Interfacial Effects in the Entrapment and Displacement of Residual Oil

Qualitative theories are developed to explain the roles of surface tension and the two surface viscosities during the entrapment of residual oil by water and during the subsequent displacement of residual oil by surfactant solutions. The results are in agreement with available experimental data concerning the effects to be observed as the oil-water surface tension is reduced. Limited data suggest an order of magnitude criterion for the critical surface tension above which no residual oil can be recovered. The two surface viscosities do not affect the entrapment of residual oil, but they are predicted to play a major role in the displacement of residual oil by surfactant solutions.

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SCOPE

Conventional petroleum production from a field usually concludes with a partial displacement of the oil remaining in the reservoir by either water or brine. At the end, there remains on the average 70% of the oil originally in place. It has been demonstrated, at least in the laboratory, that a portion of this residual oil can be recovered by displacing it with a dilute aqueous solution of a surfactant. Our purpose here is to investigate the roles of surface tension and the two surface viscosities in the entrapment of residual oil and their influence upon the efficiency with which a surfactant solution can displace this residual oil.

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. Figure 1 shows a water-oil interface moving through a particular pore that bifurcates to form two pores of unequal diameters, which in turn rejoin at some point downstream. If the interface advances through the large pore more rapidly than the small pore, residual oil will be trapped in the small pore. Conversely, if the interface advances through the small pore more rapidly, residual oil will be trapped in the large pore. Experimental evidence indicates that the water-oil interfaces advance through these pores in an episodic motion: the interface deforms until it becomes unstable, it jumps ahead a short distance, and then it stops for another period of slow deformation. Since these jumps take place very rapidly (less than 7.8 millisec.), the motion between jumps controls how rapidly the oil is displaced by the water. A qualitative theory for the entrapment of residual oil is developed based upon an integral momentum balance for the oil and water in the pore during this period of slow deformation between jumps.

Once a segment of oil has been trapped in a pore, it may or may not continue to be driven forward by the existing pressure gradient. If it does advance, it will do so in an episodic motion: the segment slowly deforms until one of the interfaces becomes unstable, the segment jumps ahead a short distance, and then it stops for another period of slow deformation. The displacement of residual oil appears to be controlled by the period of slow deformation between jumps. A qualitative theory for the displacement of residual oil is constructed upon an integral momentum balance for the oil and water in the pore during this period of slow deformation between jumps.

CONCLUSIONS AND SIGNIFICANCE

In the displacement of oil by water in an oil-wet rock, residual oil will be trapped in the smaller pores. In the free or forced displacement of oil by water in a water-wet rock, residual oil will again be trapped in the smaller pores. In a restricted displacement of oil by water in a water-wet rock, residual oil will be trapped in the larger pores. The conclusions about water-wet rock are supported entirely by the data of Handy and Datta (1966).

The residual oil saturation following displacement of oil by water in an oil-wet rock or following restricted displacement in a water-wet rock will be unaffected by a reduction in the surface tension. In the free or forced displacement of oil by water in a water-wet rock, the residual oil saturation will be decreased by lowering the surface tension, assuming that $N_\gamma + N_{\kappa+\epsilon}$ is sufficiently small (the surface tension and the surface viscosities are sufficiently small). These statements are supported by the data of Wagner and Leach (1966).

The residual oil saturation following displacement of oil by water in either oil-wet or water-wet rock will generally be unaffected by a reduction in the magnitudes of the surface viscosities.

There is a critical value for the surface tension γ or for $\gamma/|\nabla p|R^2$, above which no residual oil can be recovered by displacement in either oil-wet or water-wet rock. For the limited data of Taber et al. (1973), which includes a variety of sandstones as well as alundum, it appears that this critical value of $\gamma/|\nabla p|R^2$ has a magnitude of order 5×10^4.

When the water-oil surface tension is less than the critical value, the efficiency of residual oil recovery in both oil-wet rock and in water-wet rock will increase as the applied pressure gradient increases. This is confirmed experimentally (Wagner and Leach, 1966; Taber, 1969; Taber et al., 1973).

The efficiency of residual oil recovery in both oil-wet

and water-wet rock will increase as the surface tension continues to decrease below its critical value. This appears to be supported by some data of Wagner and Leach (1966).

For values of the surface tension less than the critical value, the efficiency of residual oil recovery will increase as the sum of the water-oil surface viscosities is decreased. This is true for both oil-wet and water-wet structures. The effects of a reduction in the surface viscosities upon the efficiency of residual oil recovery is comparable to the effect of a reduction in the surface tension, when $N^{**}_{\kappa+\epsilon}$ is sufficiently small.

Conventional petroleum production from a field usually concludes with a partial displacement of the oil remaining in the reservoir by either water or brine. At the end, there remains on the average 70% of the oil originally in place (Arnold, 1973).

It has been demonstrated, at least in the laboratory, that a portion of this residual oil can be recovered by displacing it with a dilute aqueous solution of a surfactant (Reisberg and Doscher, 1956; Taber, 1969; Taber et al., 1973). All of these studies demonstrate that a suitable surfactant should drastically reduce the oil-water interfacial tension. A practical surfactant should also be absorbed to a minimum extent by the pore walls of the rock structure, it should be stable in reservoir brines at reservoir temperatures, and it should be inexpensive.

In what follows, I begin by investigating the role of interfacial behavior in the entrapment of residual oil by water at the conclusion of conventional petroleum production. I then indicate the influence of interfacial behavior upon the efficiency with which a surfactant solution can displace this residual oil.

ENTRAPMENT OF RESIDUAL OIL

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. Figure 1 indicates a particular pore that bifurcates to form two pores of unequal diameters, which in turn rejoin at some point downstream. Let us consider the displacement of oil by water in this bifurcated pore as the flow proceeds from left to right. The character of the events that follow depend upon whether we are considering an oil-wet or a water-wet permeable structure.

In reality, the pores are not as regular as I have indicated in Figure 1. They might be better described by the irregular channels shown in Figure 2.

Experimental evidence indicates that the oil-water interface will not advance through the channels in Figure 2 as a smooth function of time. Poynting and Thomson (1902) forced mercury up a capillary tube and then gradually reduced the pressure. Instead of falling, the mercury at first adjusted itself to the reduced pressure by altering the curvature of the air-mercury interface. When the pressure gradient finally grew too large, the configuration of the meniscus became unstable and the mercury fell a short distance in the tube before stopping, repeating the deformation of the interface, and falling again when a new instability developed. Consequently, they observed the interface to move through the tube in a series of jumps. Yarnold (1938) saw this same sticking phenomena as a liquid index moved slowly through a glass capillary tube. Heller (1968) used high-speed photography to follow the advance of water-air interfaces through a porous bed as jumps in the individual pores. He found that any particular jump in a pore takes place in less than 7.8 millisec.

In Figure 2a, I have shown an advancing water-oil interface trapped at a narrow portion of a pore in an oil-wet rock (Melrose, 1970). If the pressure gradient exceeds some minimum value, the interface will slowly deform until it becomes unstable and jumps to the position shown by the dotted interface.

In the water-wet rock illustrated in Figure 2b, an advancing water-oil interface will tend to be trapped at a wide portion of a pore (Melrose, 1970). Again, the interface will deform until it becomes unstable and advances to the configuration indicated by the dotted curve.

Returning now to Figure 1, we conclude that the water-oil interfaces will advance through the two pores at unequal rates. If the water-oil interface advances through the small pore more rapidly, residual oil will tend to be trapped in the large pore. If the interface moves through the large pore more rapidly, residual oil will be trapped in the small pore.

APPROXIMATE CALCULATION FOR ENTRAPMENT OF OIL

The limited experimental evidence discussed above indicates that, when a water-oil interface advances slowly through a pore, the limiting step in its episodic motion appears to be the period in which the interface deforms to

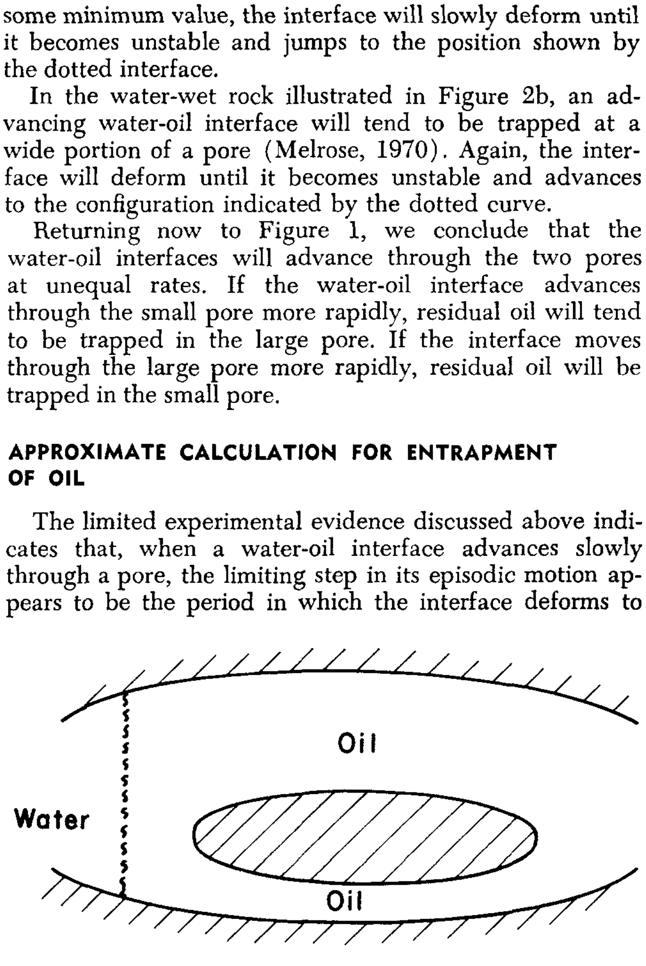

Fig. 1. Water-oil interface approaching bifurcation in pore.

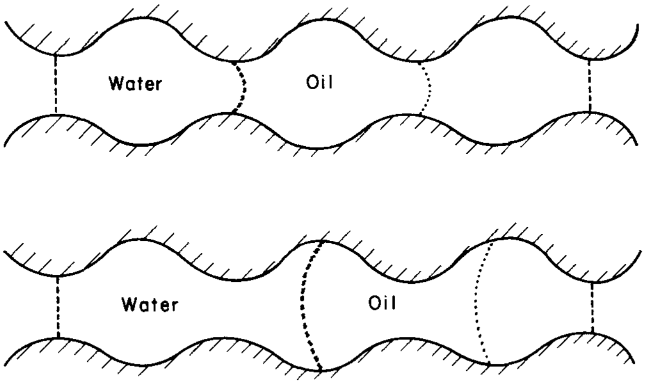

Fig. 2a. In an oil-wet rock, the water-oil interface is trapped at a narrow portion of the pore. The dotted curve indicates a subsequent position of the interface. The dashed lines denote the entrance surface $S_{(ent)}$ and the exit surface $S_{(ex)}$ of the system for which the momentum balance is written; b. In a water-wet rock, the water-oil interface is trapped at a wide portion of the pore.

the point of instability. Let us now estimate the effects of interfacial behavior upon the slow deformation of such an interface. In doing so, we shall concern ourselves only with the forces acting on the interface and not with a specific criterion for the subsequent instability.

Consider as a system all of the oil and water in the pore between the fixed entrance and exit surfaces shown as dashed lines in Figure 2. Let us write the z component of the momentum balance for this system, making the following assumptions:

1. Neglect the inertial effects. The water-oil interface deforms very slowly up to the point where it becomes unstable. Inertial effects are important only after this instability develops and during the subsequent jump.
2. The pore is horizontal.
3. Neglect the viscous forces acting at the entrance and exit cross sections. This would be completely justified if we were dealing with poiseuille flow in a cylindrical tube of uniform diameter.
4. Neglect mass transfer to and from the water-oil interface.
5. The interfacial stress is described by the linear boussinesq surface fluid model (Scriven, 1960; Slattery, 1964, 1967).
6. Both the pore wall and the oil-water phase interface are axisymmetric.

In view of the first three restrictions, the z component of the integral momentum balance (Slattery, 1972) becomes

$$\int_{S_{(\text{ent})}} (p - p_0)\,dA - \int_{S_{(\text{ex})}} (p - p_0)\,dA - F_z{}^{(p)} - F_z{}^{(v)}$$
$$- \mathbf{g}_z \cdot \int_{\Sigma} (\mathbf{T}_{(O)} \cdot \boldsymbol{\xi}_{(O)} + \mathbf{T}_{(W)} \cdot \boldsymbol{\xi}_{(W)})\,dA = 0 \qquad (1)$$

By $S_{(\text{ent})}$, $S_{(\text{ex})}$, and Σ, I mean, respectively, the entrance surface for the system, the exit surface, and the water-oil phase interface; p_0 is a constant reference or ambient pressure; $F_z{}^{(p)}$ is the z component of the pressure or form drag that the oil and water exert upon the pore walls $S_{(w)}$ beyond any force attributable to p_0

$$F_z{}^{(p)} = \mathbf{g}_z \cdot \int_{S_{(w)}} (p - p_0)\mathbf{n}\,dA \qquad (2)$$

$F_z{}^{(v)}$ is the z component of the viscous or friction drag that the oil and water exert upon $S_{(w)}$

$$F_z{}^{(v)} = \mathbf{g}_z \cdot \int_{S_{(w)}} (\mathbf{T} + p\mathbf{I}) \cdot (-\,\mathbf{n})\,dA \qquad (3)$$

where $\mathbf{n}$ is the unit normal to the pore walls $S_{(w)}$ that is outwardly directed with respect to the system, and dA indicates an area integration.

With no mass transfer to or from the oil-water interface, the jump momentum balance (Scriven, 1960; Slattery, 1964, 1967) requires

$$\mathbf{T}_{(O)} \cdot \boldsymbol{\xi}_{(O)} + \mathbf{T}_{(W)} \cdot \boldsymbol{\xi}_{(W)} + \text{div}_{(\sigma)}\,\mathbf{T}^{(\sigma)} = 0 \qquad (4)$$

The surface stress tensor for the oil-water phase interface is denoted by $\mathbf{T}^{(\sigma)}$; the surface divergence operation $\text{div}_{(\sigma)}$ is discussed in Appendix A. The jump momentum balance is the requirement of Euler's first law at the interface (Slattery, 1972). The last term on the left of Equation (1) can be usefully rearranged by using Equation (4)

$$- \mathbf{g}_z \cdot \int_{\Sigma} (\mathbf{T}_{(O)} \cdot \boldsymbol{\xi}_{(O)} + \mathbf{T}_{(W)} \cdot \boldsymbol{\xi}_{(W)})\,dA$$
$$= \mathbf{g}_z \cdot \int_{\Sigma} \text{div}_{(\sigma)}\,\mathbf{T}^{(\sigma)}\,dA$$

(Continued in column 2)

$$= \mathbf{g}_z \cdot \int_C \mathbf{T}^{(\sigma)} \cdot \boldsymbol{\mu}\,ds$$
$$= \oint_C \mathbf{g}_z \cdot \mathbf{T}^{(\sigma)} \cdot \boldsymbol{\mu}\,ds \qquad (5)$$

where C denotes the closed curve bounding the water-oil phase interface in Figure 2; ds indicates that a line integration is to be performed over C; $\boldsymbol{\mu}$ is the unit vector tangent to the phase interface, normal to C, and outwardly directed with respect to Σ. In the second line, we have employed the surface divergence theorem (McConnell, 1957); in the third line we have noted that $\mathbf{g}_z$ is independent of position on the curve C.

We can make further progress by restricting ourselves to the linear boussinesq surface model (Scriven, 1960; Slattery, 1964 and 1967)[*] for the surface stress tensor

$$\mathbf{T}^{(\sigma)} = [\gamma + (\kappa - \epsilon)\,\text{div}_{(\sigma)}\,\mathbf{v}^{(\sigma)}]\,\mathbf{P} + 2\epsilon\,\mathbf{D}^{(\sigma)} \qquad (6)$$

In this expression, γ is the thermodynamic surface tension. Assuming only that the pore wall and the water-oil phase interface are axisymmetric, we find that (see Appendix B for details)

$$\text{on } C\text{:} \quad \mathbf{g}_z \cdot \mathbf{T}^{(\sigma)} \cdot \boldsymbol{\mu} = [\gamma + (\kappa + \epsilon)\,\text{div}_{(\sigma)}\,\mathbf{v}^{(\sigma)}]\,\mu_z \qquad (7)$$

Note that, if the phase interface intersects the pore wall precisely either at its minimum or maximum radius, then $\mu_z = -\cos\varphi$, where φ is the contact angle between the water-oil interface and the pore wall measured through the oil phase. It will not be necessary for us to make this assumption.

The jump mass balance is the requirement of conservation of mass at the phase interface. If there is no mass transfer between the interface and the adjoining phases, it takes the form (Scriven, 1960; Slattery, 1964 and 1967)

$$\frac{d_{(s)}\rho^{(\sigma)}}{dt} + \rho^{(\sigma)}\,\text{div}_{(\sigma)}\,\mathbf{v}^{(\sigma)} = 0 \qquad (8)$$

where $\rho^{(\sigma)}$ is the surface mass density and $d_{(s)}/dt$ indicates a derivative following a material particle in the phase interface. This allows us to write Equation (7) as

$$\mathbf{g}_z \cdot \mathbf{T}^{(\sigma)} \cdot \boldsymbol{\mu} = \left[\gamma - (\kappa + \epsilon)\,\frac{d_{(s)} \ln \rho^{(\sigma)}}{dt}\right] \mu_z \qquad (9)$$

Equation (9) may now be used to rewrite Equation (5) in a more explicit form:

$$- \mathbf{g}_z \cdot \int_{\Sigma} (\mathbf{T}_{(O)} \cdot \boldsymbol{\xi}_{(O)} + \mathbf{T}_{(W)} \cdot \boldsymbol{\xi}_{(W)})\,dA$$
$$= 2\pi\,R_{(WO)} \left[\gamma - (\kappa + \epsilon)\,\frac{d_{(s)} \ln \rho^{(\sigma)}}{dt}\right] \mu_z \qquad (10)$$

Here $R_{(WO)}$ is the radius of the pore at the line of contact with the water-oil interface.

The first two terms on the left of Equation (1) may be more conveniently written as

$$\int_{S_{(\text{ent})}} (p - p_0)\,dA - \int_{S_{(\text{ex})}} (p - p_0)\,dA = \Delta p\;\pi R^2 \qquad (11)$$

where

$$\Delta p \equiv p_{(\text{ent})} - p_{(\text{ex})} \qquad (12)$$

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[*] Mannheimer and Schechter (1970), Wasan et al. (1971), and Hegde (1971) recommend different experiments for measuring the surface shear viscosity of liquid-liquid interfaces with the deep channel geometry. Wei et al. (1974) describe the measurement of $3\kappa + 2\epsilon$ at liquid-liquid interfaces with a rotating drop in a constant shear field.

Let us introduce as dimensionless variables

$$t^* \equiv \frac{t\, v_{(o)}}{l} \tag{13}$$

$$\mathcal{F}_z^{(p)*} \equiv \frac{\mathcal{F}_z^{(p)}}{|\Delta p|\ \pi R^2} \tag{14}$$

$$\mathcal{F}_z^{(v)*} \equiv \frac{\mathcal{F}_z^{(v)}}{\pi l \mu_{(o)}\, v_{(o)}} \tag{15}$$

where l is the length of the pores shown in Figure 1. In Equation (13) we have chosen as a characteristic time a rough measure of the time required for the water-oil interface to travel the length of the pore. The pressure drag is characterized by $|\Delta p|\ \pi R^2$ in Equation (14). The viscous drag in Equation (15) is crudely proportional to the product of $\pi R l$, a measure of the area of the pore wall, and $\mu_{(o)} \dfrac{v_{(o)}}{R}$, a measure of the viscous shear force acting on the pore wall. Making use of Equations (10) and (11), we can rewrite Equation (1) in terms of these variables as

$$\begin{aligned} v^*_{(o)} &\equiv \frac{v_{(o)}\ \mu_{(o)}}{|\Delta p|\ l} \\ &= \frac{R^{*2}\left(\dfrac{\Delta p}{|\Delta p|} - \mathcal{F}_z^{(p)*}\right) - R^* N_\gamma \left(-2\,\dfrac{R_{(wo)}}{R}\,\mu_z\right)}{2\mathcal{F}_z^{(v)*} + R^* N_{\kappa+\epsilon}\left(2\,\dfrac{R_{(wo)}}{R}\,\mu_z\,\dfrac{d_{(s)} \ln \rho^{(\sigma)}}{dt^*}\right)} \\ &= \frac{R^{*2} A - R^* N_\gamma B}{D + R^* N_{\kappa+\epsilon} E} \end{aligned} \tag{16}$$

In writing this I have introduced as definitions

$$R^* \equiv \frac{R}{l} \tag{17}$$

$$N_\gamma \equiv \frac{\gamma}{|\Delta p|\ l} \tag{18}$$

$$N_{\kappa+\epsilon} \equiv \frac{\kappa + \epsilon}{l \mu_{(o)}} \tag{19}$$

$$A \equiv \frac{\Delta p}{|\Delta p|} - \mathcal{F}_z^{(p)*} \tag{20}$$

$$B \equiv -2\,\frac{R_{(wo)}}{R}\,\mu_z \tag{21}$$

$$D \equiv 2\mathcal{F}_z^{(v)*} \tag{22}$$

$$E \equiv 2\,\frac{R_{(wo)}}{R}\,\mu_z\,\frac{d_{(s)} \ln \rho^{(\sigma)}}{dt^*} \tag{23}$$

The pore length l has been viewed as a constant in writing Equation (17) since in Figure 1 we wish to compare two pores that have the same length but different diameters.

It is helpful to observe that the magnitudes of A, B, D, and E are all of the order unity (they differ by less than a factor of ten from unity).

Let us now examine the signs of some of the terms that appear in Equation (16). We will assume that flow is always in the positive z direction and therefore

$$R^* A \geqq N_\gamma B \tag{24}$$

For oil-wet rock, B is positive; for water-wet rock, negative. We observe that $\mathcal{F}_z^{(v)*}$ and D are positive dimensionless scalars. In the oil-wet case shown in Figure 2a, the area of the water-oil interface increases as a function of time. With the assumption that there is no mass transfer from the adjoining phases, the surface mass density must decrease as a function of time. Since μ_z is also negative, we have

$$\mu_z\,\frac{d_{(s)} \ln \rho^{(\sigma)}}{dt^*} \geqq 0, \quad E \geqq 0 \tag{25}$$

A similar argument for the water-wet case shown in Figure 2b indicates that Inequality (25) is valid there as well.

Equation (16) gives us the form of the dependence of the average velocity in the oil phase during the deformation of the water-oil interface before an instability develops. Without examining the criteria for the stability of the interface, we can draw several conclusions concerning the relative rates of displacement in the two portions of the bifurcated pore pictured in Figure 1 and concerning the subsequent entrapment of residual oil by water.

ENTRAPMENT OF RESIDUAL OIL: DISTRIBUTION

From Equation (16),

$$\frac{\partial v^*_{(o)}}{\partial R^*} = \frac{R^* A(D + N_{\kappa+\epsilon} R^* E) + D(R^* A - N_\gamma B)}{(D + N_{\kappa+\epsilon} R^* E)^2} \tag{26}$$

If this derivative is positive, the oil will be displaced more rapidly in the larger pore of Figure 1 and residual oil will be trapped in the smaller pore. If this derivative is negative, the water-oil interface will advance more rapidly through the small pore, trapping residual oil in the larger pore. In view of Inequality (25), the sign of this derivative will depend upon the sign and magnitude of A.

For an oil-wet rock, Inequality (25) requires that A be positive.

1. In the displacement of oil by water in an oil-wet permeable structure, residual oil will be trapped in the smaller of those pores initially containing oil.

In a water-wet rock, if A is sufficiently large (it may be negative) that $\partial v^*_{(o)}/\partial R^*$ is positive, we will speak of a free or forced displacement of the oil by water. These terms are motivated by our estimate that, if we assume pressure to be roughly independent of position within each phase,

$$A \doteq \frac{\Delta p}{|\Delta p|}\left(\frac{R_{(wo)}}{R}\right)^2 \tag{27}$$

2. In the free or forced displacement of oil by water in a water-wet structure, residual oil will be trapped in the smaller pores.

In a water-wet rock, let A and $\partial v^*_{(o)}/\partial R^*$ be negative although Inequality (24) is still observed. The flow of water into the rock is slowed by an imposed pressure gradient. We will refer to a restricted displacement of the oil by water.

3. In a restricted displacement of oil by water in a water-wet structure, residual oil will be trapped in the larger pores.

Conclusions 2 and 3 concerning water-wet structures are supported entirely by the experiments of Handy and Datta (1966).

ENTRAPMENT OF RESIDUAL OIL: SURFACE TENSION

Returning to Equation (16), we see that

$$\frac{\partial v^*_{(o)}}{\partial N_\gamma} = \frac{-R^* B}{D + N_{\kappa+\epsilon} R^* E} \tag{28}$$

In an oil-wet structure, B is positive; a reduction in the surface tension leads to an increase in the displacement velocities in both of the pores of Figure 1. In a water-wet structure, B is negative; the displacement velocities in both pores are decreased when the surface tension is reduced. But in which pore is the effect greater?

Let us consider

$$\frac{\partial^2 v^*_{(O)}}{\partial N_\gamma \partial R^*} = \frac{-BD}{(D + N_{\kappa+\epsilon} R^* E)^2} \tag{29}$$

Note that the magnitude of $\partial v^*_{(O)}/\partial R^*$ is on the order of $N_{\kappa+\epsilon} + N_\gamma$ times that of $\partial^2 v^*_{(O)}/\partial N_\gamma \partial R^*$ (estimating that the magnitudes of A, B, D, and E are of the order unity).

4. The fraction of the oil trapped in either oil-wet or water-wet rock structures will be relatively independent of the water-oil surface tension unless $N_\gamma + N_{\kappa+\epsilon}$ is small (unless the surface tension and surface viscosities are small).

Equation (29) implies that the effect of reducing the water-oil surface tension in an oil-wet rock structure is to increase the displacement velocity in the larger pore of Figure 1 relative to that in the smaller pore.

5. The entrapment of residual oil in the smaller pores of an oil-wet rock will be reinforced by reducing the surface tension. The fraction of the oil trapped will not decrease even if $N_{\kappa+\epsilon} + N_\gamma$ is small.

From Equation (29), a reduction of the water-oil surface tension in a water-wet structure tends to decrease the displacement velocity in the larger pore of Figure 1 relative to that in the smaller pore.

6. In the free or forced displacement of oil by water in a water-wet structure, the residual saturation will be decreased by lowering the surface tension if $N_{\kappa+\epsilon} + N_\gamma$ sufficiently small.

7. In a restricted displacement of oil by water in a water-wet structure, the entrapment of residual oil in the larger pores will be enhanced by lowering the surface tension. The fraction of the oil trapped will not decrease even if $N_{\kappa+\epsilon} + N_\gamma$ is small.

Conclusion 4 is supported by the observations of Wagner and Leach (1966)* who studied displacement using the equilibrium vapor and liquid phases of the methane-*n*-pentane system. They found that, independent of whether it was the gas or liquid phase being displaced, the residual saturation was unchanged as the surface tension was lowered to 0.1 dyne/cm.

For $\gamma < 0.1$ dyne/cm, Wagner and Leach (1966) found a sharp change in the dependence of the residual saturation upon γ, which suggests a change in the nature of the physical process. For the forced displacement of the nonwetting phase by the wetting phase, the residual saturation generally decreased as the surface tension was lowered, in agreement with conclusion 6. But for the displacement of the wetting phase by the nonwetting phase, the residual saturation also decreased as the surface tension was lowered, in contrast with conclusion 5. I discuss in more detail later the possibility there may have been another physical process that was important in their experiments for $\gamma < 0.1$ dyne/cm: a portion of the oil initially trapped by the mechanism described here may have been subsequently displaced under the existing pressure gradient.

ENTRAPMENT OF RESIDUAL OIL: SURFACE VISCOSITIES

In order to investigate the effect of the interfacial viscosities, let us consider

$$\frac{\partial^2 v^*_{(O)}}{\partial N_{\kappa+\epsilon} \partial R^*} = \frac{-R^{*2} AE\,(D + N_{\kappa+\epsilon} R^* E) - 2R^* DE\,(R^* A - N_\gamma B)}{(D + N_{\kappa+\epsilon} R^* E)^3}$$

$$= \frac{R^{*2} AE\,(D + N_{\kappa+\epsilon} R^* E) - 2R^* E\,[R^* A\,(D + N_{\kappa+\epsilon} R^* E) + D(R^* A - N_\gamma B)]}{(D + N_{\kappa+\epsilon} R^* E)^3} \tag{30}$$

Let us begin by observing that the magnitude of $\partial v^*_{(O)}/\partial R^*$ is about $N_{\kappa+\epsilon}$ times that of $\partial^2 v^*_{(O)}/\partial N_{\kappa+\epsilon} \partial R^*$.

8. The fraction of the oil trapped in either oil-wet or water-wet structures will be relatively independent of the water-oil surface viscosities unless $N_{\kappa+\epsilon}$ is small (unless the surface viscosities are small).

Since Inequality (24) requires A to be positive for an oil-wet rock, $\partial^2 v^*_{(O)}/\partial N_{\kappa+\epsilon} \partial R^*$ will always be negative. When the water-oil surface viscosities are reduced, the displacement velocity in the larger pore of Figure 1 is increased in relation to that in the smaller pore.

9. The entrapment of residual oil in the smaller pores of an oil-wet rock will be enhanced by reducing the surface viscosities. The fraction of the oil trapped will not decrease, even if $N_{\kappa+\epsilon}$ is small.

Let us now consider a free or forced displacement of oil by water in a water-wet rock. The derivative $\partial v^*_{(O)}/\partial R^*$ must always be positive although A may be either positive or negative. If A is positive, $\partial^2 v^*_{(O)}/\partial N_{\kappa+\epsilon} \partial R^*$ will be negative. If A is negative, Equation (26) and Inequality (30_2) require that $\partial^2 v^*_{(O)}/\partial N_{\kappa+\epsilon} \partial R^*$ again be negative.

10. In a free or forced displacement of oil by water in a water-wet structure, the entrapment of residual oil in the smaller pores will be reinforced by reducing the surface viscosities. The fraction of the oil trapped will not decrease even if $N_{\kappa+\epsilon}$ is small.

For a restricted displacement of oil by water in a water-wet structure, $\partial^2 v_{(O)}/\partial N_{\kappa+\epsilon} \partial R^*$ may be either positive or negative and no general conclusions may be drawn.

The available experimental evidence is not definitive. Kimbler et al. (1966) reported for a water-wet porous bed three different water floods with three qualitatively different surface viscosities. With a rigid oil-water interface, they found appreciably more residual oil than with an expanded one. Unfortunately, they do not report the corresponding surface tensions. Their observations can be explained by a large reduction in the water-oil surface tension (conclusion 6).

DISPLACEMENT OF RESIDUAL OIL

Up to this point, our concern has been to explore a mechanism by which residual oil may be trapped by water in a displacement. Let us now ask: under what conditions will the short segment of oil shown trapped in Figure 3 continue to be displaced by the water?

The displacement of a segment of one fluid by another in a straight capillary tube of uniform diameter has been described several times in the literature (Jamin, 1860; West, 1911; Gardescu, 1930; Yarnold, 1938; Jacobs, 1962, 1963, and 1966; Schwartz et al., 1964). West (1911), Yarnold (1938), and Schwartz et al. (1964) give a good qualitative picture of the motion inside the segment. The primary concern with all of these workers has been the contact angle resistance encountered in straight tubes. Jamin (1860) and Gardescu (1930) give some attention to the resistance encountered in forcing a segment through a constriction in a tube. Gardescu's (1930) expression for the pressure difference over the drop shown in Figure 3 at equilibrium may be written as

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* In the paper of Wagner and Leach (1966), the drawings shown as Figures 11, 12, and 13 are actually Figures 13, 11, and 12, respectively.

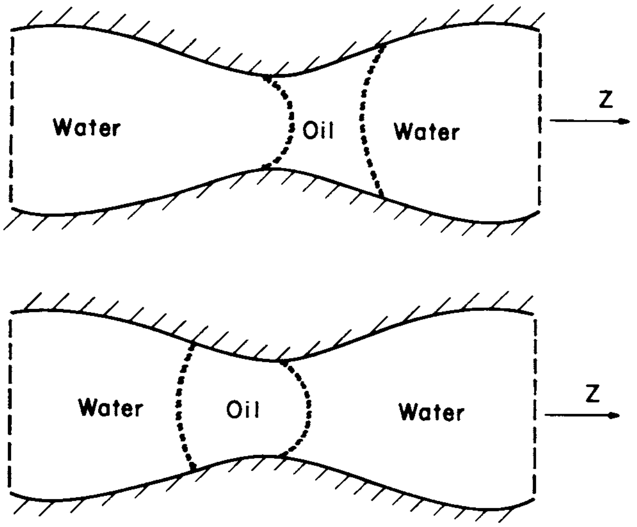

Fig. 3a. In an oil-wet rock, a drop of residual oil will be trapped with its trailing interface at a narrow portion of the pore. The dashed lines denote the entrance surface $S_{(\text{ent})}$ and the exit surface $S_{(\text{ex})}$ of the system for which the momentum balance is written; b. In a water-wet rock, a drop of residual oil will be trapped with its advancing interface at a narrow portion of the pore.

$$\Delta p \equiv p_{(\text{ent})} - p_{(\text{ex})} = -\frac{\gamma \mu_{(a)z}}{R_{(a)}} - \frac{\gamma \mu_{(t)z}}{R_{(t)}} \tag{31}$$

where $_{(a)}$ refers to the advancing interface (on the right in Figure 3) and $_{(t)}$ to the trailing interface. Apparently no one has described the displacement of a liquid segment in a capillary tube whose diameter varies with axial position.

Yarnold (1938) noted that a liquid segment tends to stick as it is moved slowly through a capillary tube. Poynting and Thomson (1902) found that an air-mercury interface advanced in a series of jumps as the mercury was displaced from a glass tube. Heller (1968) observed air-water interfaces to move in finite jumps through a porous bed. These reports prompt the following description of the displacement of a residual oil drop by water in an irregular pore.

Figure 3a in agreement with Equation (31) shows a pore in an oil-wet rock in which a segment of oil is trapped with its trailing interface at a narrow portion of the pore. If the pressure gradient exceeds some critical value, the oil segment will slowly deform until one of the interfaces becomes unstable and the entire segment moves to the position shown by the dotted interfaces. In Figure 3b, we see a pore in a water-wet rock containing a segment of oil trapped with its advancing interface at a restriction in the pore as suggested by Equation (31). If the pressure gradient exceeds some critical value, the oil drop will slowly deform until an instability develops in one of the interfaces. At that point, the drop will appear to jump to another position downstream indicated by the dotted curves. If the pressure gradient in the permeable structure is less than this critical value, there will be no flow in the pore and the oil segment will remain trapped.

This modeling of the displacement process is simplified to the extent that we have not considered residual oil trapped as a film on the walls of the pore or as pendular rings at the contact points between the particles of which the structure is composed, as in a sandstone. It does suggest that the efficiency of the displacement will be enhanced by anything we can do to lower the critical value of the overall pressure gradient necessary for continued deformation of the segment. Furthermore, displacement efficiency will be improved if we can increase the rate at which the drop deforms since this appears to be the controlling step in the movement of a drop through a pore.

APPROXIMATE CALCULATION FOR DISPLACEMENT OF RESIDUAL OIL

Although the experimental evidence is limited, I assume here that the limiting step in the episodic advance of an oil segment through a pore is that period in which it deforms to the point of instability. Let us now estimate the effects of interfacial behavior upon the slow deformation of a drop in a pore. In doing so, we shall concern ourselves only with the forces acting on the drop, and not with a specific criterion for the subsequent instability.

Looking at either Figure 3a for an oil-wet rock or at Figure 3b for a water-wet rock, consider as a system all of the oil and water in the pore between the fixed entrance and exit surfaces shown as dashed lines. The z component of the momentum balance for this system takes the form [the assumptions and calculation are analogous to those leading to Equation (16)]

$$v^{**}_{(O)} \equiv \frac{v_{(O)}\,\mu_{(O)}}{|\Delta p|\,R}$$

$$= \frac{\left(\dfrac{\Delta p}{|\Delta p|} - F_z{}^{(p)*}\right) - 2N_\gamma{}^{**}\left(-\dfrac{R_{(a)}}{R}\,\mu_{(a)z} - \dfrac{R_{(t)}}{R}\,\mu_{(t)z}\right)}{2\dfrac{l}{R}F_z{}^{(v)*} + 2\dfrac{R}{l}N^{**}_{\kappa+\epsilon}\left[\dfrac{R_{(a)}}{R}\,\mu_{(a)z}\dfrac{d_{(s)}\ln\rho^{(\sigma)}_{(a)}}{dt^*} + \dfrac{R_{(t)}}{R}\,\mu_{(t)z}\dfrac{d_{(s)}\ln\rho^{(\sigma)}_{(t)}}{dt^*}\right]}$$

$$= \frac{A - N_\gamma{}^{**}\,G}{l^{**}\,D + N^{**}_{\kappa+\epsilon}\,H/l^{**}} \tag{32}$$

where I have introduced as definitions

$$G \equiv 2\left(-\frac{R_{(a)}}{R}\,\mu_{(a)z} - \frac{R_{(t)}}{R}\,\mu_{(t)z}\right) \tag{33}$$

$$H \equiv 2\left[\frac{R_{(a)}}{R}\,\mu_{(a)z}\frac{d_{(s)}\ln\rho^{(\sigma)}_{(a)}}{dt^*} + \frac{R_{(t)}}{R}\,\mu_{(t)z}\frac{d_{(s)}\ln\rho^{(\sigma)}_{(t)}}{dt^*}\right] \tag{34}$$

$$N_\gamma{}^{**} \equiv \frac{\gamma}{|\Delta p|\,R} \tag{35}$$

$$N^{**}_{\kappa+\epsilon} \equiv \frac{\kappa + \epsilon}{R\mu_{(O)}} \tag{36}$$

$$l^{**} \equiv \frac{l}{R} \tag{37}$$

Equations (20) and (22) can still serve as a definition for A and D.

Our motivation in deriving Equation (32) is to describe the motion of an oil segment that has been trapped by water within a single pore. We will not be comparing the motion in two pores of equal lengths but different diameters as we did with Equation (16). For this reason, it is more convenient here to use R rather than l as the characteristic length describing the porous structure. Dimensionless variables defined in terms of R are marked by ** in order to distinguish them from similar quantities defined earlier in terms of l.

Note that the magnitudes of A, D, G, and H are all of the order unity.

Let us now examine the signs of some of the terms that appear in Equation (32). We will assume that flow is always in the positive z direction and therefore

$$A - N_\gamma{}^{**}\;G \geqq 0 \tag{38}$$

For an oil-wet rock, we assume that the trailing interface is controlling ($-\mu_{(t)z} >> \mu_{(a)z}$ in Figure 3a) and

$$G > 0 \tag{39}$$

TABLE 1. CRITICAL VALUES FOR $\frac{\gamma}{|\nabla p| R^2}$, ABOVE WHICH NO RESIDUAL OIL CAN BE RECOVERED (TABER ET AL., 1973)[a]

Core type	R cm $\times 10^{5}$[b]	Critical $\frac{\gamma}{|\nabla p| R^2} \times 10^{-4}$
—	2.01	8.05
—	2.27	4.27
—	3.07	1.97
Jelm	4.32	1.45
—	4.89	1.62
—	5.62	3.48
Tensleep	6.13	2.30
Berea	5.84	2.12
—	7.05	5.20
St. Peters	7.25	4.42
alundum	7.60	2.01
St. Peters	7.78	6.53
—	7.92	3.51
Berea	8.62	3.59
—	12.0	4.24
—	14.7	6.61

[a] With the exception of the alundum core, all of the rock samples were sandstones. Nine were not identified for proprietary reasons.

[b] The characteristic length of the pore is interpreted here as the square root of the permeability of the core to air.

For a water-wet rock, we estimate that the advancing interface is controlling ($-\mu_{(a)z} >> \mu_{(t)z}$ in Figure 3b) and Inequality (39) still applies. Considerations similar to those that led to Inequalities (25) indicate that for both oil-wet and water-wet rock

$$H \geqq 0 \tag{40}$$

DISPLACEMENT OF RESIDUAL OIL: CONCLUSIONS

Equation (32) gives us the form of the dependence of the average velocity in the oil phase during its deformation and before an instability develops. Without examining the criteria for the stability of the phase interfaces, we can say that everything done to enhance the average velocity in the oil phase will increase the efficiency of the displacement process. Several conclusions can be drawn.

From Inequality (38), we see that

11. The dimensionless group N_γ^{**} must be less than some critical value before any residual oil can be recovered by displacement in either oil-wet or water-wet permeable structures.

Inequality (38) also tells us that the critical value for N_γ^{**} has a magnitude of order unity. However, this is not of any practical value to us, since $|\Delta p|$ is not available for direct experimental measurement. A related quantity that we can measure is $|\nabla p|$, the magnitude of the pressure gradient in the rock structure. But in general we should expect that $|\nabla p| << |\Delta p|/l$.

Taber et al. (1973) reported that $|\nabla p|/\gamma$ must exceed some critical value before any residual oil can be recovered by displacement. Their data, interpreted as critical values of $\gamma/|\nabla p|\, R^2$ are shown in Table 1. It is interesting that the order of magnitude of $\gamma/|\nabla p|\, R^2$ (5×10^4) is independent of pore size for their data. Inequality (38) suggests that it should depend upon the wetting characteristics and detailed geometry of the structure, no measures of which were given.

Let us assume that N_γ^{**} is less than the critical value. We can see from

$$\frac{\partial}{\partial N_\gamma^{**-1}} \left(v_{(o)}^{**} \; N_\gamma^{**-1}\right) = \frac{A}{l^{**} D + N_{\kappa+\epsilon}^{**} \; H/l^{**}} \tag{41}$$

the effect of increasing the pressure gradient while holding the water-oil surface tension constant. Since this derivative must be positive and since A must be proportional to the applied pressure gradient, we have

12. For values of N_γ^{**} less than the critical value, the efficiency of residual oil recovery will increase as the applied pressure gradient increases in both oil-wet and water-wet structures.

This is confirmed experimentally (Wagner and Leach, 1966; Taber, 1969; Taber et al., 1973).

We can also ask about the effect of lowering the surface tension while maintaining the pressure gradient constant:

$$\frac{\partial v_{(o)}^{**}}{\partial N_\gamma^{**}} = \frac{-G}{l^{**} D + N_{\kappa+\epsilon}^{**} \; H/l^{**}} \tag{42}$$

We conclude

13. For values of N_γ^{**} less than the critical value, the efficiency of residual oil recovery will increase as the water-oil surface tension is decreased in both oil-wet and water-wet structures.

We discussed in conjunction with conclusions 5 and 6 the anomalous behavior observed by Wagner and Leach (1966).* When the surface tension was decreased below a critical value, the residual saturation was found to decrease both in their simulated oil-wet tests and in their simulated water-wet tests. This is in contrast with conclusion 5. But their findings are in agreement with conclusion 13, if we assume that some of the simulated oil phase, after initially being trapped, is subsequently displaced. This would imply that some of their simulated oil was recovered after breakthrough. Their experiment was not designed to sense recovery after breakthrough in the simulated water-wet tests.

The effect of lowering the surface viscosities is indicated by

$$\frac{\partial v_{(o)}^{**}}{\partial N_{\kappa+\epsilon}^{**}} = \frac{-(A - N_\gamma^{**}\, G)\,(H/l^{**})}{(l^{**} D + N_{\kappa+\epsilon}^{**} \; H/l^{**})^2} \tag{43}$$

This means

14. For values of N_γ^{**} less than the critical value, the efficiency of residual oil recovery will increase as the sum of the water-oil surface viscosities is decreased. This is true both for oil-wet and for water-wet structures.

There is at the present time no direct experimental evidence concerning the effect of $N_{\kappa+\epsilon}^{**}$ upon the efficiency with which residual oil is displaced by surfactant solutions.

The conditions under which we would expect the effect of the surface viscosities to be important is suggested by comparing Equations (42) and (43). We see that the magnitude of $\frac{\partial v_{(o)}^{**}}{\partial N_\gamma^{**}}$ is about $N_{\kappa+\epsilon}^{**}$ times that of $\frac{\partial v_{(o)}^{**}}{\partial N_{\kappa+\epsilon}^{**}}$. In making this estimate, we recognize that the critical value of N_γ^{**} has a magnitude of order unity [see Inequality (39)].

15. The effect of a reduction in the surface viscosities upon the efficiency of residual oil recovery is comparable to the effect of a reduction in the surface tension when $N_{\kappa+\epsilon}^{**}$ is sufficiently small.

Gladden and Neustadter (1972) report that for the in-

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* See footnote on page 1147.

terface between Kuwait crude ($\mu_{(O)} \doteq 0.13$ dyne s/cm^2) and a 1% salt solution, $\epsilon = 0.04$ to 0.19 dyne s/cm; between Iranian heavy crude ($\mu_{(O)} \doteq 0.12$ dyne s/cm^2) and a 1% salt solution, $\epsilon = 0.49$ to 2.48 dyne s/cm. From the second law, it can be shown that $\kappa \geqq 0$.* For a typical oil-bearing rock structure, $R = 5 \times 10^{-5}$ cm (square root of the salt water permeability for a 250 millidarcy rock). This allows us to estimate that $N^{**}_{\kappa+\epsilon} > 6 \times 10^3$ for the Kuwait crude-brine interface and $N^{**}_{\kappa+\epsilon} > 8 \times 10^4$ for the Iranian heavy crude-brine interface.

Gupta and Wasan (1974) have observed that the surface shear viscosity for many phase interfaces is small ($\sim 10^{-4}$ dyne s/cm) even when a surfactant is introduced. They suggest that significant surface shear viscosities may often be associated with a mixture of surfactants, at least one of which is relatively insoluble. The significant magnitude of the crude oil-brine surface shear viscosity may be attributable to the mixture of natural surfactants in the oil, identified by Strassner (1968) as polar asphaltenes and resins. Strassner's observations indicate that commercial surfactants added to a waterflood can displace some of the natural surfactants from the crude oil-water interface and reduce its surface viscosity. Gupta and Wasan (1974) have shown that the surface shear viscosity may both decrease and increase upon the continued addition of another surfactant to such a mixed surfactant system. More important, their work indicates that the concentrations in a mixed surfactant system at which both the surface tension and the surface shear viscosity are minimized can not be identified by measurements of the surface tension alone.

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NOTATION

A, B, D, E, G, H = dimensionless terms defined by Equations (20) to (23) and (33) to (34)
C = closed curves bounding discontinuous portions of Σ
$\mathbf{D}^{(\sigma)}$ = surface rate of deformation tensor (see Appendix A)
$F_z^{(p)}$ = z component of the viscous or friction drag that oil and water exert upon the pore walls; see Equation (2)
$F_z^{(p)*}$ defined by Equation (14)
$F_z^{(v)}$ = z component of the pressure or form drag that the oil and water exert upon the pore walls; see Equation (3)
$F_z^{(v)*}$ defined by Equation (15)
$\mathbf{g}_z$ = unit vector in z direction
$\mathbf{I}$ = identity tensor
l = pore length
l^{**} defined by Equation (37)
$\mathbf{n}$ = unit normal to pore walls directed into wall
N_γ defined by Equation (18)
N_γ^{**} defined by Equation (35)
$N_{\kappa+\epsilon}$ defined by Equation (19)
$N^{**}_{\kappa+\epsilon}$ defined by Equation (36)
p = pressure
p_0 = reference or ambient pressure
$p_{(\text{ent})}$ = average pressure at $S_{(\text{ent})}$
$p_{(\text{ex})}$ = average pressure at $S_{(\text{ex})}$
Δp = pressure drop over pore; defined by Equation (12)
$|\nabla p|$ = magnitude of pressure gradient in porous rock structure
$\mathbf{P}$ = projection tensor that transforms any vector on interface into its tangential component
R = radius of entrance and exit surfaces in Figures 2 and 3; characteristic pore radius
R^* = defined by Equation (17)
$R_{(a)}, R_{(t)}$ = radii of pore at the lines of contact with the advancing and trailing interface
$R_{(WO)}$ = radius of pore at the line of contact with the water-oil interface
$S_{(\text{ent})}$ = entrance surface, represented by dashed lines on left in Figures 2 and 3
$S_{(\text{ex})}$ = exit surface, represented by dashed lines on right in Figures 2 and 3
$S_{(w)}$ = pore walls
t = time
t^* = dimensionless time defined by Equation (13)
$\mathbf{T}$ = stress tensor
$\mathbf{T}_{(O)}$ = stress tensor in oil phase at water-oil interface
$\mathbf{T}_{(W)}$ = stress tensor in water phase at water-oil interface
$\mathbf{T}^{(\sigma)}$ = surface stress tensor
$v_{(O)}$ = average z component of velocity in oil phase
$v^*_{(O)}$ defined by Equation (16)
$v^{**}_{(O)}$ defined by Equation (32)
$\mathbf{v}^{(\sigma)}$ = surface velocity vector

Greek Letters

γ = surface tension
ϵ = surface shear viscosity
κ = surface dilatational viscosity
$\boldsymbol{\mu}$ = unit vector tangent to Σ, normal to C, and outwardly directed with respect to Σ
μ_z = z component of $\boldsymbol{\mu}$
$\mu_{(a)z}, \mu_{(t)z}$ = z component of $\boldsymbol{\mu}$ at advancing and trailing interfaces, respectively
$\mu_{(O)}$ = viscosity of oil phase
$\boldsymbol{\xi}_{(O)}$ = unit normal to water-oil interface pointing into oil phase
$\boldsymbol{\xi}_{(W)}$ = unit normal to water-oil interface pointing into water phase
$\rho^{(\sigma)}$ = surface density, mass per unit area
$\rho^{(\sigma)}_{(a)}, \rho^{(\sigma)}_{(t)}$ = surface densities for advancing and trailing interfaces
Σ = water-oil interfaces in system
$\text{div}_{(\sigma)}$ = surface divergence operation (see Appendix A)
$\dfrac{d_{(s)}}{dt}$ = derivative following a material particle in phase interface

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* The proof is analogous to that for the signs of the two coefficients appearing in newtonian model for bulk stress-deformation behavior (Slattery, 1972).

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APPENDIX A: COMMENTS ON NOTATION

Some of the notation used in the text represents an extension to differential geometry of the coordinate-free notation of tensor analysis (Slattery, 1972). The results are completely consistent with the presentation of McConnell (1957) including the use of the summation convention with repeated indices.

A surface is the locus of a point whose position vector $\mathbf{z}$ is a function of two parameters y^1 and y^2:

$$\mathbf{z} = \mathbf{p}^{(\sigma)}\,(y^1, y^2) \tag{A1}$$

Since the two numbers y^1 and y^2 uniquely determine a point on the surface, we call them *surface coordinates.*

At every point on the surface, the values of the spatial vector fields

$$\mathbf{a}_\alpha \equiv \frac{\partial \mathbf{p}^{(\sigma)}}{\partial y^\alpha} = \frac{\partial x_i}{\partial y^\alpha}\,\mathbf{g}_i \quad (\alpha = 1,2) \tag{A2}$$

are tangent to the y^α coordinate curves and therefore tangent to the surface. These two vectors are linearly independent and every vector tangent to the surface can be written as a linear combination of them. We can refer to them as the *natural basis* fields.

Let us define

$$a_{\alpha\beta} \equiv \mathbf{a}_\alpha \cdot \mathbf{a}_\beta \tag{A3}$$

These are often referred to as the covariant components of the metric tensor (McConnell, 1957). Let a be the determinant whose elements are the $a_{\alpha\beta}$ and let $a^{\alpha\beta}$ be the cofactor of $a_{\alpha\beta}$ in a, divided by a. The dual basis fields

$$\mathbf{a}^\alpha = a^{\alpha\beta}\,\mathbf{a}_\beta, (\alpha = 1, 2) \tag{A4}$$

are also linearly independent. Every vector tangent to the surface can be written as a linear combination of them as well.

The surface velocity vector $\mathbf{v}^{(\sigma)}$ is an example of a vector defined on the dividing surface that has normal and tangential components:

$$\begin{aligned}\mathbf{v}^{(\sigma)} &= v^{(\sigma)\alpha}\,\mathbf{a}_\alpha + (\mathbf{v}^{(\sigma)} \cdot \boldsymbol{\xi})\boldsymbol{\xi} \\ &= v_\alpha{}^{(\sigma)}\,\mathbf{a}^\alpha + (\mathbf{v}^{(\sigma)} \cdot \boldsymbol{\xi})\boldsymbol{\xi}\end{aligned} \tag{A5}$$

The $v^{(\sigma)\alpha}$ are said to be the *contravariant tangential* components of $\mathbf{v}^{(\sigma)}$; the $v_\alpha{}^{(\sigma)}$ are the *covariant tangential* components.

The *projection* tensor

$$\mathbf{P} = \mathbf{a}_\alpha\,\mathbf{a}^\alpha = \mathbf{a}^\alpha\,\mathbf{a}_\alpha \tag{A6}$$

transforms every vector on the surface into its tangential component.

The *surface gradient* of a scalar such as surface tension is defined as

$$\nabla_{(\sigma)}\gamma = \frac{\partial \gamma}{\partial y^\alpha}\,\mathbf{a}^\alpha \tag{A7}$$

A vector such as surface velocity $\mathbf{v}^{(\sigma)}$ is an explicit function of position on the dividing surface. The *surface gradient* of such a vector is similarly

$$\nabla_{(\sigma)}\mathbf{v}^{(\sigma)} = \frac{\partial \mathbf{v}^{(\sigma)}}{\partial y^\alpha}\,\mathbf{a}^\alpha \tag{A8}$$

We have a particular interest in the surface rate of deformation tensor, which becomes

$$\begin{aligned}\mathbf{D}^{(\sigma)} &\equiv \frac{1}{2}\,[\mathbf{P} \cdot \nabla_{(\sigma)}\,\mathbf{v}^{(\sigma)} + (\nabla_{(\sigma)}\,\mathbf{v}^{(\sigma)})^T \cdot \mathbf{P}] \\ &= \frac{1}{2}\,(\underset{\alpha,\beta}{v^{(\sigma)}} + \underset{\beta,\alpha}{v^{(\sigma)}})\mathbf{a}^\alpha\mathbf{a}^\beta\end{aligned} \tag{A9}$$

where the comma denotes surface covariant differentiation (McConnell, 1957). Finally, the *surface divergence* of a vector such as $\mathbf{v}^{(\sigma)}$ is

$$\mathrm{div}_{(\sigma)}\,\mathbf{v}^{(\sigma)} \equiv tr(\nabla_{(\sigma)}\,\mathbf{v}^{(\sigma)}) = v^{(\sigma)\alpha}{}_{,\alpha} - 2H\mathbf{v}^{(\sigma)} \cdot \boldsymbol{\xi} \tag{A10}$$

The surface stress tensor $\mathbf{T}^{(\sigma)}$ is a type of tensor defined on the dividing surface that transforms tangential vectors into tangential vectors and normal vectors into the zero vector:

$$\mathbf{T}^{(\sigma)} = \underset{\alpha\beta}{\mathbf{T}^{(\sigma)}}\,\mathbf{a}^\alpha\mathbf{a}^\beta \tag{A11}$$

We can define the surface gradient of such a tensor in a manner very similar to our definitions for the surface gradient of a scalar and the surface gradient of a vector. Of particular interest to us here is the surface divergence of this type of tensor:

$$\mathrm{div}_{(\sigma)}\,\mathbf{T}^{(\sigma)} = T_{\alpha\beta,\gamma}\,a^{\beta\gamma}\mathbf{a}^\alpha + T_{\mu\beta}B_{\nu\gamma}a^{\mu\nu}a^{\beta\gamma}\boldsymbol{\xi} \tag{A12}$$

The comma again denotes surface covariant differentiation (McConnell, 1957). The $B_{\alpha\beta}$ are the components of the second groundform tensor (McConnell, 1957).

APPENDIX B: DERIVATION OF EQUATION (7)

Let us assume that both the pore wall and the oil-water phase interface are axisymmetric. We can describe the interface in the form of Equation (A1) as

$$z = f(y^1, t)$$

$$y^1 = r$$

$$y^2 = \theta \qquad \text{(B1)}$$

These restrictions allow us to say

$$\text{on } C: \quad \mathbf{g}_z \cdot \mathbf{T}^{(\sigma)} \cdot \boldsymbol{\mu} = (\mathbf{g}_z \cdot \mathbf{a}_\alpha) T^{(\sigma)\alpha\beta} (\mathbf{a}_\beta \cdot \boldsymbol{\mu})$$

$$= \frac{\partial f}{\partial y^1} T^{(\sigma)11} \mu_1 \qquad \text{(B2)}$$

where from Equation (6)

$$T^{(\sigma)11} = [\gamma + (\kappa - \epsilon) \operatorname{div}_{(\sigma)} \mathbf{v}^{(\sigma)}] a^{11} + 2\epsilon D^{(\sigma)11} \qquad \text{(B3)}$$

Using Equation (A9), we can calculate that

$$D^{(\sigma)}_{22} = y^1 \left(v_r{}^{(\sigma)} + \frac{\partial v_\theta{}^{(\sigma)}}{\partial y^2} \right) \qquad \text{(B4)}$$

The definition for the surface divergence of a vector given in Equation (A10) may alternatively be written

$$\operatorname{div}_{(\sigma)} \mathbf{v}^{(\sigma)} = tr\, \mathbf{D}^{(\sigma)}$$

$$= a^{11} D^{(\sigma)}_{11} + a^{22} D^{(\sigma)}_{22} \qquad \text{(B5)}$$

We can consequently state that, because $\mathbf{v}^{(\sigma)} = 0$ at the pore wall,

$$\text{on } C: \quad \operatorname{div}_{(\sigma)} \mathbf{v}^{(\sigma)} = a^{11} D^{(\sigma)}_{11}$$

$$\operatorname{div}_{(\sigma)} \mathbf{v}^{(\sigma)} a^{11} = D^{(\sigma)11}$$

From Equation (B3), this means

$$\text{on } C: \quad \mathbf{T}^{(\sigma)11} = [\gamma + (\kappa + \epsilon) \operatorname{div}_{(\sigma)} \mathbf{v}^{(\sigma)}] a^{11} \qquad \text{(B7)}$$

Let us now observe that

$$\frac{\partial f}{\partial y^1} a^{11} \mu_1 = \mu_z \qquad \text{(B8)}$$

Equations (B7) and (B8) permit us to express Equation (B2) in the form of Equation (7).

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Modified One-at-a-Time Optimization

An optimization method has been developed that searches one variable at a time under the conditions that previously searched variables are at their approximate optimum and variables to be searched later are constant. This method provides the optimum and also information on the effects of the variables. The method is based on the Partan and Powell methods and on assuming linear partial derivatives of the objective function with respect to any given variable. The procedure involves searching each variable separately with other variables either constant or varied so that they remain at their estimated optimum for the given conditions. This method provides useful information on the effects of independent variables as well as locating the overall optimum and a number of partial optimums and requires a comparable number of trials.

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SCOPE

This paper reports on a study undertaken to develop and evaluate a search method of optimization that would provide information not only on the location of the optimum, but also on the effects of the individual independent variables on the objective function to be maximized or minimized. The principle of the method is to search one variable $Z_{(J=K)}$ at a time, with previously searched variables $Z_{(J<K)}$ at their estimated partial optimum for any given search point in $Z_{(J=K)}$, while variables to be searched later $Z_{(J>K)}$ are held constant. A partial optimum in this paper is taken to mean the optimum of 1 or more variables at given nonoptimum values of other variables. That is, the best value of $Z_{(1)}$ at given constant nonoptimum values of $Z_{(2)}$, $Z_{(3)}$, $Z_{(4)}$ would be a partial optimum of $Z_{(1)}$. The information obtained in this type search of 4 variables would provide the overall 4-variable optimum plus a number of 3-variable, 2-variable, and 1-variable optimums under various conditions. It would also show the effects of each variable, combined with interaction effects of that