$$\eta_o = \sum_m^\infty \sum_n^\infty \left\{ \frac{2\,\mathrm{Sin}^2\lambda_n\,\mathrm{Sin}^2\kappa_m/(\lambda_n^2\kappa_m^2 b_{mn})}{(\coth b_{mn} + b_{mn}/\alpha_{gLs})\left[a_m^2 + (1-a_m^2)\left(\frac{1}{2}+\frac{1}{4\kappa_m}\sin 2\kappa_m\right)\right]\left(\frac{1}{2}+\frac{1}{4\lambda_n}\sin 2\lambda_n\right)} + \frac{\mathrm{Sin}^2\lambda_n\,\mathrm{Sin}^2\lambda_m/(\lambda_m^2\lambda_n^2 g_{mn})}{\left(\frac{1}{2}+\frac{1}{4\lambda_n}\mathrm{Sin}\,2\lambda_n\right)\left(\frac{1}{2}+\frac{1}{4\lambda_m}\mathrm{Sin}\,2\lambda_m\right)} \left[\frac{1}{l_{mn} + g_{mn}/\alpha_{gLs} + (1 + l_{mn}g_{mn}/\alpha_{gLs})\coth g_{mn}} + \frac{1}{d_{mn} + g_{mn}/\alpha_{gs} + (1 + d_{mn}g_{mn}/\alpha_{gs})\coth g_{mn}}\right] \right\} \quad \text{(A1)}$$

where

$$\frac{1}{\alpha_{gLs}} = \frac{1}{\alpha_{gL}} + \frac{1}{\alpha_{Ls}} \quad \text{(A2)}$$

$$b_{mn} = (\lambda_n^2 + \kappa_m^2 + \phi_c^2)^{1/2} \quad \text{(A3)}$$

$$g_{mn} = (\lambda_n^2 + \lambda_m^2 + \phi_c^2)^{1/2} \quad \text{(A4)}$$

$$d_{mn} = \frac{g_{mn}\tanh g_{mn} + \alpha_{gLs}}{g_{mn} + \alpha_{gLs}\tanh g_{mn}} \quad \text{(A5)}$$

$$l_{mn} = \frac{\alpha_{gs} + g_{mn}\tanh g_{mn}}{\alpha_{gs}\tanh g_{mn} + g_{mn}} \quad \text{(A6)}$$

and λ_n and κ_m are the roots of

$$\lambda_n \tan\lambda_n = \alpha_{gLs}; \quad n = 1, 2, \cdots \quad \text{(A7)}$$

$$\left(\kappa_m + \frac{\alpha_{gLs}}{\alpha_{gs}}\right)\tan^2\kappa_m - 2\left(\alpha_{gLs} - \frac{\kappa_m^2}{\alpha_{gs}}\right)\tan\kappa_m - \left(\frac{\alpha_{gLs}}{\alpha_{gs}} + 1\right)\kappa_m = 0; \quad m = 1, 2, \cdots \quad \text{(A8)}$$

Similar relations were obtained for the cases $f = 1/6, 2/6, 3/6, 4/6$ and can be found in Herskowitz (1978).

Manuscript received June 2, 1978; revision received October 23, and accepted November 13, 1978.

Interfacial Effects in the Displacement of Residual Oil by Foam

A qualitative theory is developed to explain the roles of surface tension and the two surface viscosities in the displacement of foams through porous media. There is a critical value of the surface tension above which a foam cannot be displaced under a given pressure gradient. The displacement efficiency of a foam can be raised by increasing the surface tension to only slightly less than this critical value, by increasing the viscosity of the aqueous surfactant solution from which the foam is formed and by increasing the surface viscosities. These predictions are in agreement with available experimental data.

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SCOPE

Petroleum is found in the microscopic pores of sedimentary rocks such as sandstones and limestones. Not all of the pores are filled with petroleum. Some of the pores contain water or brine that is saturated with minerals from the local rock structure.

In the primary stage of production, oil and brine are driven into a well from the surrounding rock by the relatively large difference between the initial field pressure and the pressure in the well. In the secondary stage of conventional production, water or steam is pumped into a selected pattern of wells in a field forcing a portion of the oil toward the production wells.

A number of tertiary recovery techniques have been proposed (Geffen, 1973). The one with which we shall concern ourselves here is a gas drive, in which the residual oil is displaced by a gas. The most favorable conditions for displacement would occur if the gas were miscible with the oil at the reservoir temperature and pressure. But even if the gas is not miscible with the oil, it will still be soluble in the oil under reservoir conditions. This can result in a reduced viscosity of the oil, a reduced density of the oil (the volume of the oil would be increased), and possibly a reduced gas-oil interfacial tension. Any combination of these factors can enhance the displacement of residual oil.

A major disadvantage of a gas drive is that the mobility of the gas (the ratio of the relative permeability of the gas to its viscosity) is much larger than the mobility of the oil. This results in an unstable displacement, with the gas fingering ahead through the oil and water and bypassing the majority of it.

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It has been suggested that this unfavorable mobility ratio could be reversed by incorporating the gas in a foam which would be used to displace the crude oil and water (Bernard, 1963; Holm, 1970; Raza, 1970; Minssieux, 1974). In practice, either an aqueous surfactant solution and gas could be injected simultaneously or injection of surfactant solution could alternate with injection of gas allowing the foam to form in place within the porous rock as the gas fingered through the surfactant solution.

Our objective here is to study the factors controlling the efficiency of a foam displacement, both its local efficiency and its sweep efficiency or conformance. The local efficiency describes the degree to which the foam is able to displace residual oil from all of the pores within the immediate neighborhood of any point within the rock. The sweep efficiency or conformance describes the degree to which the foam is able to move through all of the pores with nearly the same speed, minimizing any tendency to finger ahead in one macroscopic region and bypass the residual oil in another.

CONCLUSIONS AND SIGNIFICANCE

The dimensionless gas-aqueous surfactant solution surface tension N_γ must be less than some critical value before any residual oil can be recovered by displacement with a foam under a given pressure gradient. This agrees with Minssieux's (1974) report of a critical pressure gradient below which a continuous foam flow could not be achieved. For displacement in a typical oil bearing reservoir rock, this critical interfacial tension is estimated to be of the order 8 × 10^{-2} dyne/cm. In most foams, the surface tension is considerably larger. This appears to explain why foams are frequently described as blocking agents to seal leaks in gas storage reservoirs, to prevent gas coning in the neighborhood of a production well, or to reduce the flow through high permeability zones in heterogeneous reservoirs. Because of this latter ability to reduce the flow through high permeability zones in heterogeneous reservoirs, even relatively high tension foams may be useful in controlling a gas drive to recover residual oil.

For values of N_γ less than the critical value, the rate of displacement of a foam can be enhanced by decreasing the surface tension and the surface viscosities. This is consistent with Kanda and Schechter's (1976) observations.

For values of N_γ less than the critical value, a foam will preferentially flow through the larger pores, failing to displace portions of the residual oil in smaller pores. The efficiency of a foam displacement can be raised by decreasing the magnitude of the pressure gradient and increasing the surface tension, which implies that the optimum value for N_γ is only slightly less than the critical value. Displacement efficiency can also be raised by increasing the viscosity of the aqueous surfactant solution and by increasing the surface viscosities. Kanda and Schechter (1976) observed that displacement efficiency was raised as the surface shear viscosity increased.

The agreement between the effect of the surface viscosities upon foam displacement predicted here and that observed by Kanda and Schechter (1976) gives added support to the predictions of a similar analysis (Slattery, 1974) regarding the effects of the interfacial viscosities in the recovery of residual oil by surfactant water flooding.

The void volume in a permeable rock, such as that in which oil is found, is composed of many intersecting irregular pores, the mean neck 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 structure a foam has the same ordered structure of thin films intersecting in plateau borders which we observe when the same liquid and gas are shaken together in a graduate cylinder.* Within the pore structure, the aqueous surfactant solution from which the foam is formed is likely dispersed in the form of blobs or ganglia occupying a large set of neighboring pores.

Visualize two neighboring pore networks having different mean radii that offer parallel paths for displacement. If the oil is displaced by the foam more rapidly in the network having the larger mean pore radius, a portion of the oil in the network having the smaller mean pore radius will be bypassed and lost.

Consider two blobs of surfactant solution in adjacent, parallel pore networks. Assume for the moment that the blob in the pore network having the larger mean pore radius is displaced more rapidly than the blob in the network having smaller diameter pores. This would lead to more rapid displacement of the oil in the network having the larger pores, with a portion of the oil in the network having smaller pores being bypassed. The sweep efficiency or conformance of a foam displacement can be improved to the extent that we can cause the blobs of surfactant solution to move through all portions of the pore network with nearly the same rate of displacement.

It is easier to discuss this mechanism for foam displacement on a smaller scale. Figure 1 shows a pore that bifurcates to form two pores of unequal diameters which

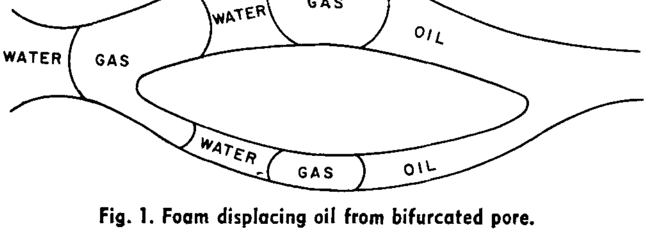

Fig. 1. Foam displacing oil from bifurcated pore.

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* As a result, the properties of a foam as observed in a macroscopic experiment (stability of a foam upon standing in a graduate cylinder; viscosity or rheology inferred from displacements in pipes or tubes) are at best indirect indications of the behavior of the liquid-gas mixture in a porous rock.

rejoin downstream. Assume that displacement takes place from left to right.

In constructing our detailed analysis, several observations will be useful. The pores in a permeable rock are irregular channels whose diameters vary with axial position. We must be able to displace the water segments in both the large and the small pores, if the local efficiency of the foam displacement is to be improved. If the water segment advances through the small pore more rapidly, residual oil will tend to be bypassed in the large pore. If the water segment moves through the large pore more rapidly, residual oil will tend to be bypassed in the small pore. We can improve both the local and the sweep efficiencies of a foam displacement to the extent that we can cause the water segments to move through the large and small pores at nearly the same speeds.

We have previously suggested that a liquid segment is displaced through an irregular pore in a series of jumps (Slattery, 1974; Oh and Slattery, 1979). We might expect that these jumps have the same character as those observed by Haines (1930), Miller and Miller (1956), Melrose (1965), and Heller (1968) as a single interface advanced through an irregular pore.

Following a jump, a water segment will creep forward a short distance until an instability develops and the next jump occurs. This creeping motion between jumps probably takes place in that portion of the pore where the pressure difference required to hold the segment in a static configuration increases as the segment advances (Oh and Slattery, 1979). Figure 2 shows a small liquid segment undergoing a creeping motion through a water wet pore. In Figure 3, a liquid segment is shown in creeping motion through a gas wet pore. The portion of the pore in which a water segment undergoes creeping motion will depend upon the volume of the water segment, the wettability condition, and the contact angle hysteresis (Oh and Slattery, 1979).

Experiments suggest that the water segments will not advance smoothly as a function of time even during this creeping motion. Yarnold (1938) observed that, when a liquid segment is slowly displaced through a glass capillary, it moves in an irregular, episodic fashion, appearing to periodically stick to the tube wall.

These irregular, stick-slip motions can be understood in terms of the contact angle hysteresis to be expected on contaminated or roughened surfaces. Let us consider the water segments shown in Figures 2 and 3. The water advances when either of two conditions is satisfied.

1. When the contact angle measured through the gas at the leading interface is less than the receding contact angle, the gas retreats and the common line formed by the intersection of the leading interface with the pore wall advances.
2. When the contact angle measured through the gas at the trailing interface is greater than the advancing contact angle, the gas advances and the common line formed by the intersection of the trailing interface with the pore wall advances.

A water segment that appears to be stuck to the pore wall will slowly deform until one of these conditions is satisfied and it advances. Inertia will carry the segment to a position where neither of these conditions is satisfied, where both of the common lines are stationary, and where the segment again appears to stick to the wall. Time is required for the segment to slowly deform until one of these conditions is again satisfied and the common lines can again advance.

This suggests that we reexamine the creeping motion between jumps as a water segment advances through a pore. It may consist of one or more pauses during which the contact angle measured through the gas at the leading interface decreases and the contact angle measured through the gas at the trailing interface increases. These pauses are followed by an irregular motion when either of these contact angles finally equals their critical values required for advance.

APPROXIMATE ANALYSIS

The rate limiting steps in the episodic advance of a water segment through an irregular pore are the periods in which the segment creeps forward between jumps.

In this analysis, we will go even further and assume that the rate limiting steps are the pauses which occur during this creeping motion as the contact angle measured through the gas phase at the leading interface decreases and the contact angle measured through the gas phase at the trailing interface increases. Let us estimate the effects of interfacial behavior upon the slow deformation that occurs during one of these pauses. In carrying out this analysis, we shall not be concerned either with the jump or with the development of any instability which leads to the jump.

Consider as a system all of the water and gas in the pore between the fixed entrance and exit surfaces shown as dashed lines in Figures 2 and 3. The z component of the momentum balance for this system can be arranged in the form [for a detailed derivation of nearly the same result in a slightly different context, see Equation (32) in Slattery, 1974]:

$$\begin{aligned} v^*_{(w)} &\equiv \frac{v_{(w)}\mu_{(w)}}{|\nabla p| l^2} \\ &= \frac{R^{*2}A - R^* N_\gamma G}{L^*_{(w)}D + (1 - L^*_{(w)}) \dfrac{\mu_{(g)}}{\mu_{(w)}} E + R^* N_{\kappa+\epsilon} H} \\ &= \frac{R^{*2}A - R^* N_\gamma G}{\tilde{D} + R^* N_{\kappa+\epsilon} H} \end{aligned} \tag{1}$$

where I have introduced as definitions

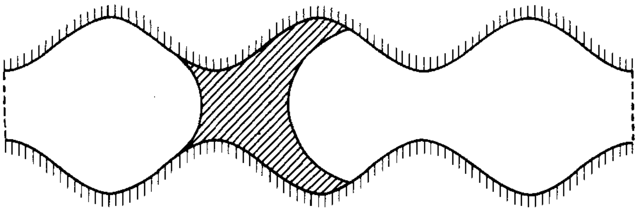

Fig. 2. Water segment undergoing creeping motion through water wet pore following a jump (OH and Slattery, 1979). Morrow's (1975) class III contact angle hysteresis is assumed with the advancing and receding contact angles measured through the aqueous phase taken to be 50 and 5 deg, respectively.

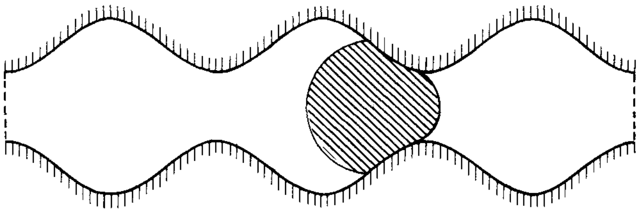

Fig. 3. Water segment undergoing creeping motion through gas wet pore following a jump (Oh and Slattery, 1979). Morrow's (1975) class III contact angle hysteresis is assumed with the advancing and receding contact angles measured through the aqueous phase taken to be 176 and 140 deg, respectively.

$$R^* \equiv \frac{R}{l} \tag{2}$$

$$L^*_{(w)} \equiv \frac{L_{(w)}}{l} \tag{3}$$

$$t^* \equiv \frac{t v_{(w)}}{l} \tag{4}$$

$$N_\gamma \equiv \frac{\gamma}{|\nabla p| l^2} \tag{5}$$

$$N_{\kappa+\epsilon} \equiv \frac{\kappa+\epsilon}{l \mu_{(w)}} \tag{6}$$

$$A \equiv \frac{\Delta p}{|\nabla p| l} - F^{(p)*} \tag{7}$$

$$D \equiv 2F^{(v)*}_{(w)} \tag{8}$$

$$E \equiv 2F^{(v)*}_{(g)} \tag{9}$$

$$G \equiv -2\left[\frac{R_{(l)}}{R}\mu_{(l)z} + \frac{R_{(t)}}{R}\mu_{(t)z}\right] \tag{10}$$

$$H \equiv 2\left[\frac{R_{(l)}}{R}\frac{d_{(s)} \ln \rho^{(\sigma)}_{(l)}}{dt^*}\mu_{(l)z} + \frac{R_{(t)}}{R}\frac{d_{(s)} \ln \rho^{(\sigma)}_{(t)}}{dt^*}\mu_{(t)z}\right] \tag{11}$$

$$\widetilde{D} \equiv L^*_{(w)} D + (1 - L^*_{(w)}) \frac{\mu_{(g)}}{\mu_{(w)}} E \tag{12}$$

$$F^{(p)*} \equiv \frac{F^{(p)}}{|\nabla p| \pi R^2 l} \tag{13}$$

$$F^{(v)*}_{(w)} \equiv \frac{F^{(v)}_{(w)}}{2\pi L_{(w)} \mu_{(w)} v_{(w)}} \tag{14}$$

$$F^{(v)*}_{(g)} \equiv \frac{F^{(v)}_{(g)}}{2\pi (l - L_{(w)}) \mu_{(g)} v_{(w)}} \tag{15}$$

$$\Delta p \equiv p_{(\text{ent})} - p_{(\text{ex})} \tag{16}$$

is the pressure drop over the system.

We will assume that we have chosen our dimensionless variables such that the magnitudes of A, D, E, G, H, and $\widetilde{D}$ are all of order unity (they differ by less than a factor of ten from unity).

Let us begin by examining the signs of some of the terms that appear in Equation (1). We will assume that the flow is always in the positive z direction, and consequently

$$R^* A - N_\gamma G \geqq 0 \tag{17}$$

In the water wet case shown in Figure 2, the trailing interface is dominant, and[†]

$$G \geqq 0 \tag{18}$$

For the gas wet case shown in Figure 3, the leading interface is dominant, and (19) again applies. Inequalities (17) and (18) together imply that in order to hold the water segment in a static configuration

$$A \geqq 0 \tag{19}$$

The dimensionless scalars D and E are positive. In the gas wet case shown in Figure 3, the area of the leading interface increases as a function of time, and the area of the trailing interface decreases as a function of time. With the assumption that there is no appreciable mass transfer from the adjoining phases, the surface mass density must decrease as a function of time on the leading interface and increase as a function of time on the trailing interface. Since $\mu_{(l)z}$ is negative and $\mu_{(t)z}$ positive, we have

$$\frac{d_{(s)} \ln \rho^{(\sigma)}_{(l)}}{dt^*}\mu_{(l)z} + \frac{d_{(s)} \ln \rho^{(\sigma)}_{(t)}}{dt^*}\mu_{(t)z} \geqq 0 \quad H \geqq 0 \tag{20}$$

A similar argument for the water wet case shown in Figure 2 indicates that (20) is valid there as well.

Equation (1) describes the average velocity within the aqueous phase during a pause in the creeping motion between jumps. Since we visualize that these pauses are the rate limiting steps, we can use Equation (1) to draw several conclusions concerning the relative rates of displacement in the two portions of the bifurcated pore pictured in Figure 1 and the efficiency with which a foam will displace a gas.

CRITICAL VALUE FOR INTERFACIAL TENSION

From Equation (1) and inequality (17), we observe that the dimensionless interfacial tension N_γ must be less than some critical value before any residual oil can be recovered by displacement. The critical value of N_γ has a magnitude of order unity.

Minssieux (1974) reported a critical pressure gradient below which a continuous foam flow could not be achieved. The corresponding value of N_γ is estimated from his data to be a little less than unity.

We can write

$$N_\gamma \equiv \frac{\gamma}{|\nabla p| l^2} = \frac{\gamma R^{*2}}{|\nabla p| R^2} \tag{21}$$

For a typical displacement, $|\nabla p| \sim 1$ lb/in.^{2}/ft (2.26×10^3 dyne/cm^3). Let us take $R^{*-1} = 6$, the length of a repeating unit of irregular pore (Payatakes et al., 1973). Let us choose R to be the neck radius for the irregular pore. For a rock whose permeability is 250 millidarcies (2.47×10^{-9} cm^2), a reasonable value for R appears to be 10 μ (Batra and Dullien, 1973). Taking $N_\gamma = 1$, we estimate the critical value for the surface tension γ above which a foam could not be displaced through the porous rock structure as 8×10^{-2} dyne/cm.

For most foams, the gas-aqueous surfactant solution surface tension is considerably larger. This appears to explain why foams are frequently described as blocking agents to seal leaks in gas storage reservoirs (Bernard and Holm, 1970; Albrecht and Marsden, 1970), to prevent gas coning in the neighborhood of a production well (Raza, 1970), or to reduce the flow through high permeability zones in heterogeneous reservoirs (Holm, 1970). Because of this latter ability to reduce the flow through high permeability zones in heterogeneous reservoirs, even relatively high tension foams may be useful in controlling a gas drive to recover residual oil.

[†] For a capillary of uniform diameter

$$\mu_{(l)z} = \cos \Theta_A$$

$$\mu_{(t)z} = -\cos \Theta_R$$

where Θ_A and Θ_R are, respectively, the advancing and receding contact angles measured through the aqueous phase. Therefore

$$G = 2(\cos \Theta_R - \cos \Theta_A)$$

in agreement with inequality (18), since the receding contact angle will always be smaller than the advancing contact angle.

For Holm's (1968) experiments, N_γ (based upon the mean pore diameter) is estimated to be greater than unity. The flows recorded in these experiments may have proceeded by a different mechanism than the one assumed here. He observed that the gas flowed as the result of bubbles or short liquid segments breaking and reforming. We can visualize that the liquid segments thinned by draining became unstable and finally broke. There is nothing in Holm's (1968) description or Mast's (1972) characterization of flow in smaller pores to suggest that these liquid segments broke and reformed as the result of jumps.

DISTRIBUTION OF BYPASSED OIL

From (1)

$$\frac{\partial v^*_{(w)}}{\partial R^*} = \frac{R^*A[\tilde{D} + R^*N_{\kappa+\epsilon}H] + \tilde{D}[R^*A - N_\gamma G]}{[\tilde{D} + R^*N_{\kappa+\epsilon}H]^2} \tag{22}$$

which must be positive, in view of (17), (19), (20) and the observation that $\tilde{D}$ is positive. This means that the water segment shown in the larger pore of Figure 1 will be displaced more rapidly. The implication is that, for values of N_γ less than the critical value, a foam will preferentially flow through the larger pores, failing to displace portions of the residual oil in smaller pores.

In order to improve the displacement efficiency of a foam, we must reduce $\partial v^*_{(w)}/\partial R^*$, forcing the water segments to move through the large and small pores at more nearly the same speed.

EFFECT OF PRESSURE GRADIENT

The effect of increasing the magnitude of the pressure gradient while holding the gas-water surface tension constant can be seen from

$$\frac{\partial[v^*_{(w)}N_\gamma^{-1}]}{\partial N_\gamma^{-1}} = \frac{R^{*2}A}{\tilde{D} + R^*N_{\kappa+\epsilon}H} \tag{23}$$

Because of (19), (20), and the observation that $\tilde{D}$ is positive, the rate at which a water segment is displaced increases as the magnitude of the pressure gradient is increased. Of greater concern here is the efficiency with which the displacement proceeds. In particular, for which of the pores shown in Figure 1 is the effect more significant?

Consider

$$\frac{\partial^2[v^*_{(w)}N_\gamma^{-1}]}{\partial N_\gamma^{-1}\partial R^*} = \frac{\partial v^*_{(w)}}{\partial R^*} + \frac{N_\gamma G\tilde{D}}{[\tilde{D} + R^*N_{\kappa+\epsilon}H]^2} \tag{24}$$

In view of (18), (22), and the observation that $\tilde{D}$ is positive, we see that this derivative is always positive, suggesting that, for values of N_γ less than the critical value, the efficiency of a foam displacement can be increased by decreasing the magnitude of the pressure gradient. The optimum value for N_γ is only slightly less than the critical value.

EFFECT OF VISCOSITY RATIO

The effect of changing the gas-aqueous solution viscosity ratio is seen from (1) to be

$$\frac{\partial[v^*_{(w)}\mu_{(g)}/\mu_{(w)}]}{\partial[\mu_{(g)}/\mu_{(w)}]} = \frac{(R^{*2}A - R^*N_\gamma G)[L^*_{(w)}D + R^*N_{\kappa+\epsilon}H]}{[\tilde{D} + R^*N_{\kappa+\epsilon}H]^2} \tag{25}$$

Inequalities (17) and (20) and the observation that D is positive combine to require this derivative to be positive. The speed at which an aqueous segment is displaced decreases as the viscosity of the aqueous phase is increased (as $\mu_{(g)}/\mu_{(w)}$ is decreased).

In order to examine the effect upon efficiency, consider

$$\frac{\partial^2[v^*_{(w)}\mu_{(g)}/\mu_{(w)}]}{\partial[\mu_{(g)}/\mu_{(w)}]\partial R^*} = \Big\{ R^*(R^*A - N_\gamma G)[1 - L^*_{(w)}] \frac{\mu_{(g)}}{\mu_{(w)}} N_{\kappa+\epsilon}EH + (R^*A - N_\gamma G)[L^*_{(w)}D + R^*N_{\kappa+\epsilon}H]\tilde{D} + R^*A[L^*_{(w)}D + R^*N_{\kappa+\epsilon}H](\tilde{D} + R^*N_{\kappa+\epsilon}H) \Big\} \{\tilde{D} + R^*N_{\kappa+\epsilon}H\}^{-3} \tag{26}$$

Using (17), (19), and (20) and noting that D, $\tilde{D}$, and E are all positive, we conclude that this derivative is positive, which allows us to say that, for values of N_γ less than the critical value, the efficiency of a foam displacement can be raised by increasing the viscosity of the aqueous solution (decreasing $\mu_{(g)}/\mu_{(w)}$).

This suggests that the displacement efficiency of a foam might be enhanced if it were formed from an aqueous solution of an appropriate polymer. The effect can be a large one, since $\partial^2[v^*_{(w)}\mu_{(g)}/\mu_{(w)}]/\partial[\mu_{(g)}/\mu_{(w)}]\partial R^*$ is on the order of $\mu_{(w)}/\mu_{(g)}$ times $\partial[v^*_{(w)}\mu_{(g)}/\mu_{(w)}]/\partial R^*$ (estimating that the magnitudes of A, D, E, G, and H are of the order unity).

EFFECT OF SURFACE TENSION

Returning to (1), we see that

$$\frac{\partial v^*_{(w)}}{\partial N_\gamma} = \frac{-R^*G}{\tilde{D} + RN_{\kappa+\epsilon}H} \tag{27}$$

Because of (18), (20), and the observation that $\tilde{D}$ is positive, this derivative must always be negative. We find that, for values of N_γ less than the critical value, the rate of displacement of a foam can be enhanced by decreasing the gas-water surface tension. This agrees with Kanda and Schechter's (1976) observation that breakthrough time is increased by increasing the gas-water surface tension.

In order to investigate the effect upon efficiency, consider

$$\frac{\partial^2 v^*_{(w)}}{\partial N_\gamma \partial R^*} = \frac{-G\tilde{D}}{[\tilde{D} + R^*N_{\kappa+\epsilon}H]^2} \tag{28}$$

In view of (18) and the observation that $\tilde{D}$ is positive, this must also be negative, which means that, for values of N_γ less than the critical value, the efficiency of a foam displacement can be raised by increasing the gas-aqueous solution surface tension. The optimum value for N_γ is only slightly less than the critical value. Since the magnitude of $\partial v^*_{(w)}/\partial R^*$ is on the order of $R^{*2}N_{\kappa+\epsilon}$ times that of $\partial^2 v^*_{(w)}/\partial N_\gamma \partial R^*$ (estimating N_γ to be of order unity), the effect will be largest when the surface viscosities are small.

In contrast, Kanda and Schechter (1976) state that in their experimental studies the efficiency of a foam displacement was raised by decreasing the surface tension. From their data, it appears that N_γ based upon the mean pore diameter was considerably larger than unity. Consequently, they may have seen displacement only in the larger pores. As the interfacial tension was decreased, displacement took place in a larger fraction of the pores, resulting in an enhanced displacement efficiency.

EFFECT OF SURFACE VISCOSITIES

From (1)

$$\frac{\partial v^*_{(w)}}{\partial N_{\kappa+\epsilon}} = -R^{*2}H(R^*A - N_\gamma G)(\widetilde{D} + R^* N_{\kappa+\epsilon} H)^{-2} \tag{29}$$

By (17) and (20), this derivative must always be negative, and we can say that, for values of N_γ less than the critical value, the rate of displacement of a foam can be enhanced by decreasing the gas-water surface viscosities. This agrees with Kanda and Schechter's (1976) observation that breakthrough time increased as the surface shear viscosity increased. As suggested above, the foam may not have been displaced within the smaller pores in their experiments. The interpretation is that breakthrough time increased for the larger pores in which the foam was displaced.

From (17), (19), and (20) and the observation that $\widetilde{D}$ is positive, we reason that

$$\frac{\partial^2 v^*_{(w)}}{\partial N_{\kappa+\epsilon}\partial R^*} = -[R^{*2}AH(\widetilde{D} + R^* N_{\kappa+\epsilon} H) + 2R^*\widetilde{D}H(R^*A - N_\gamma G)][\widetilde{D} + R^* N_{\kappa+\epsilon} H]^{-3} \tag{30}$$

must also be negative. We conclude that, for values of N_γ less than the critical value, the efficiency of a foam displacement can be raised by increasing the gas-aqueous solution surface viscosities. This also agrees with the observations of Kanda and Schechter (1976). Since the magnitude of $\partial v^*_{(w)}/\partial R^*$ is on the order of $N_{\kappa+\epsilon}$ times that of $\partial^2 v^*_{(w)}/\partial N_{\kappa+\epsilon}\partial R^*$, the effect will be largest when the surface viscosities are small.

ACKNOWLEDGMENT

This work was supported by the Department of Energy (Contract No. ET-76-S-03-1809).

NOTATION

A = defined by Equation (7)
$d_{(s)}/dt$ = derivative with respect to time following a particle in the interface
D = defined by Equation (8)
$\widetilde{D}$ = defined by Equation (12)
E = defined by Equation (9)
$F^{(p)}$ = z component of the pressure force exerted by the water and gas phases on the pore wall.
$F^{(p)*}$ = defined by Equation (13)
$F^{(v)}_{(w)}$ = z component of the viscous force exerted by the water on the pore wall
$F^{(v)*}_{(w)}$ = defined by Equation (14)
$F^{(v)}_{(g)}$ = z component of the viscous force exerted by the gas on the pore wall
$F^{(v)*}_{(g)}$ = defined by Equation (15)
G = defined by Equation (10)
H = defined by Equation (11)
l = length of pores shown in Figure 1
$L_{(w)}$ = length of water segment
$L^*_{(w)}$ = defined by Equation (3)
N_γ = dimensionless surface tension defined by Equation (5)
$N_{\kappa+\epsilon}$ = dimensionless sum of surface viscosities defined by Equation (6)
$p_{(\text{ent})}$ = average pressure at entrance to system
$p_{(\text{ex})}$ = average pressure at exit from system
Δp = pressure drop over system, defined by Equation (16)
$|\nabla p|$ = magnitude of pressure gradient in porous medium
R = radius of the entrance and exit surfaces shown in Figures 2 and 3
R^* = defined by Equation (2)
$R_{(l)}, R_{(t)}$ = radii of the pore at the common lines formed with the leading and trailing phase interfaces
t = time
t^* = defined by Equation (4)
$v_{(w)}$ = average z component of velocity in aqueous phase
$v^*_{(w)}$ = defined by Equation (1)

Greek Letters

γ = gas-aqueous surfactant solution surface tension
ϵ = gas-aqueous surfactant solution surface shear viscosity
κ = gas-aqueous surfactant solution surface dilatational viscosity
$\mu_{(g)}$ = viscosity of gas
$\mu_{(w)}$ = viscosity of aqueous surfactant solution or water
$\mu_{(l)z}, \mu_{(t)z}$ = z component of the unit vectors that are tangent to the leading and trailing interfaces, normal to the common lines formed by these interfaces with the pore wall, and outwardly directed with respect to these interfaces
$\overset{(\sigma)}{\rho}_{(l)}, \overset{(\sigma)}{\rho}_{(t)}$ = surface mass densities of the leading and trailing interfaces

Superscript

$*$ = dimensionless quantity

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Manuscript received May 16, 1977; revision received April 6, and accepted October 5, 1978.

The Dynamic Behavior of a CSTR: Some Comparisons of Theory and Experiment

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Mathematical methods employed recently in a theoretical study by Uppal et al. (1974) are applied to the second-order homogeneous reaction between sodium thiosulfate and hydrogen peroxide and are combined with experimental investigations of that reaction using a nonadiabatic continuous stirred tank reactor (CSTR). A complete portrayal of the expected behavior of that reaction system is presented in parameter space. Some new experimental studies of reactor instabilities are presented and linked to that portrayal. Close agreement is shown between theoretical predictions and experimental data.

SCOPE

Recent publications by Uppal et al. (1974, 1976) have summarized, added to, and given order to the plethora of prior theoretical information on the classical problem regarding steady state multiplicity, stability, and oscillations in a continuous stirred tank reactor (CSTR) for a first-order, exothermic Arrhenius reaction. Publications of experimental investigations of these phenomena in homogeneous reaction systems had appeared, though they were sparse at that time. Among these were experiments by Vetjtasa and Schmitz (1970) and Chang and Schmitz (1975a,b) which employed the second-order liquid phase reaction between sodium thiosulfate and hydrogen peroxide. The present investigation employs this reaction system and amounts to a union between experimental studies and the analytical methods employed by Uppal et al. The general intention was to enhance the significance of both lines of research. Specifically, the objectives of the work were to elucidate completely the possible behavioral traits for the thiosulfate-peroxide reaction system, which has proved to be useful for laboratory tests and demonstrations of CSTR behavioral characteristics, and to relate these findings to previously reported experimental results; to examine the feasibility of using the existing experimental facility for conducting experimental tests of behavior predicted theoretically but not previously observed; and to conduct, with the guidance of theoretical results, feasible laboratory tests.

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0001-1541-79-2125-0289-$01.15.