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# Effect of Interfacial Viscosities upon Displacement in Capillaries with Special Application to Tertiary Oil Recovery

Washburn's equation has been generalized to explain the relative effects of the interfacial viscosities, interfacial tension, and wetting during displacement in a single, cylindrical capillary. The effect of the interfacial viscosities is to increase the resistance to displacement regardless of the wetting condition. The predictions of a prior qualitative theory for the relative effects of the interfacial viscosities and of interfacial tension during tertiary oil recovery are fully supported by this analysis. This discussion further indicates that the interfacial dilatational viscosity may be relatively more important than the interfacial shear viscosity.

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## SCOPE

Conventional production of light crudes usually concludes with a partial displacement of the oil remaining in the reservoir by either water or brine. The void volume in a permeable rock, such as that in which oil is found, may be thought of as many intersecting pores of varying diameters. Consider two neighboring pore networks having different mean radii that offer parallel paths for displacement. Oil (residual oil) will be trapped in that pore network through which the oil is displaced more slowly. For carefully selected, well-designed, good performing operations, at the end of conventional petroleum production there remains trapped in this way 50–70% of the oil originally in place (Geffen, 1973).

Slattery (1974, 1979) developed a qualitative theory for the

relative effects of interfacial tension, the interfacial viscosities, and wetting upon the displacement of this residual oil. He concludes that, when the interfacial tension is less than the critical value required for displacement and when the interfacial viscosities are large, the rate of displacement will be adversely affected by the interfacial viscosities.

There are no experimental data that either support or reject this theory.

The objective in what follows is to test this theory by developing a more complete, quantitative analysis for the relative effects of the interfacial viscosities, interfacial tension, and wetting during displacement in a single, cylindrical pore.

## CONCLUSIONS AND SIGNIFICANCE

Washburn's (1921) equation has been generalized to include the effects of the interfacial viscosities. The result is limited by assumptions that the Reynolds number  $N_{Re}$ , the capillary number  $N_{Ca}$ , and the Bond number  $N_{Bo}$  are all small compared with unity and that surface viscous forces dominate bulk viscous forces in the interface (the dimensionless sum of the interfacial viscosities  $N_{\sigma+\epsilon} \gg 1$ ).

The limited data available for the interfacial viscosities of proposed tertiary oil recovery systems indicate that the dimensionless sum of the interfacial viscosities  $N_{\sigma+\epsilon} \gg 1$ .

Tertiary oil displacements would normally be conducted with

relatively constant pressure differences between injection and production wells. The effect of the interfacial viscosities is to decrease the speed of displacement for a given pressure drop regardless of the wetting condition. Of the two interfacial viscosities, the interfacial dilatational viscosity may play the dominant role. This suggests that for a successful tertiary oil recovery system the interfacial viscosities, particularly the interfacial dilatational viscosity, should be as small as possible.

The conclusion of Slattery's (1974, 1979) qualitative theory for the effects of the interfacial viscosities in tertiary oil recovery is fully supported by this quantitative analysis, although this discussion further indicates that the interfacial dilatational viscosity may be relatively more important than the interfacial shear viscosity.

Residual oil is trapped in the form of blobs, each of which occupies possibly a large set of neighboring pores. Once such a blob has been trapped, it may or may not continue to be driven forward by the existing pressure gradient (Slattery, 1974; Oh and Slattery, 1979). If one of its many phase interfaces does advance, it will do so in an episodic fashion: it will slowly creep forward until an instability develops somewhere in the system, it will jump ahead a short distance, and it will begin another period of creeping motion. Since these Haines (1930) jumps take place very rapidly (Heller, 1968), the displacement of residual oil appears to be controlled by the period of slow advancement between jumps.

Slattery (1974, 1979) constructed a qualitative analysis of this displacement process. He postulated that the slow flow between jumps is an irregular, stick-slip motion (Yarnold, 1938). Such a motion can be understood in terms of the contact angle hysteresis to be expected on contaminated or roughened surfaces. It may consist of one or more pauses during which the contact angle measured through the advancing phase increases. These pauses are followed by an irregular motion, when the contact angle finally equals the critical value required for advancement of the common line or three-phase line of contact. In order to simplify his analysis, Slattery assumed that the rate limiting steps in this displacement process are the pauses during the creeping motion between jumps. His analysis is for that period of time in which the common line is stationary.

A number of conclusions were drawn from this qualitative analysis (Slattery, 1974). For present purposes, two are important:

- There is a critical value for the surface tension above which no residual oil can be recovered by displacement.
- When the interfacial tension is less than the critical value and the interfacial viscosities are large, equal percentage reductions of the interfacial tension and the interfacial viscosities are equally important. When the interfacial viscosities are small, it is more important to reduce the interfacial tension.

This is a stronger statement about the effects of the surface viscosities than that made previously (Slattery, 1974). Equation 42 of that article may be written as

$$\frac{\partial v_{(0)}^*}{\partial \ln N_{\gamma}^*} = - \frac{GN_{\gamma}^*}{l^{**}D + N_{\gamma}^*H/l^{**}}$$

Similarly, Eq. 43 may be expressed as

$$\frac{\partial v_{(0)}^*}{\partial \ln N_{\gamma}^*} = - \frac{N_{\gamma}^* (A - N_{\gamma}^* G) (H/l^{**})}{(l^{**}D + N_{\gamma}^*H/l^{**})^2}$$

Since the magnitudes of  $A$ ,  $G$ ,  $D$ ,  $H$ , and  $l^{**}$  are all of the order unity and since the critical value of  $N_{\gamma}^*$  is unity, conclusion (ii) follows.

At the present time, there are no experimental data that either support or reject conclusion ii. It is only encouraging that the predictions of a similar analysis for foam displacement (Slattery, 1979) are supported by the limited observations of Kanda and Schechter (1976).

In the absence of experimental data and to provide a better basis for analyzing experimental data as it does become available, we develop in what follows a *quantitative* analysis for the relative effects of interfacial viscosities, interfacial tension, and wetting during displacement in a single, cylindrical pore. In contrast with the prior *qualitative* analysis of this problem (Slattery, 1974, 1979), the common line will be assumed to advance with a constant speed of displacement.

## STATEMENT OF PROBLEM

Figure 1 shows phase 1 displacing phase 2 in a cylindrical capillary of radius  $R^*$ . The common line  $C$ , formed by the intersection of the fluid-fluid interface  $\Sigma$  with the capillary wall, moves with a speed of displacement  $V^*$ . The contact angle  $\alpha$  is measured

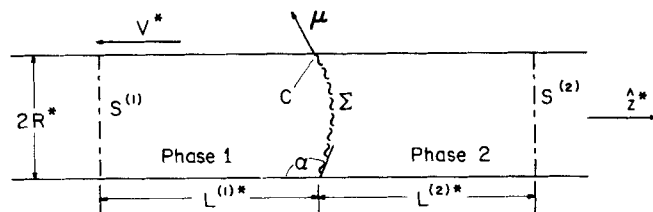


Figure 1. Phase 1 displacing phase 2 in a cylindrical capillary viewed with respect to a frame of reference in which the common line  $C$  is stationary.

through phase 1. The imaginary surfaces  $S^{(1)}$  and  $S^{(2)}$  are fixed with respect to  $\Sigma$ .

Our objective is to estimate the speed of displacement as a function of the pressure drop between  $S^{(1)}$  and  $S^{(2)}$ .

The following physical assumptions will be made in our development.

- The fluids are incompressible and Newtonian:

$$\begin{aligned} S^{(j)*} &\equiv T^{(j)*} + p^{(j)*} I \\ &= 2\mu^{(j)*} D^{(j)*} \end{aligned} \quad (1)$$

Here  $S^{(j)*}$  is the viscous portion of the stress tensor in phase  $j$ ;  $T^{(j)*}$  is the stress tensor;  $p^{(j)*}$  the pressure;  $I$  the identity tensor that transforms vectors into themselves;  $\mu^{(j)*}$  the shear viscosity for phase  $j$ ;

$$D^{(j)*} \equiv \frac{1}{2} [\nabla v^{(j)*} + (\nabla v^{(j)*})^T] \quad (2)$$

is the rate of deformation tensor and  $v^{(j)*}$  is the velocity vector.

- The fluid-fluid interfacial stress-deformation behavior can be represented by the linear Boussinesq surface fluid model (Boussinesq, 1913; Scriven, 1960)

$$\begin{aligned} S^{(\sigma)*} &\equiv T^{(\sigma)*} - \gamma^* P \\ &= [\kappa^* - \epsilon^* \text{div}_{(\sigma)} v^{(\sigma)*}] P + 2\epsilon^* D^{(\sigma)*} \end{aligned} \quad (3)$$

Here  $S^{(\sigma)*}$  is the viscous portion of the surface stress tensor;  $T^{(\sigma)*}$  the surface stress tensor;  $\gamma^*$  the interfacial tension;  $P$  the projection tensor that transforms vectors defined on the dividing surface into their tangential components;  $\kappa^*$  the interfacial dilatational viscosity;  $\epsilon^*$  the interfacial shear viscosity;  $v^{(\sigma)*}$  the surface viscosity vector;

$$D^{(\sigma)*} \equiv \frac{1}{2} [P \cdot \nabla_{(\sigma)} v^{(\sigma)*} + (\nabla_{(\sigma)} v^{(\sigma)*})^T \cdot P] \quad (4)$$

the surface rate of deformation tensor;  $\nabla_{(\sigma)}$  the surface gradient operator and  $\text{div}_{(\sigma)}$  the corresponding surface divergence operation (Wei et al., 1974; Briley et al., 1976).

- The location of the dividing surface can be arbitrarily specified for any choice of reference state (see footnote 1 of Slattery et al., 1980). We will take our reference state to be the static state corresponding to the limit in which the speed of displacement of the fluid-fluid interface is zero. Let  $\rho^{(\sigma)*}$  denote the total surface mass density and  $\rho_0^{(\sigma)*}$  the total surface mass density in the reference state. The dividing surface in this reference state is located such that it is sensibly coincident with the interface and

$$\frac{\rho_0^{(\sigma)*}}{\rho^{(2)*} R^*} \ll 1 \quad (5)$$

where  $\rho^{(2)*}$  is the total mass density in phase 2.

- Inertial forces are neglected with respect to viscous forces within the bulk phases, which implies in the following analysis that

$$N_{Re}^{(j)} \equiv \frac{\rho^{(j)*} V^* R^*}{\mu^{(j)*}} \ll 1 \quad (6)$$

where  $N_{Re}^{(j)}$  is the Reynolds number for phase  $j$ .

- The displacement is stable in the sense that, in the frame of reference fixed with respect to the common line, the flow is independent of time.

- We require

$$N_{Bo} \equiv \frac{|\rho^{(1)*} - \rho^{(2)*}| g^* R^{*2}}{\gamma^*} \ll 1 \quad (7)$$

which means that the effect of gravity upon the configuration of the interface can be neglected. In our analysis, we shall also neglect the effect of gravity upon the bulk phases. If one wishes to include this effect in considering a vertical capillary, it is necessary only to substitute the modified pressure  $P^* = p^* + \rho^* \varphi^*$  for pressure  $p^*$  in Cauchy's first law (46), where  $\varphi^*$  is the potential energy per unit mass (Slattery, 1981). Besides  $p^*$  being replaced by  $P^*$  in Eqs. 61, 62, 64, and 65, additional terms arise that correct for the difference in potential energy per unit volume  $\rho^* \varphi^*$  at the interfaces.

(g) In the dividing surface, interfacial viscous forces dominate bulk viscous forces, since we will demand

$$N_{\kappa+\epsilon} \equiv \frac{\kappa^* + \epsilon^*}{\mu^{(2)*} R^*} \gg 1 \quad (8)$$

(h) The capillary number  $N_{ca}$  is small,

$$N_{ca} \equiv \frac{\mu^{(2)*} V^*}{\gamma^*} \ll 1 \quad (9)$$

(i) The speed of displacement  $V^*$  is sufficiently small that surfactant concentration in the dividing surface may be considered nearly independent of position and that interfacial tension and the two interfacial viscosities may be treated as constants. Appendix A suggests that this is reasonable in the context of oil displacement.

(j) The surfaces  $S^{(1)}$  and  $S^{(2)}$  are sufficiently far away from the phase interface  $\Sigma$  that the bulk phases may be assumed to be in Poiseuille flow at these surfaces.

(k) Consider the system composed of those portions of phases 1 and 2 in the tube between  $S^{(1)}$  and  $S^{(2)}$ . In forming the integral mechanical energy balance for this system, we have estimated the rate of viscous dissipation of mechanical energy within the bulk phases in this system as though these phases were in Poiseuille flow everywhere.

(l) In this integral mechanical energy balance, we have neglected the effect of the viscous surface stress acting on the common line, assuming that the contact angle measured at the common line is unaffected by small perturbations of the capillary number  $N_{ca}$  from zero. This assumption is supported by experimental observations of the contact angle at a small distance from the common line. [See for example Jiang et al. (1979) for a review.] Alternatively, we may argue that the interfacial velocity at the common line is continuous with the wall velocity. In this case, the work done by the surface viscous stresses on the wall is again zero in a frame of reference in which the wall is stationary. This is consistent with Berry (1974) and White (1977), who have argued that for a liquid-gas-solid system the van der Waals forces between the solid and liquid restrict the contact angle measured within the immediate neighborhood of the common line to be  $0^\circ$  or  $180^\circ$ .

(m) We have also neglected the area integral of the interfacial viscous dissipation in the inner region near the common line compared to the dissipation in the rest of the interface. This appears reasonable, since in any well posed problem the viscous dissipation must be everywhere bounded and the area of the interface in the inner region is negligible compared to the remainder of the interface (see following discussion for explanation of inner and outer expansions).

(n) In forming this integral mechanical energy balance, we have further assumed that the configuration of the fluid-fluid interface may be represented as a spherical segment (correct to the lowest order in  $N_{ca}$ ).

When velocity is assumed to be continuous across all phase interfaces, unbounded forces are predicted within the neighborhood of a common line moving over a rigid solid (Moffatt, 1964; Huh and Scriven, 1971; Dussan V. and Davis, 1974). These unbounded forces can be eliminated, by relaxing the no-slip boundary condition on the solid within the immediate vicinity of the common line (Hocking, 1976, 1977; Dussan V., 1976; Huh and Mason, 1977; Levine et al., 1980).

The slip length, a measure of the distance over which slip is postulated to be important, varies with the slip model, but it is assumed to be of the order of molecular dimensions. The slip ratio, the ratio of the slip length to a macroscopic length scale of the system, is invariably small.

In certain cases, one can obtain solutions valid for all slip ratios (Hocking, 1976; Dussan V., 1976). More generally, one should expect to seek a perturbation solution valid only for small values of the slip ratio. This expansion is singular, since the lowest order approximation, which corresponds to the no-slip problem, predicts unbounded forces. By using matched asymptotic expansions, the flowfield separates into two regions: the inner region, scaled by the slip length and valid in the immediate neighborhood of the common line, and the outer region, scaled by a macroscopic dimension of the system and valid throughout the remainder of the flowfield. The singular perturbation analysis indicates that at the lowest order the velocity in the outer region is not directly affected by the dynamics in the inner region (Kafka and Dussan V., 1979).

In the analysis that follows, we will be interested only in the flow outside the immediate neighborhood of the common line. The slip ratio is assumed to be so small, that we seek only the lowest order approximate solution as a function of this variable. For these reasons, we need not specify the details of the slip model.

## INTERFACIAL VELOCITY DISTRIBUTION IN OUTER REGION

In our analysis, all starred variables are dimensional. It will be convenient to introduce as dimensionless variables

$$\begin{aligned} \bar{r} &\equiv \bar{r}^*/R^* \\ H &\equiv R^* H^* \\ \mathbf{v}^{(j)} &\equiv \frac{\mathbf{v}^{(j)*}}{V^*} \\ \mathbf{v}^{(\sigma)} &\equiv \frac{\mathbf{v}^{(\sigma)*}}{V^*} \\ S^{(\sigma)} &\equiv \frac{R^* S^{(\sigma)*}}{(\kappa^* + \epsilon^*) V^*} \\ p^{(j)} &\equiv \frac{R^* p^{(j)*}}{\gamma^*} \\ S^{(j)} &\equiv \frac{R^* S^{(j)*}}{\mu^{(j)*} V^*} \end{aligned} \quad (10)$$

in which  $(\bar{r}, \bar{\theta}, \bar{\varphi})$  are the spherical coordinates referred to in Figure 2 and  $H^*$  is the mean curvature of the interface.

Our first objective is to construct a perturbation solution for the displacement shown in Figure 1, correct to the zeroth order in  $N_{ca}$ .  $(N_{\kappa+\epsilon})^{-1}$ ,  $N_{Re}^{(1)}$ ,  $N_{Re}^{(2)}$ ,  $N_{Bo}$ , and the slip ratio. We shall identify  $p_0$ ,  $\mathbf{v}_0$ ,  $\mathbf{v}_0^{(\sigma)}$ , and  $H_0$  as variables that are zeroth order in all perturbation parameters.

The Navier-Stokes equation for each phase requires

$$\begin{aligned} N_{Re}^{(1)} N_{ca} N_\mu (\nabla \mathbf{v}^{(1)} \cdot \mathbf{v}^{(1)}) &= -\nabla p^{(1)} + N_{ca} N_\mu \text{div}(\nabla \mathbf{v}^{(1)}) \\ N_{Re}^{(2)} N_{ca} (\nabla \mathbf{v}^{(2)} \cdot \mathbf{v}^{(2)}) &= -\nabla p^{(2)} + N_{ca} \text{div}(\nabla \mathbf{v}^{(2)}) \end{aligned} \quad (11)$$

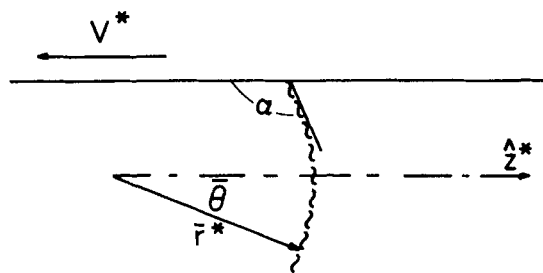


Figure 2. Spherical coordinate system for frame of reference in which the common line at  $\bar{\theta} = \pi/2$  is stationary. When  $N_{ca} = 0$ , the spherical phase interface coincides with a coordinate surface.

where we have introduced the bulk viscosity ratio

$$N_\mu \equiv \mu^{(1)*}/\mu^{(2)*} \quad (12)$$

At the lowest order in all perturbation parameters, Eq. 11 reduces to

$$\nabla p_0^{(j)} = 0 \quad (13)$$

which means that the pressure in each phase is a constant independent of position.

In view of assumptions (c) and (i), the overall mass balance at the phase interface and the mass balance for surfactant at the phase interface (Scriven, 1960; Slattery, 1967, 1980; Deemer and Slattery, 1978) place no constraints on the surface viscosity distribution. They are satisfied by saying that the normal component of velocity in each phase measured relative to the dividing surface is zero in the limit as the dividing surface is approached.

The normal component of the jump momentum balance requires (Scriven, 1960; Slattery, 1967, 1980; Deemer and Slattery, 1978)

$$2H\xi - p^{(1)}\xi^{(1)} - p^{(2)}\xi^{(2)} + N_{ca}(N_{x+\epsilon}\text{div}_{(o)}S^{(o)} + N_\mu S^{(1)} \cdot \xi^{(1)} + S^{(2)} \cdot \xi^{(2)}) = 0 \quad (14)$$

Here  $\xi$  is the unit normal to the phase interface and  $\xi^{(j)}$  is the unit normal to the phase interface pointing into phase  $j$ ; the product  $H\xi$  has the same sign, independent of the direction chosen for  $\xi$ . To the lowest order in all perturbation parameters, Eq. 14 reduces to

$$2H_0\xi_0 - p_0^{(1)}\xi_0^{(1)} - p_0^{(2)}\xi_0^{(2)} = 0 \quad (15)$$

so long as we assume that  $N_{ca}N_{x+\epsilon} \ll 1$ . Since the pressures in each phase are constants independent of position, the interface is a segment of a sphere at the lowest order.

The tangential component of the jump momentum balance requires (Scriven, 1960; Slattery, 1967, 1980; Deemer and Slattery, 1978)

$$P \cdot (N_{x+\epsilon}\text{div}_{(o)}S^{(o)} + N_\mu S^{(1)} \cdot \xi^{(1)} + S^{(2)} \cdot \xi^{(2)}) = 0 \quad (16)$$

To the zeroth order in  $(N_{x+\epsilon})^{-1}$  and the other perturbation parameters, it appears that the effect of the bulk viscous forces on the interface can be neglected with respect to the surface viscous forces and Eq. 16 reduces to

$$P \cdot \text{div}_{(o)}S_0^{(o)} = 0 \quad (17)$$

Assuming that the zeroth perturbation of the surface velocity distribution takes the form

$$\begin{aligned} v_{0\theta}^{(o)} &= v_{0\theta}^{(o)}(\bar{\theta}) \\ v_{0r}^{(o)} &= v_{0r}^{(o)} = 0 \end{aligned} \quad (18)$$

the zeroth perturbation of Eq. 17 reduces to (Scriven, 1960)

$$\frac{d}{d\bar{\theta}} \left[ \frac{1}{\sin \bar{\theta}} \frac{d}{d\bar{\theta}} (v_{0\theta}^{(o)} \sin \bar{\theta}) \right] + \frac{2\epsilon^*}{\kappa + \epsilon^*} v_{0\theta}^{(o)} = 0 \quad (19)$$

We will require

$$\text{at } \bar{\theta} = \left| \alpha - \frac{\pi}{2} \right|: \quad v_{0\theta}^{(o)} = A \quad (20)$$

leaving  $A$  for the moment unspecified. The solution to Eq. 19 consistent with Eq. 20 is

$$v_{0\theta}^{(o)} = A \frac{P_\nu^{-1}(\cos \bar{\theta})}{P_\nu^{-1}(\sin \alpha)} \quad (21)$$

in which  $P_\nu^{-1}$  is the associated Legendre function of the first kind (Abramowitz and Stegun, 1965) and  $\nu$  satisfies

$$\nu(\nu + 1) = \frac{2\epsilon^*}{\kappa^* + \epsilon^*} \quad (22)$$

## SOLUTION FOR A

In order to determine  $A$  in Eq. 20, we must examine the implications of conservation of mass and of momentum within the adjacent bulk phases.

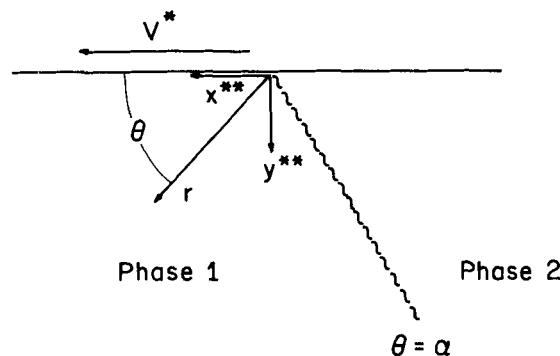


Figure 3. Polar coordinate system centered on common line viewed with respect to a frame of reference in which the common line is stationary.

Let us begin by thinking in terms of a cylindrical coordinate system  $(\hat{r}^*, \theta, \hat{z}^*)$  in which the axis of the tube coincides with the  $\hat{z}^*$  coordinate axis and the  $\hat{z}^*$  axis points in the direction of displacement. Let

$$\hat{r} \equiv \hat{r}^*/R^* \quad \hat{z} \equiv \hat{z}^*/R^* \quad (23)$$

be the corresponding dimensionless coordinates. We seek a two-dimensional solution for the velocity distribution in the two bulk phases ( $j = 1, 2$ ):

$$\begin{aligned} v_{0r}^{(j)} &= v_{0r}^{(j)}(\hat{r}, \hat{z}) \\ v_{0z}^{(j)} &= v_{0z}^{(j)}(\hat{r}, \hat{z}) \\ v_{0\theta}^{(j)} &= 0 \end{aligned} \quad (24)$$

Since our particular concern is to identify  $A$ , we will focus our attention upon the outer solution for the velocity distribution in the limit as the common line is approached. Let  $\delta^*$  be a length much greater than the slip length that characterizes a small neighborhood surrounding the common line, in the majority of which the outer solution must be used to describe the velocity distribution. Define

$$\begin{aligned} x^{**} &\equiv -\frac{\hat{z}}{N_\delta} & y^{**} &\equiv \frac{1 - \hat{r}}{N_\delta} \\ N_{x+\epsilon}^{**} &\equiv \frac{N_{x+\epsilon}}{N_\delta} \end{aligned} \quad (25)$$

where

$$N_\delta \equiv \delta^*/R^* \quad (26)$$

To the lowest order in  $N_\delta$ , the displacement problem simplifies to the flow shown in Figure 3: flow in the immediate neighborhood of the common line formed as a flat plate passes through a fluid-fluid interface at an angle  $\alpha$  such that the interface remains a plane.

This problem is more conveniently analyzed in terms of the dimensionless polar coordinates  $(r, \theta)$  centered on the common line in Figure 3 and defined such that

$$\begin{aligned} x^{**} &= r \cos \theta \\ y^{**} &= r \sin \theta \end{aligned} \quad (27)$$

The equation of continuity for each of the incompressible bulk phases may be identically satisfied by expressing the velocity distributions in terms of  $\psi^{(j)}$  ( $j = 1, 2$ ), the lowest order terms in expansions for the stream functions in terms of  $N_\delta$ :

$$\begin{aligned} v_{0r}^{(j)} &= -\frac{1}{r} \frac{\partial \psi^{(j)}}{\partial \theta} \\ v_{0\theta}^{(j)} &= \frac{\partial \psi^{(j)}}{\partial r} \end{aligned} \quad (28)$$

The only nonzero component of the curl of the Navier-Stokes equation may consequently be expressed as

$$\left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right] \psi^{(j)} = 0 \quad (29)$$

The frame of reference is defined such that the common line is stationary and the tube wall is in motion, which implies

$$\text{at } \theta = 0: \quad \frac{1}{r} \frac{\partial \psi^{(1)}}{\partial \theta} = -1 \quad (30)$$

$$\text{at } \theta = \pi: \quad \frac{1}{r} \frac{\partial \psi^{(2)}}{\partial \theta} = 1 \quad (31)$$

The tangential component of velocity must be continuous at the fluid-fluid interface,

$$\text{at } \theta = \alpha: \quad \frac{\partial \psi^{(1)}}{\partial \theta} = \frac{\partial \psi^{(2)}}{\partial \theta} \quad (32)$$

Very far upstream of the fluid-fluid interface, we have Poiseuille flow. Since we are free to specify  $\psi^{(1)} = 0$  at one point on the tube wall, this implies

$$\text{as } \hat{z} \rightarrow -\infty: \quad \text{The Stream Function} \rightarrow -\frac{\hat{r}^2}{2} (1 - \hat{r}^2) \quad (33)$$

Because the normal component of velocity is zero on the tube wall, it follows that

$$\text{at } \theta = 0: \quad \psi^{(1)} = 0 \quad (34)$$

Equation 33 tells us that along the centerline streamline the stream function equals zero. We require that this centerline streamline be continuous with all of the streamlines in the fluid-fluid phase interface consistent with the two-dimensional flow (Eq. 24) and that the component of velocity normal to the interface be zero:

$$\text{at } \theta = \alpha: \quad \psi^{(1)} = \psi^{(2)} = 0 \quad (35)$$

Reversing this same argument in phase 2, we conclude

$$\text{at } \theta = \pi: \quad \psi^{(2)} = 0 \quad (36)$$

To the lowest order in  $N_\delta$ , the normal component of the jump momentum balance at the fluid-fluid interface is satisfied identically. The tangential component reduces to

at  $\theta = \alpha$ :

$$N_{\delta}^{**} \frac{\partial^2}{\partial r^2} \left( \frac{1}{r} \frac{\partial \psi^{(1)}}{\partial \theta} \right) + \frac{1}{r^2} \frac{\partial^2 \psi^{(2)}}{\partial \theta^2} - \frac{N_\mu}{r^2} \frac{\partial^2 \psi^{(1)}}{\partial \theta^2} = 0 \quad (37)$$

The work of Huh and Scriven (1971) suggests that

$$\psi_p^{(1)} = r(C_1 \sin \theta + C_2 \theta \sin \theta + C_3 \theta \cos \theta) \quad (38)$$

$$\psi_p^{(2)} = r(C_4 \sin \theta + C_5 \cos \theta + C_6 \theta \sin \theta + C_7 \theta \cos \theta) \quad (39)$$

$$C_1 = -1 - C_3$$

$$C_2 = \frac{\sin^2 \alpha}{D} \left\{ \sin^2 \alpha - (\alpha - \pi)^2 + \frac{1}{N_\mu} [\alpha(\alpha - \pi) - \sin^2 \alpha] \right\}$$

$$C_3 = \frac{\sin 2\alpha}{2D} \left\{ \sin^2 \alpha - (\alpha - \pi)^2 + \frac{1}{N_\mu} [\alpha(\alpha - \pi) - \sin^2 \alpha - \pi \tan \alpha] \right\}$$

$$C_4 = -1 - \pi C_6 - C_7$$

$$C_5 = \pi C_7$$

$$C_6 = \frac{\sin^2 \alpha}{D} \left[ \sin^2 \alpha - \alpha(\alpha - \pi) + \frac{1}{N_\mu} (\alpha^2 - \sin^2 \alpha) \right]$$

$$C_7 = \frac{\sin 2\alpha}{2D} \left[ \sin^2 \alpha - \alpha(\alpha - \pi) - \pi \tan \alpha + \frac{1}{N_\mu} (\alpha^2 - \sin^2 \alpha) \right]$$

$$D \equiv \left( \frac{1}{2} \sin 2\alpha - \alpha \right) [(\alpha - \pi)^2 - \sin^2 \alpha] + \frac{1}{N_\mu} \left( \alpha - \pi - \frac{1}{2} \sin 2\alpha \right) (\alpha^2 - \sin^2 \alpha) \quad (40)$$

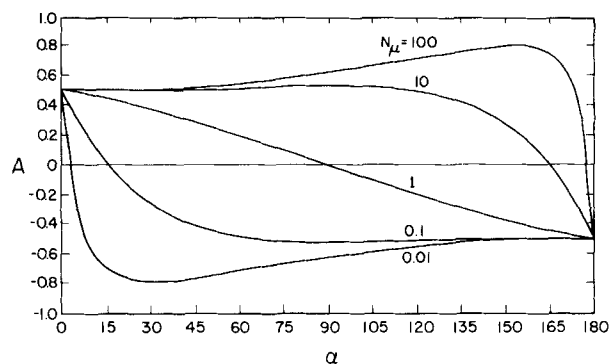


Figure 4. Function A defined by Eq. 45.

is a particular solution to Eqs. 29–32 and 34–37.

The general solution takes the form

$$\psi^{(j)} = \psi_p^{(j)} + \sum_{m=1}^{\infty} B_m^{(j)} \Phi_m^{(j)} \quad (41)$$

where the eigenfunctions  $\Phi_m^{(j)}$  are solutions of Eq. 29 consistent with the homogeneous boundary conditions

$$\text{at } \theta = 0: \quad \frac{\partial \psi^{(1)}}{\partial \theta} = 0 \quad (42)$$

$$\text{at } \theta = \pi: \quad \frac{\partial \psi^{(2)}}{\partial \theta} = 0 \quad (43)$$

as well as Eqs. 32 and 34–37. The constants  $B_m^{(j)}$  are arbitrary, since boundary conditions have not been specified as  $r \rightarrow \infty$ . The eigensolutions may be found by separation of variables. In the limit as  $r \rightarrow 0$ , the eigenvalues are roots of (Giordano, 1980)

$$\begin{aligned} & \{\sin(\lambda_m \alpha) \sin[(\lambda_m - 2)\alpha] - \lambda_m(\lambda_m - 2) \sin^2 \alpha\} \\ & \{\sin[\lambda_m(\pi - \alpha)] \sin[(\lambda_m - 2)(\pi - \alpha)] \\ & - \lambda_m(\lambda_m - 2) \sin^2 \alpha\} = 0 \quad (44) \end{aligned}$$

In order that velocities be bounded, we discard all roots whose real part is less than 1. There are no roots of Eq. 44 whose real part equals 1. This means that the particular solution  $\psi_p^{(j)}$  ( $j = 1, 2$ ), which is  $O(r)$ , dominates the eigensolutions as the common line is approached.

From Eqs. 28 and 38–41, we conclude that

$$\begin{aligned} A & \equiv - \lim_{r \rightarrow 0} v_r^{(\sigma)} \\ & = -\{N_\mu(\alpha \cos \alpha - \sin \alpha)[\sin^2 \alpha - (\alpha - \pi)^2] \\ & \quad + [(\alpha - \pi) \cos \alpha - \sin \alpha](\alpha^2 - \sin^2 \alpha)\} \\ & \quad \{N_\mu(\sin \alpha \cos \alpha - \alpha)[(\alpha - \pi)^2 - \sin^2 \alpha] \\ & \quad + (\alpha - \pi - \sin \alpha \cos \alpha)(\alpha^2 - \sin^2 \alpha)\}^{-1} \quad (45) \end{aligned}$$

Figure 4 shows A as a function of  $N_\mu$  and  $\alpha$ .

The values for A in the limits as  $\alpha \rightarrow 0^\circ$  and  $\alpha \rightarrow 180^\circ$  initially appear to be incorrect in Figure 4, since we would expect the interfacial velocity to approach the velocity of the wall. The answer is that this is a result of an analysis for the outer solution of the velocity distribution. Compatibility with the velocity boundary condition at the wall would be imposed in the inner solution.

## INTEGRAL MECHANICAL ENERGY BALANCE

Our objective is to estimate the pressure drop between  $S^{(1)}$  and  $S^{(2)}$  in Figure 1 required to displace phase 2 at a given volume rate of flow. The surfaces  $S^{(1)}$  and  $S^{(2)}$  move with the speed of displacement of the common line. This estimate will be based upon an integral mechanical energy balance for the system  $R_{(sys)}$  consisting of those portions of phases 1 and 2 in the tube between  $S^{(1)}$  and  $S^{(2)}$ . We will examine this system in a frame of reference in which the wall is fixed.

This integral mechanical energy balance may be derived by taking the scalar product of Cauchy's first law with the velocity vector and integrating the result over the volume occupied by the system. Since inertial forces have been neglected (assumption d), Cauchy's first law reduces for each phase to ( $j = 1, 2$ )

$$\text{div } \mathbf{T}^{(j)*} = 0 \quad (46)$$

Taking the scalar product of this with the velocity vector and integrating the result over the volume occupied by the system  $R_{(\text{sys})}$ , we find

$$\begin{aligned} \int_{R(\text{sys})} \mathbf{v}^* \cdot \text{div } \mathbf{T}^* dV \\ = - \int_{R(\text{sys})} \text{tr}(\mathbf{S}^* \cdot \nabla \mathbf{v}^*) dV^* + \int_{S(\text{sys})} \mathbf{v}^* \cdot \mathbf{T}^* \cdot \mathbf{n} dA^* \\ - \int_{\Sigma} \mathbf{v}^{(\sigma)*} \cdot (\mathbf{T}^{(1)*} \cdot \boldsymbol{\xi}^{(1)} + \mathbf{T}^{(2)*} \cdot \boldsymbol{\xi}^{(2)}) dA^* = 0 \end{aligned} \quad (47)$$

in which  $S_{(\text{sys})}$  is the closed surface bounding the system. In arriving at Eq. 47, we have applied Green's transformation (Slattery, 1981) separately to each phase and we have recognized that the equation of continuity requires for each of these incompressible fluids ( $j = 1, 2$ )

$$\text{div } \mathbf{v}^{(j)*} = 0 \quad (48)$$

Let us examine each of the terms in Eq. 47 separately.

Since both inertial forces and the effects of gravity have been neglected, the jump momentum balance requires (Slattery, 1980)

$$\text{on } \Sigma: \text{div}_{(\sigma)} \mathbf{T}^{(\sigma)*} + \mathbf{T}^{(1)*} \cdot \boldsymbol{\xi}^{(1)} + \mathbf{T}^{(2)*} \cdot \boldsymbol{\xi}^{(2)} = 0 \quad (49)$$

In view of Eq. 49, we can rearrange the final integral in Eq. 47 as

$$\begin{aligned} \int_{\Sigma} \mathbf{v}^{(\sigma)*} \cdot (\mathbf{T}^{(1)*} \cdot \boldsymbol{\xi}^{(1)} + \mathbf{T}^{(2)*} \cdot \boldsymbol{\xi}^{(2)}) dA^* \\ = - \int_{\Sigma} \mathbf{v}^{(\sigma)*} \cdot \text{div}_{(\sigma)} \mathbf{T}^{(\sigma)*} dA^* \\ = \int_{\Sigma} [\gamma^* \text{div}_{(\sigma)} \mathbf{v}^{(\sigma)*} + \text{tr}(\mathbf{S}^{(\sigma)*} \cdot \mathbf{D}^{(\sigma)*})] dA^* \\ - \int_C (\gamma^* \mathbf{v}^{(\sigma)*} \cdot \boldsymbol{\mu} + \mathbf{v}^{(\sigma)*} \cdot \mathbf{S}^{(\sigma)*} \cdot \boldsymbol{\mu}) ds^* \end{aligned} \quad (50)$$

In the second line, we have employed Green's transformation for a surface (McConnell, 1957).

By another application of Green's transformation for a surface, we can observe

$$\begin{aligned} \int_{\Sigma} \text{div}_{(\sigma)} \mathbf{v}^{(\sigma)*} dA^* \\ = \int_C \mathbf{v}^{(\sigma)*} \cdot \boldsymbol{\mu} ds^* - \int_{\Sigma} 2H^* \mathbf{v}^{(\sigma)*} \cdot \boldsymbol{\xi} dA^* \end{aligned} \quad (51)$$

By means of Eqs. 50 and 51, Eq. 47 can be written in terms of dimensionless variables as

$$\begin{aligned} \int_{S(\text{sys})} (-p \mathbf{v} \cdot \mathbf{n} + N_{ca} \mathbf{v} \cdot \mathbf{S} \cdot \mathbf{n}) dA \\ = N_{ca} \int_{R(\text{sys})} \text{tr}(\mathbf{S} \cdot \nabla \mathbf{v}) dV \\ + \int_{\Sigma} [-2H \mathbf{v}^{(\sigma)} \cdot \boldsymbol{\xi} + N_{ca} N_{x+\epsilon} \text{tr}(\mathbf{S}^{(\sigma)} \cdot \mathbf{D}^{(\sigma)})] dA \\ - N_{ca} N_{x+\epsilon} \int_C \mathbf{v}^{(\sigma)} \cdot \mathbf{S}^{(\sigma)} \cdot \boldsymbol{\mu} ds \end{aligned} \quad (52)$$

In view of assumption (j),

$$\int_{S(\text{sys})} (-p \mathbf{v} \cdot \mathbf{n} + N_{ca} \mathbf{v} \cdot \mathbf{S} \cdot \mathbf{n}) dA = \frac{\pi R^* \Delta p^*}{\gamma^*} \quad (53)$$

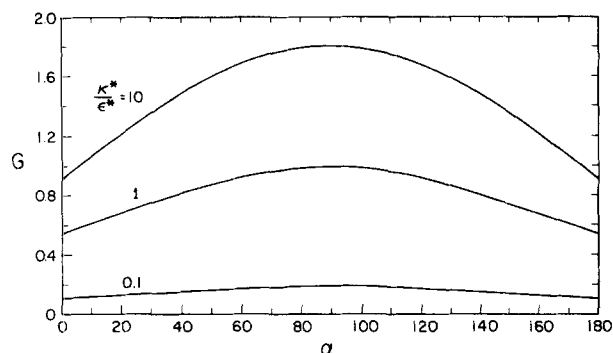


Figure 5. Function G defined by Eq. 58.

Here  $\Delta p^*$  is the pressure drop between  $S^{(1)}$  and  $S^{(2)}$  in Figure 1.

We will estimate the viscous dissipation within the bulk phases as though both phases were in Poiseuille flow everywhere (assumption k):

$$\int_{R(\text{sys})} \text{tr}(\mathbf{S} \cdot \nabla \mathbf{v}) dV = 8\pi \left\{ N_{\mu} \frac{L^{(1)*}}{R^*} + \frac{L^{(2)*}}{R^*} \right\} \quad (54)$$

Assumption (l) leads us to say

$$\int_C \mathbf{v}^{(\sigma)} \cdot \mathbf{S}^{(\sigma)} \cdot \boldsymbol{\mu} ds = 0 \quad (55)$$

With the approximation that the configuration of the interface can be represented as a spherical segment (assumption n)

$$\int_{\Sigma} 2H \mathbf{v}^{(\sigma)} \cdot \boldsymbol{\xi} dA = 2\pi \cos \alpha \quad (56)$$

Using Eq. 21 we can compute to the zeroth order in  $N_{ca}$

$$\int_{\Sigma} \text{tr}(\mathbf{S}_0^{(\sigma)} \cdot \mathbf{D}_0^{(\sigma)}) dA = 2\pi A^2 G \quad (57)$$

where we have defined

$$G \equiv (1 - \nu) \frac{p_{v-1}^{-1}(\sin \alpha)}{P_v^{-1}(\sin \alpha)} + (1 - \nu^2) \sin \alpha \quad (58)$$

Figure 5 shows G as a function of  $\kappa^*/\epsilon^*$  and  $\alpha$ . It is noteworthy that

$$\lim_{\frac{\kappa^*}{\epsilon^*} \rightarrow \infty} G \rightarrow 1 + \sin \alpha \quad (59)$$

and

$$\lim_{\frac{\kappa^*}{\epsilon^*} \rightarrow 0} G \rightarrow 0 \quad (60)$$

Finally, we can use Eqs. 53–57 in expressing Eq. 52 as

$$\begin{aligned} \frac{R^* \Delta p^*}{\gamma^*} = 8N_{ca} \left( N_{\mu} \frac{L^{(1)*}}{R^*} + \frac{L^{(2)*}}{R^*} \right) \\ - 2 \cos \alpha \left( 1 - N_{ca} N_{x+\epsilon} \frac{A^2 G}{\cos \alpha} \right) \end{aligned} \quad (61)$$

or

$$\begin{aligned} \frac{V^* \mu^{(2)*}}{|\Delta p^*| R^*} = \left[ \frac{\Delta p^*}{|\Delta p^*|} + 2N_{\gamma} \cos \alpha \right] \\ \left[ 8 \left( N_{\mu} \frac{L^{(1)*}}{R^*} + \frac{L^{(2)*}}{R^*} \right) + 2N_{x+\epsilon} A^2 G \right]^{-1} \end{aligned} \quad (62)$$

where

$$N_{\gamma} \equiv \frac{\gamma^*}{|\Delta p^*| R^*} \quad (63)$$

The function A is given by Eq. 45 (Figure 4) and the function G is given by Eq. 58 (Figure 5). Note that  $\Delta p^*$  as computed from Eq. 61 is approximately correct to first order in  $N_{ca}$ .

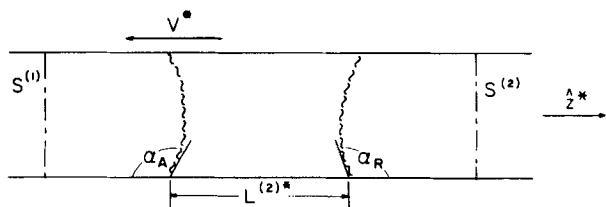


Figure 6. Segment of phase 2 being displaced through a capillary filled with phase 1. System is viewed with respect to a frame of reference in which the common lines are stationary.

For the displacement of a segment of phase 2 through a capillary filled with phase 1 in Figure 6, we can immediately say by analogy either

$$\frac{R^* \Delta p^*}{\gamma^*} = 8N_{ca} \left( N_{\mu} \frac{L^{(1)*}}{R^*} + \frac{L^{(2)*}}{R^*} \right) + 2(\cos \alpha_R - \cos \alpha_A) + 2N_{ca}N_{x+\epsilon} (A_A^2 G_A + A_R^2 G_R) \quad (64)$$

or

$$\frac{V^* \mu^{(2)*}}{|\Delta p^*| R^*} = \left[ \frac{\Delta p^*}{|\Delta p^*|} - 2N_{\gamma} (\cos \alpha_R - \cos \alpha_A) \right] \times \left[ 8 \left( N_{\mu} \frac{L^{(1)*}}{R^*} + \frac{L^{(2)*}}{R^*} \right) + 2N_{x+\epsilon} (A_A^2 G_A + A_R^2 G_R) \right]^{-1} \quad (65)$$

where

$$A_A = A(\alpha_A, N_{\mu})$$

$$A_R = A(\pi - \alpha_R, N_{\mu}^{-1}) \quad (66)$$

and

$$G_A = G(\alpha_A, x^*/\epsilon^*)$$

$$G_R = G(\pi - \alpha_R, x^*/\epsilon^*) \quad (67)$$

The subscript A refers to the advancing (left) interface in Figure 6 and the subscript R refers to the receding (right) interface. By  $L^{(1)*}$  we now refer to that portion of the capillary occupied by phase 1.

## DISCUSSION

Equation 61 reduces to the Washburn (1921) equation, when  $N_{x+\epsilon} = N_{\mu}^{-1} = 0$ . The Washburn equation describes the displacement of a gas by a liquid, when the effect of the interfacial viscosities can be neglected. Its validity has been tested experimentally for "clean" liquid-gas interfaces (Ligenza and Bernstein, 1951; Oliva and Joye, 1975; Fisher and Lark, 1979).

Tertiary oil displacements would normally be conducted with relatively constant pressure differences between injection and production wells. Equations 62 and 65 together with Figures 4 and 5 show that the effect of the interfacial viscosities is to decrease the speed of displacement for a given pressure drop regardless of the contact angle. The dimensionless group  $N_{x+\epsilon}$ , which characterizes the ratio of interfacial viscous forces to bulk viscous forces, has been assumed to be very large compared with unity in deriving these results (assumption g).

Limited data are available for the interfacial shear viscosities of proposed tertiary oil recovery systems (Wasan, 1978; Wasan et al., 1978; Jones et al., 1978). If we assume that  $R^* = 10 \mu\text{m}$  (Batra and Dullien, 1973), then  $N_{x+\epsilon} \gg 1$  for these systems.

The conclusion of Slattery's (1974, 1979) analysis for the effects of the interfacial viscosities in tertiary oil recovery (see ii of INTRODUCTION) is fully supported by this analysis. Appendix B (Sen and Slattery) further points out that, while both interfacial viscosities play important roles, the interfacial dilatational viscosity may be the more important of the two. In screening surfactant systems for potential use in tertiary oil recovery, we recommend those for which the interfacial viscosities are small and in particular

those for which the interfacial dilatational viscosity is small. Unfortunately, we currently know even less about the interfacial dilatational viscosity than we do about the interfacial shear viscosity.

Caution is advised in acting upon these conclusions, since it remains to be demonstrated *experimentally* that there is a correlation between recovery efficiency and the interfacial viscosities.

Equations 61 and 64 together with Figures 4 and 5 indicate that the effect of the interfacial viscosities is to increase the pressure drop for a given speed of displacement regardless of the contact angle. But in the context of tertiary oil recovery, their effect upon pressure drop for a given speed of displacement is not as dramatic as their effect upon the speed of displacement for a given pressure drop. Economic field displacement speeds are typically of the order  $3.5 \mu\text{m/s}$  (1 ft/d). The speed of displacement of an interface during the creeping motion between jumps in a single pore will be considerably smaller. Consequently,  $N_{ca}$  will be small (see also assumption h) and  $N_{ca}N_{x+\epsilon}$ , which characterizes the ratio of interfacial viscous forces to interfacial tension forces, may be either small or large compared with unity even though  $N_{x+\epsilon}$  is relatively large.

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## NOTATION

A	= defined by Eq. 45
$A_A, A_R$	= defined by Eq. 66
$B_m^{(j)}$	= constant appearing in Eq. 41
C	= common line (Figure 1)
$C_1, C_2, C_3, C_4$	= defined by Eq. 40
$C_5, C_6, C_7$	
d	= defined by Eq. B6
D	= defined by Eq. 40
$D^{(\sigma)*}$	= surface diffusion coefficient of surfactant
$D^{(i)*}$	= bulk diffusion coefficient of surfactant within phase i
$D^{(j)*}$	= rate of deformation tensor in phase j
$g^*$	= acceleration of gravity
G	= defined by Eq. 58
$G_A, G_R$	= defined by Eq. 67
$H^*$	= mean curvature of interface
H	= dimensionless mean curvature of interface defined by Eq. 10
I	= identity tensor that transforms every spatial vector field into itself
$j_{(s)}^{(\sigma)*}$	= surface mass flux of surfactant with respect to the surface mass-averaged velocity
$j_{(s)}^{(\sigma)}$	= dimensionless surface mass flux of surfactant, defined by Eq. A2
$k^{(i)*}$	= mass transfer coefficient used in Eq. A6
$L^{(1)*}$	= length shown in Figure 1; with respect to Figure 6, $L^{(1)*}$ refers to that portion of the system occupied by phase 1
$L^{(2)*}$	= length shown in Figures 1 and 6
n	= unit normal directed outward
$n_{(s)}^{(i)*}$	= mass flux of surfactant within phase i measured with respect to a fixed frame of reference
$n_{(s)}^{(i)}$	= dimensionless mass flux of surfactant within phase i measured with respect to a fixed frame of reference, defined by Eq. A2
$n_{(s)}^{(i)*}$	= characteristic magnitude of $n_{(s)}^{(i)*} \cdot \xi^{(i)}$

$N_{Bo}$  = Bond number, defined by Eq. 7  
 $N_{ca}$  = capillary number, defined by Eq. 9  
 $N^{(\sigma)}, N^{(i)}$  = dimensionless numbers defined by Eq. A3  
 $N_{Re}^{(j)}$  = Reynolds number of phase  $j$ , defined by Eq. 6  
 $N_\gamma$  = dimensionless interfacial tension, defined by Eq. 63  
 $N_\delta$  = dimensionless number defined by Eq. 26  
 $N_{\kappa+\epsilon}, N_\kappa, N_\epsilon$  = dimensionless interfacial viscosities defined by Eqs. 8 and B5  
 $N_{\kappa+\epsilon}^*$  = dimensionless number defined by Eq. 25  
 $N_\mu$  = viscosity ratio, defined by Eq. 12  
 $p^{(j)*}$  = pressure in phase  $j$   
 $p^{(j)}$  = dimensionless pressure in phase  $j$ , defined by Eq. 10  
 $\Delta p^*$  = pressure drop between  $S^{(1)}$  and  $S^{(2)}$  in Figure 1  
 $|\Delta p^*|$  = absolute value of  $\Delta p^*$   
 $P$  = projection tensor that transforms vectors defined on the dividing surface into their tangential components  
 $P_\nu^{-1}, P_{\nu-1}^{-1}$  = associated Legendre functions of the first kind  
 $r$  = dimensionless polar coordinate shown in Figure 3  
 $\bar{r}^*$  = spherical coordinate (Figure 2)  
 $\bar{r}$  = dimensionless spherical coordinate defined by Eq. 10  
 $\hat{r}^*$  = cylindrical radial coordinate  
 $\hat{r}$  = dimensionless cylindrical radial coordinate, defined by Eq. 23  
 $R_{sys}$  = portions of phases 1 and 2 between  $S^{(1)}$  and  $S^{(2)}$  in Figure 1  
 $R^*$  = capillary radius (Figure 1)  
 $S_{(sys)}$  = closed bounding surface of system in Figure 1  
 $S^{(1)}, S^{(2)}$  = imaginary surfaces shown in Figure 1  
 $S^{(j)*}$  = viscous portion of the stress tensor in phase  $j$   
 $S^{(j)}$  = dimensionless viscous portion of stress tensor in phase  $j$ , defined by Eq. 10  
 $S^{(\sigma)*}$  = viscous portion of the surface stress tensor  
 $S^{(\sigma)}$  = dimensionless viscous portion of the surface stress tensor defined by Eq. 10  
 $t^*$  = time  
 $t$  = dimensionless time, defined by Eq. A2  
 $T^{(j)*}$  = stress tensor in phase  $j$   
 $T^{(\sigma)*}$  = surface stress tensor  
 $v^{(j)*}$  = velocity vector in phase  $j$   
 $v^{(j)}$  = dimensionless velocity vector in phase  $j$ , defined by Eq. 10  
 $v^{(\sigma)*}$  = surface velocity vector  
 $v^{(\sigma)}$  = dimensionless surface velocity vector defined by Eq. 10 in text and by Eq. A2 in Appendix A  
 $v_{0r}^{(\sigma)}, v_{0\theta}^{(\sigma)}, v_{0\phi}^{(\sigma)}$  = dimensionless spherical components of the surface velocity vector which are zero order in  $N_{ca}$ ,  $(N_{\kappa+\epsilon})^{-1}$ ,  $N_{Re}^{(1)}, N_{Re}^{(2)}, N_{Bo}$ , and the slip ratio  
 $v_{0r}^{(j)}, v_{0\theta}^{(j)}, v_{0\phi}^{(j)}$  = dimensionless cylindrical components of the velocity vector in phase  $j$  which are zero order in  $N_{ca}$ ,  $(N_{\kappa+\epsilon})^{-1}$ ,  $N_{Re}^{(1)}, N_{Re}^{(2)}, N_{Bo}$ , and the slip ratio  
 $V^*$  = speed of displacement  
 $V$  = dimensionless speed of displacement defined by Eq. B2  
 $x^{**}$  = coordinate defined by Eq. 25 and shown in Figure 3  
 $y^{**}$  = coordinate defined by Eq. 25 and shown in Figure 3  
 $\hat{z}^*$  = cylindrical axial coordinate (Figure 1)  
 $\hat{z}$  = dimensionless cylindrical axial coordinate, defined by Eq. 23

#### Greek Letters

$\alpha$  = contact angle (Figure 1)  
 $\alpha_A$  = advancing contact angle in Figure 6  
 $\alpha_R$  = receding contact angle in Figure 6  
 $\gamma^*$  = interfacial tension

$\delta^*$  = length characterizing neighborhood around common line in outer solution  
 $\epsilon^*$  = interfacial shear viscosity  
 $\nu$  = defined by Eq. 22  
 $\xi^{(j)}$  = unit normal vector pointing into phase  $j$   
 $\pi$  = 3.14...  
 $\rho^{(j)*}$  = total mass density of phase  $j$   
 $\rho_{(s)}^{(j)*}$  = mass density of surfactant in phase 1  
 $\rho^{(\sigma)*}$  = total surface mass density  
 $\rho_{(s)}^{(\sigma)*}$  = surface mass density of surfactant  
 $\rho_{(s)}^{(\sigma)}$  = dimensionless surface mass density of surfactant, defined by Eq. A2  
 $\rho_{(s)o}^{(\sigma)*}$  = equilibrium surface mass density of surfactant in the limit  $N_{ca} \rightarrow 0$   
 $\rho_o^{(\sigma)*}$  = surface mass density in reference state  
 $\Sigma$  = fluid-fluid interface (Figure 1)  
 $\theta$  = polar coordinate shown in Figure 3  
 $\bar{\theta}$  = spherical coordinate (Figure 2)  
 $\hat{\theta}$  = cylindrical angular coordinate  
 $\kappa^*$  = interfacial dilatational viscosity  
 $\lambda_m$  = Eigenvalue, determined by Eq. 44  
 $\mu$  = unit vector that is normal to  $C$  and both tangent and outwardly directed with respect to the interface  
 $\mu^{(j)*}$  = shear viscosity for phase  $j$   
 $\phi$  = spherical coordinate of system in Figure 2  
 $\Phi_m^{(j)}$  = Eigenfunctions appearing Eq. 41  
 $\psi^{(j)}$  = stream function for phase  $j$ , defined by Eq. 28  
 $\psi_p^{(1)}, \psi_p^{(2)}$  = particular stream functions defined by Eqs. 38 and 39

#### Others

div

 = divergence operation  

div<sub>(\sigma)</sub>

 = surface divergence operation (Wei et al., 1974; Briley et al., 1976)  
 $dA^*$  = differential area  
 $dA$  = dimensionless differential area  
 $ds^*$  = differential arc length  
 $ds$  = dimensionless differential arc length  
 $dV^*$  = differential volume  
 $dV$  = dimensionless differential volume  
 $tr$  = trace operation  
 $\nabla$  = gradient operator  
 $\nabla_{(\sigma)}$  = surface gradient operator (Wei et al., 1974; Briley et al., 1976)  
 $\dots T$  = superscript denoting transpose operation  
 $\dots 0$  = subscript denoting variable is zero order in  $N_{ca}, N_{Re}^{(1)}, N_{Re}^{(2)}, N_{Bo}, (N_{\kappa+\epsilon})^{-1}$ , and the slip ratio

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## APPENDIX A: EFFECT OF INTERFACIAL TENSION GRADIENTS

Interfacial tension gradients are the result of concentration gradients within the interface. Rather than looking directly at the development of interfacial tension gradients, we will focus on the concentration distribution within the interface.

The mass balance for surfactant S in the fluid-fluid interface in Figure 1 is (Slattery, 1980)

$$\frac{\partial \rho_{(s)}^{(\sigma)}}{\partial t} + \nabla_{(\sigma)}(\rho_{(s)}^{(\sigma)} \cdot \mathbf{v}^{(\sigma)}) + \rho_{(s)}^{(\sigma)} \text{div}_{(\sigma)} \mathbf{v}^{(\sigma)} + N^{(\sigma)} \text{div}_{(\sigma)} \mathbf{j}_{(s)}^{(\sigma)} + N^{(1)} \mathbf{n}_{(s)}^{(1)} \cdot \boldsymbol{\xi}^{(1)} + N^{(2)} \mathbf{n}_{(s)}^{(2)} \cdot \boldsymbol{\xi}^{(2)} = 0 \quad (\text{A1})$$

in which

$$\begin{aligned} \rho_{(s)}^{(\sigma)} &\equiv \frac{\rho_{(s)}^{(\sigma)*}}{\rho_{(s)0}^{(\sigma)*}} & t &\equiv \frac{V^* t^*}{R^*} \\ \mathbf{v}^{(\sigma)} &\equiv \frac{\mathbf{v}^{(\sigma)*}}{V^*} & \mathbf{j}_{(s)}^{(\sigma)} &\equiv \frac{R^* \mathbf{j}_{(s)}^{(\sigma)*}}{\mathcal{D}^{(\sigma)*} \rho_{(s)0}^{(\sigma)*}} \\ \mathbf{n}_{(s)}^{(i)} &\equiv \frac{\mathbf{n}_{(s)}^{(i)*}}{n_{(s)}^{(i)*}} \end{aligned} \quad (\text{A2})$$

and

$$N^{(\sigma)} \equiv \frac{\mathcal{D}^{(\sigma)*}}{R^* V^*} \quad N^{(i)} \equiv \frac{n_{(s)}^{(i)*} R^*}{\rho_{(s)0}^{(\sigma)*} V^*} \quad (\text{A3})$$

Here  $\rho_{(s)}^{(\sigma)*}$  is the surface mass density of surfactant;  $\rho_{(s)0}^{(\sigma)*}$  the equilibrium surface concentration of surfactant in the limit  $N_{ca} \rightarrow 0$ ;  $\mathbf{j}_{(s)}^{(\sigma)*}$  surface mass flux of surfactant with respect to the mass-averaged velocity;  $\mathcal{D}^{(\sigma)*}$  the surface diffusion coefficient for surfactant;  $\mathbf{n}_{(s)}^{(i)*}$  the mass flux of surfactant within phase  $i$  measured with respect to a fixed frame of reference;  $n_{(s)}^{(i)*}$  a characteristic magnitude of  $\mathbf{n}_{(s)}^{(i)*} \cdot \boldsymbol{\xi}^{(i)}$ .

The only term in Eq. A1 that is inconsistent with uniform concentrations of surfactant within each phase and in the interface is a portion of those terms representing surface convection:  $\rho_{(s)}^{(\sigma)} \text{div}_{(\sigma)} \mathbf{v}^{(\sigma)}$ . If  $N^{(\sigma)} \gg 1$ , mass transfer of surfactant from the bulk phases will dominate the effects of surface convection and the concentration of surfactant within the interface will be nearly independent of position. If  $N^{(\sigma)} \gg 1$ , surface diffusion will dominate surface convection, again resulting in a nearly uniform concentration of surfactant within the interface.

Let us examine three cases within the context of tertiary oil recovery. Phase 1 will be identified as the aqueous phase and phase 2 as the oil phase. Let  $\rho_{(s)0}^{(1)*}$  be the equilibrium concentration of surfactant in phase 1 in the limit  $N_{ca} \rightarrow 0$ . We will assume that  $\rho_{(s)0}^{(1)*} = 0.01 \text{ g/cm}^3$ , the diffusion coefficient for surfactant within phase 1 is  $\mathcal{D}^{(1)*} = 10^{-6} \text{ cm}^2/\text{s}$ ,  $R^* = 10 \text{ } \mu\text{m}$  (Batra and Dullien, 1973), and  $V^*/R^* = 10^{-2} \text{ to } 10^{-1} \text{ s}^{-1}$ . (See Discussion.)

### Case 1: Diffusion Controls

If diffusion controls the rate of mass transfer from the adjacent bulk phases, we define

$$n_{(s)}^{(i)*} \equiv \frac{\mathcal{D}^{(i)*} \rho_{(s)0}^{(i)*}}{R^*} \quad (\text{A4})$$

For a monomolecular film of surfactant having a molecular weight

of 400,  $\rho_{(s)0}^{(\sigma)*} < 4 \times 10^{-7}$  g/cm<sup>2</sup> based upon a limiting area of 20 Å<sup>2</sup>/molecule (Adamson, 1967). From Eqs. A3 and A4

$$N^{(1)} = \frac{\rho_{(s)0}^{(1)*} \mathcal{D}^{(1)*}}{\rho_{(s)0}^{(\sigma)*} V^*} \gg 1 \quad (\text{A5})$$

suggesting that mass transfer of surfactant from the bulk phases will dominate the effects of surface convection and the concentration of surfactant within the interface will be nearly independent of position.

### Case 2: Adsorption Controls

If the adsorption process is modelled in terms of mass transfer coefficient  $k^{(i)*}$  such that

$$n_{(s)}^{(i)*} \cdot \xi^{(i)} = k^{(i)*} (\rho_{(s)}^{(\sigma)*} - \rho_{(s)0}^{(\sigma)*}) \quad (\text{A6})$$

we define

$$n_{(s)}^{(i)*} \equiv k^{(i)*} \rho_{(s)}^{(\sigma)*} \quad (\text{A7})$$

Available experimental data (Posner and Alexander, 1953a,b; Tsionopoulos et al., 1971; Pierson and Whitaker, 1976) suggest that  $k^{(i)*} \gg 0.1$  s<sup>-1</sup>. From Eqs. A3 and A7,

$$N^{(i)} = \frac{k^{(i)*} R^*}{V^*} \gg 1 \quad (\text{A8})$$

and we again conclude that the concentration of surfactant within the interface will be nearly independent of position.

### Case 3: Surface Diffusion Controls

Limited experimental data indicate that  $\mathcal{D}^{(\sigma)*}$  is of the order 10<sup>-5</sup> to 10<sup>-4</sup> cm<sup>2</sup>/s (Sakata and Berg, 1969). In this case,  $N^{(\sigma)} \gg 1$  and we again conclude that surface mass density gradients are small.

## APPENDIX B: RELATIVE EFFECTS OF INTERFACIAL VISCOSITIES UPON DISPLACEMENT (B. L. SEN and J. C. SLATTERY)

As explained in the INTRODUCTION, Slattery (1974, 1979) constructed qualitative analyses of the displacement process assuming that the rate limiting steps are the pauses during the creeping motion between jumps. His arguments were based upon the axial component of an integral momentum balance for that period of time in which the common line is stationary.

We are now in the position to repeat those arguments, assuming that the rate limiting steps are the creeping motions between jumps and that for simplicity the integral mechanical energy balance in the forms of Eqs. 61 and 65 apply. The results are substantially the same with one exception. Whereas Slattery (1974, 1979) was not able to distinguish between the effects of the interfacial dilatational and shear viscosities, we can with Eqs. 61 and 65.

As an example, let us consider the effect upon the rate of displacement of a liquid segment when the concentration  $\rho_{(s)}^{(1)*}$  of surfactant in phase 1 is changed. From Eq. 65,

$$\frac{dV}{d\rho_{(s)}^{(1)*}} = \frac{\partial V}{\partial N_\gamma} \frac{dN_\gamma}{d\rho_{(s)}^{(1)*}} + \frac{\partial V}{\partial N_x} \frac{dN_x}{d\rho_{(s)}^{(1)*}} + \frac{\partial V}{\partial N_\epsilon} \frac{dN_\epsilon}{d\rho_{(s)}^{(1)*}} + \dots \quad (\text{B1})$$

where

$$V \equiv \frac{V^* \mu^{(2)*}}{|\Delta p^*| R^*} \quad (\text{B2})$$

$$\frac{\partial V}{\partial N_x} = -\frac{V}{d} \left\{ 2(A_A^2 G_A + A_R^2 G_R) + 2 \left( \frac{\kappa^*}{\epsilon^*} + 1 \right) \left[ A_A^2 \frac{\partial G_A}{\partial (\kappa^*/\epsilon^*)} + A_R^2 \frac{\partial G_R}{\partial (\kappa^*/\epsilon^*)} \right] \right\} \quad (\text{B3})$$

$$\frac{\partial V}{\partial N_\epsilon} = -\frac{V}{d} \left\{ 2(A_A^2 G_A + A_R^2 G_R) - 2 \frac{\kappa^*}{\epsilon^*} \left( \frac{\kappa^*}{\epsilon^*} + 1 \right) \left[ A_A^2 \frac{\partial G_A}{\partial (\kappa^*/\epsilon^*)} + A_R^2 \frac{\partial G_R}{\partial (\kappa^*/\epsilon^*)} \right] \right\} \quad (\text{B4})$$

$$N_x \equiv \frac{\kappa^*}{\mu^{(2)*} R^*} \quad N_\epsilon \equiv \frac{\epsilon^*}{\mu^{(2)*} R^*} \quad (\text{B5})$$

and

$$d \equiv 8 \left( N_\mu \frac{L^{(1)*}}{R^*} + \frac{L^{(2)*}}{R^*} \right) + 2N_{\kappa+\epsilon} (A_A^2 G_A + A_R^2 G_R) \quad (\text{B6})$$

The effects of the two interfacial viscosities are characterized by the relative magnitudes of  $\partial V / \partial N_x$  and  $\partial V / \partial N_\epsilon$ . There are several cases to consider.

If  $\kappa^*/\epsilon^*$  remains a constant as  $\kappa^*$  and  $\epsilon^*$  change, we see from Eqs. B3 and B4 that

$$\frac{\partial V / \partial N_x}{\partial V / \partial N_\epsilon} = 1 \quad (\text{B7})$$

This may be considered to be the case treated by Slattery (1974, 1979).

If  $\kappa^*/\epsilon^*$  changes, say as the result of a change in  $\rho_{(s)}^{(1)*}$ , Eqs. B3 and B4 and Figure 5 demand

$$\frac{\partial V / \partial N_x}{\partial V / \partial N_\epsilon} > 1 \quad (\text{B8})$$

If  $\kappa^*/\epsilon^* \leq 1$  numerical computations show

$$\frac{\partial V / \partial N_x}{\partial V / \partial N_\epsilon} \gg 1 \quad (\text{B9})$$

If  $\kappa^*/\epsilon^* = 0$ , it follows from Eqs. 60, B3 and B4 that

$$\frac{\partial V}{\partial N_\epsilon} = 0 \quad (\text{B10})$$

and

$$\lim_{\kappa^* \rightarrow 0} \frac{\kappa^*}{\epsilon^*} \rightarrow 0: \quad \frac{\partial V / \partial N_x}{\partial V / \partial N_\epsilon} \rightarrow \infty \quad (\text{B11})$$

Our conclusion is that, while both interfacial viscosities play important roles, the interfacial dilatational viscosity may be the more important of the two. Unfortunately, this is the one about which we currently know the least.

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