Colloid Sci.*, **16**, 150 (1961).

Barber, A. D., and S. Hartland, "The Effects of Surface Viscosity on the Axisymmetric Drainage of Planar Liquid Films," *Can. J. Chem. Eng.*, **54**, 279 (1976).

Batra, V. K., and F. A. L. Dullien, "Correlation Between Pore Structure of Sandstones and Tertiary Oil Recovery," *Soc. Petrol. Eng. J.*, **13**, 256 (1973).

Bernard, G. G., and L. W. Holm, "Effect of Foam on Permeability of Porous Media to Gas," *Soc. Petrol. Eng. J.*, **4**, 267 (1964).

———, "Model Study of Foam as a Sealant for Leaks in Gas Storage Reservoirs," *Soc. Petrol. Eng. J.*, **10**, 9 (1970).

Burrill, K. A., and D. R. Woods, "Film Shapes for Deformable Drops at Liquid-Liquid Interfaces. III. Drop Rest Times," *J. Colloid Interface Sci.*, **42**, 35 (1973).

Chen, J. D., P. S. Hahn, and J. C. Slattery, "Coalescence Time for a Small Drop or Bubble at a Fluid-Fluid Interface," *AIChE J.*, **30**, 622 (July, 1984).

Chureav, N. V., "Molecular Forces in Wetting Films of Nonpolar Liquid: 1. Thick Films," *Colloid J. USSR* (Engl. transl.), **36**, No. 2, 283 (1974a).

———, "Molecular Forces in Wetting Films of Nonpolar Liquids: 2. Thin Films," *Colloid J. USSR* (Engl. transl.), **36**, No. 2, 287 (1974b).

Djabbarah, N. F., and D. T. Wasan, "Dilational Viscoelastic Properties of Fluid Interfaces. III. Mixed Surfactant Systems," *Chem. Eng. Sci.*, **37**, 175 (1982).

Flumerfelt, R. W., J. P. Oppenheim, and J. R. Son, "Magnitude and Role of Dynamic Interfacial Effects in Low Tension Flooding," *AIChE Symp. Ser.*, **78**(212), 113 (1982).

Giordano, R. M., and J. C. Slattery, "Effect of the Interfacial Viscosities Upon Displacement in Capillaries with Special Application to Tertiary Oil Recovery," *AIChE J.*, **29**, 483 (1983).

Gupta, L., and D. T. Wasan, "Surface Shear Viscosity and Related Properties of Adsorbed Surfactant Films," *Ind. Eng. Chem. Fundam.*, **13**, 26 (1974).

Hahn, P. S., and J. C. Slattery, "Effects of Surface Viscosities upon the Stability of a Draining Plane Parallel Liquid Film as a Small Bubble Approaches a Fluid-Fluid Interface," *AIChE J.*, **31** (June, 1985).

Hahn, P. S., J. D. Chen, and J. C. Slattery, "Effects of London-van der Waals Forces on the Thinning and Rupture of a Dimpled Liquid Film as a Small Drop or Bubble Approaches a Fluid-Fluid Interface," *AIChE J.* (1985).

Holm, L. W., "The Mechanism of Gas and Liquid Flow Through Porous Media in the Presence of Foam," *Soc. Petrol. Eng. J.*, **10**, 359 (1968).

———, "Foam Injection Test in the Siggins Field, Illinois," *J. Petrol. Technol.*, **1499 (Dec. 1970).**

Ivanov, I. B., B. Radoev, E. Manev, and A. Scheludko, "Theory of the Critical Thickness of Rupture of Thin Liquid Films," *Trans. Faraday Soc.*, **66**, 1262 (1970).

Kanda, M., and R. S. Schechter, "On the Mechanism of Foam Formation in Porous Media," paper SPE 6200, Soc. Petrol. Eng., Dallas (1976).

Lin, C. Y., and J. C. Slattery, "Thinning of a Liquid Film as a Drop or Bubble Coalesces at a Fluid-Fluid Interface," *AIChE J.*, **28**, 786 (1982).

MacKay, G. D. M., and S. G. Mason, "The Gravity Approach and Coalescence of Fluid Drops at Liquid Interfaces," *Can. J. Chem. Eng.*, **41**, 203 (1963).

Marrucci, G., "A Theory of Coalescence," *Chem. Eng. Sci.*, **24**, 975 (1969).

Marsden, S. S., and S. A. Khan, "The Flow of Foam Through Short Porous Media and Apparent Viscosity Measurements," *Soc. Petrol. Eng. J.*, **6**, 17 (1966).

Mast, R. F., "Microscopic Behavior of Foam in Porous Media," paper SPE 3997, Soc. Petrol. Eng., AIME, Dallas (1972).

Minssieux, L., "Oil Displacement by Foams in Relation to Their Physical Properties in Porous Media," *J. Petrol. Technol.*, **100** (Jan. 1974).

Raza, S. H., "Foam in Porous Media: Characteristics and Potential Applications," *Soc. Petrol. Eng. J.*, **10**, 328 (1970).

Ruckenstein, E., and R. K. Jain, "Spontaneous Rupture of Thin Liquid Films," *J. Chem. Soc., Faraday Trans. II*, **70**, 132 (1974).

Slattery, J. C., "Interfacial Effects in the Entrapment and Displacement of Residual Oil," *AIChE J.*, **20**, 1145 (1974).

———, "Interfacial Effects in the Displacement of Residual Oil by Foam," *AIChE J.*, **25**, 283 (1979).

Stoodt, T. S., and J. C. Slattery, "Experimental Study of the Effect of the Interfacial Viscosities Upon Displacement, *AIChE J.*, **30**, 564 (1984).

Vrij, A., "Possible Mechanism for the Spontaneous Rupture of Thin, Free Liquid Films," *Disc. Faraday Soc.*, **42**, 23 (1966).

Manuscript received Aug. 24, 1982; revision received Mar. 27, 1984, and accepted July 2.