Role of Capillary Forces in Determining Microscopic Displacement Efficiency for Oil Recovery by Waterflooding

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Abstract

The factors controlling the distribution of two immiscible fluids, such as oil and water, within the interstices of a porous solid are reviewed. It is shown that an improved understanding of these factors forms the basis of much recent work aimed at the development of new methods for reducing capillary forces and, consequently, eliminating residual oil saturations.

Introduction

The Petroleum Industry has for many years devoted much research effort to the development of new processes for achieving improved oil recovery efficiencies. The current status of the most promising of these new processes has been reviewed by Elkins(1) and by Arnold(2). For the most part, the research leading to these processes has developed along lines pointed out by Muskat(3) in a review published about 20 years ago. In addition to thermal processes, which are used primarily to overcome adverse crude oil viscosity characteristics, a variety of processes are designed to eliminate or reduce the so-called "surface forces" within the crude-oil-displacing fluid-reservoir rock system.

Hydrostatics, Capillarity and Residual Saturations

Hydrostatic Principles in Multiphase Fluid Systems

Two or more fluid phases confined within a porous solid phase of very small average pore size will generally be microscopically commingled. The fluid-fluid interfacial areas associated with fluid distributions of this type are large and characterized by high curvatures. The precise configurations of the individual segments of the total fluid-fluid interfacial area in such a system are described by two equations derivable from the fundamental principle of fluid hydrostatics(9). For simplicity, in what follows, only the case of two immiscible and relatively incompressible
fluids, e.g., oil and water, will be explicitly discussed. The extension to cases involving three fluids presents some complexities\(^{11}\), but, in principle, can be carried out without recourse to any additional fundamental considerations.

The first of the two hydrostatic equations is the Laplace equation:

\[
P_o - P_w = \gamma_{ow} \cos \theta_{ow} \tag{1}
\]

Here, \(P\) denotes pressure in a fluid phase, \(\gamma\) the interfacial tension and \(J\) the curvature of the fluid-fluid interface (c.f. Fig. 1). The subscripts \(o\) and \(w\) refer to oil and water, and the double subscript \(ow\) refers to the corresponding interface. The thermodynamic derivation of Equation (1) provides a context within which the effects of temperature, pressure and interfacial curvature on the interfacial tension can be interrelated\(^{10, 12}\). These considerations also apply, of course, to interfaces for which one of the contiguous fluids is a gas (denoted by the subscript \(g\)). In this case, the quantities \(\gamma_{ow}\) and \(\gamma_{og}\) are referred to as surface tensions.

The second hydrostatic equation is the Young equation,

\[
\gamma_{os} = \gamma_{ws} + \gamma_{ow} \cos \theta_{ow} \tag{2}
\]

Here, \(\theta_{ow}\) represents the angle of contact, as measured through the water phase, which the oil-water interface (fluid meniscus) makes with the solid surface, denoted by the subscript \(s\) (c.f. Fig. 1). The contact angle, hereafter denoted simply as \(\theta\), is clearly a property characterizing the three-phase line of contact. Measurements of this property typically display hysteresis effects\(^{15}\). It should also be pointed out that a more rigorous version of Equation (2) will include a term accounting for the line-tension in the three-phase line of contact\(^{11}\). This “line property” is the analogue of the interfacial tension for surfaces.

The contact angle provides the only direct and unambiguous specification of the so-called “wettability” property characteristic of a given oil-water-reservoir rock system. If the angle \(\theta\) is small, say less than 40 degrees, the system is usually said to be water-wet. Similarly, an oil-wet system is characterized by an angle \(\theta\) greater than 140 degrees. For angles of intermediate magnitude the wettability is best described as intermediate.

The measurement of the interfacial properties defined by Equations (1) and (2) under the temperature and pressure conditions typical of petroleum reservoirs presents a number of difficulties. Even for systems of relatively simple composition, such data are only gradually being reported in the literature. Recent studies of this type which should be noted are those of Jennings\(^{13, 14}\) and McCaffery\(^{14, 17}\). An earlier study by Hocott\(^{15}\) reported surface and interfacial tension data for several field systems. Measurements of contact angles for crude oil - reservoir water systems on flat, polished surfaces of quartz and calcite have been carried out by Treiber, Archer and Owens\(^{16}\). This work indicates that many petroleum reservoirs may be intermediate in wettability type, a conclusion which is in disagreement with the commonly held belief that water-wet conditions prevail in nearly all cases.

**APPLICATION TO POROUS SOLIDS**

The application of Equations (1) and (2) to determine the configurations of the fluid-fluid interfaces within porous solids presents difficulties not readily apparent from the usual textbook treatments of the problem. Because the average pore size is assumed to be small, the pressures in the two fluid phases may be taken as constant over distances comparable to the dimensions of an average pore. Also, the interfacial tension may be taken as independent of the magnitude of the curvature\(^{10}\). According to Equation (1), then, the interfacial configurations will correspond to surfaces of constant curvature. Even under this simplification, the algebraic expression for the curvature, \(J\), is not a simple one. The expression includes terms which involve the various first and second partial derivatives of the function representing the shape of the interface. In fact, the expression corresponds to a second-order non-linear differential equation for which general solutions in terms of known functions are not available. The problem is generally circumvented by the use of highly simplified geometrical models to represent the shape of the actual pores involved. The necessary boundary conditions are then provided by the assumed configuration of the pore walls and by the contact angle, \(\theta\), defined by Equation (2).

For example, in the case of a porous solid formed by a random packing of uniform spherical particles, the pore openings may be approximated by the inner surface of a torus\(^{16, 17}\). In such a model, the radius of the torus ring corresponds to the radius of the particles forming the packing. The equatorial distance from the axis of symmetry to the ring surface is then adjusted to provide pore openings of the appropriate sizes.

A further problem arises in connection with the stability of the fluid-fluid interfacial configuration which results from the solution of the differential equation represented by Equation (1). For typical pore models, such as packings of spherical particles of uniform size, it is easily shown\(^{19, 20}\) that a limited range of such configurations are stable (c.f. Fig. 2). This fact accounts for the hysteresis in the relationship between the capillary pressure, \(P = P_o - P_w\), and the saturation of the aqueous phase, expressed as \(S_w = V_w/(V_o + V_w)\), where \(V\) is the volume of a particular fluid in a test sample. (Under the implicit assumption that \(\theta = 0\), the quantity \(S\) is often referred to as the wetting-phase saturation.) The oil-phase saturation, \(S_o\), is similarly defined, so that \(S_w + S_o = 1\).
If the limits of stability are exceeded for a given pore, the system will respond by a sudden and localized flow in which one fluid is displaced from the pore by the other fluid. Such microscopic flow processes were first discussed by Haines(24) and are usually referred to in the field of soil physics as "Haines jumps"(25). The alternative designation of "rheon" has been suggested(12), and this term is used by Morrow(26), although in a more restricted sense than originally proposed. Rheons can be easily observed visually by allowing air to displace a liquid phase (or vice versa) from the pore space formed by packing small glass beads in a glass capillary tube. A study of the pressure oscillations associated with a displacement experiment of this type has been reported by Crawford and Hoover(27).

The stability limits applicable to interfacial configurations with axial symmetry have recently been investigated by Dyson and co-workers(28-30). This work has shown that the conjugate-point criterion of the calculus of variations leads to explicit solutions for the limiting interfacial configurations which are obtained experimentally. A thermodynamic approach to this problem, which is applicable to more general interfacial shapes, has been initiated by Everett and Haynes(31, 32). An intuitive treatment(12), also thermodynamic in nature, suggests that the appropriate condition for configurational stability can be expressed as

\[ \frac{dJ_{w}}{dV_{w}} < 0, \text{ for } \theta < 40^\circ \] (3a)

\[ \frac{dJ_{w}}{dV_{w}} > 0, \text{ for } \theta > 140^\circ \] (3b)

As mentioned previously, solutions to Equation (1) can only be obtained for highly simplified models of the pore geometry thought to be characteristic of porous solids(26, 27). Regardless of the particular geometrical forms which may be adopted as the basis of such a model, the meniscus configurations corresponding to the limiting conditions for stability will be given by Equations (3). The maximum and minimum curvatures so obtained are referred to as drainage and imbibition curvatures, \( J_{dr} \) and \( J_{imb} \), respectively. The effect of varying contact angle can then be expressed(12) in terms of a \( \cos \theta \) factor and normalized function, \( Z(\theta) \), as follows:

\[ J_{dr} = 2 H_{dr} Z_{dr}(\theta) \cos \theta / R \] (4a)

\[ J_{imb} = 2 H_{imb} Z_{imb}(\theta) \cos \theta / R \] (4b)

Here, \( H_{dr} \) and \( H_{imb} \) are the normalized values of the two limiting curvatures for the case of zero contact angle. The normalization factor is \( 2/R \), where \( R \) is a characteristic distance for the pore model. For example, if the model is a random packing of uniform spherical particles, \( R \) may be taken to be the particle radius.

Experimental systems approximating this model indicate that \( H_{dr} \cong 2.70 \) and \( H_{imb} \cong 1.75 \). The model calculations(41) also show that, for drainage conditions,

\[ Z_{dr}(\theta) > 1 \text{ if } \theta > 0 \] (5a)

and for imbibition conditions,

\[ Z_{imb}(\theta) < 1 \text{ if } \theta > 0 \] (5b)

Under the definitions adopted for \( H_{dr} \) and \( H_{imb} \), it is clear that both \( Z_{dr}(\theta) \) and \( Z_{imb}(\theta) \) approach unity as the contact angle, \( \theta \), vanishes.

**CAPILLARY PRESSURE VERSUS FLUID SATURATION RELATIONSHIPS**

Consider a sample of reservoir rock or similar porous solid which is fully saturated with an aqueous phase, and assume that the condition \( \theta = 0 \) holds. The quasi-static displacement of this phase by a non-wetting phase is then defined by the set of increasing values of the capillary pressure, \( P_c \), and a corresponding set of decreasing values of the wetting-phase saturation, \( S_w \). The pressure-versus-saturation relationship defined by such data is called the drainage capillary pressure curve. The pressure-versus-saturation relationship for the reverse process, in which the wetting phase displaces the non-wetting phase, is known as the imbibition capillary pressure curve. Because, for a typical pore configuration, the imbibition pressure is of the order of half of the drainage pressure, the curves will display considerable hysteresis(24, 33).

Excellent examples of such curves, with well-defined interior scanning loops, have been reported by Morrow and Harris(24), Topp and Miller(25) and Bomba(26). A review emphasizing the fundamental physical principles underlying such hysteresis behaviour has been given by Morrow(26). An earlier, but illuminating, account of the manner in which interface stability conditions give rise to rheons or Haines jumps, on the microscopic or pore-size level, and to hysteresis effects on the macroscopic level is due to Miller and Miller(27).

As rheons are associated with both branches of the capillary pressure curve, it may be convenient to distinguish between the two resulting types of rheons. On the drainage branch, the rheons correspond to a process in which the wetting-phase saturation is decreasing; hence such rheons may be referred to as xerons. Similarly, rheons on the imbibition branch correspond to an increasing wetting-phase saturation and may be referred to as hygrons.

A characteristic feature of the drainage capillary pressure curve for two nearly incompressible fluids, such as oil and water, is the minimum value of the wetting-phase saturation. It appears that this residual saturation, \( S_{res} \), is reached asymptotically as the capillary pressure is increased indefinitely. In the case of a typical unconsolidated pack of closely sized sand particles, the wetting-phase fluid corresponding to the minimum saturation is largely in configurations known as pendular rings. These are individually isolated segments of fluid surrounding the particle-to-particle contact points. As the particle size distribution is made broader, or possibly bimodal in character, it is possible to develop local, small-scale packing heterogeneities. If this occurs, the magnitude of the residual wetting...
Narrow Pore Size Distribution

Figure 3a — Capillary pressure versus wetting-phase saturation — narrow pore size distribution.

Figure 3b — Capillary pressure versus wetting-phase saturation — wide pore size distribution.

Phase saturation for a drainage process increases, as Morrow\(^{(31,38)}\) has recently shown (c.f. Fig. 3b). The additional fluid is now trapped in such a way that small clusters of pores remain entirely filled. The relationship between the residual wetting-phase saturation, as measured in the laboratory, and the water saturation in a petroleum reservoir at the time of discovery (the connate water saturation) is discussed by Morrow\(^{(39)}\).

In a manner somewhat analogous to the drainage case, the imbibition capillary pressure curve is characterized by a minimum value of the non-wetting-phase saturation. The residual non-wetting fluid is, however, trapped in configurations which are quite different from those of the residual wetting fluid under drainage conditions. In an imbibition process, the non-wetting fluid is trapped in such a way as to nearly fill individual pores, or small clusters of neighbouring pores. This trapping occurs because any given pore will have only a limited number of openings leading to other pores. There is then a finite probability that any given pore will be by-passed\(^{(40)}\). Evidence has been reported\(^{(41)}\) which indicates that this probability increases as the larger pores of the pore-size distribution are subjected to displacement; i.e., as the capillary pressure decreases.

As was pointed out some time ago by Frisch and Hammersley\(^{(42)}\), a rather sophisticated theory for treating the statistical aspects of the trapping process has been developed. This theory, known as the theory of percolation processes, is closely related to the well-known problem of treating a random, self-avoiding "walk" on an idealized lattice system. It is apparent from a recent review\(^{(43)}\) that a direct application of this theory to the prediction of residual non-wetting-phase saturations for porous solids has not yet been developed.

Experimental results for various porous systems clearly show that the broader the pore-size distribution, the larger is the residual non-wetting-phase saturation. For typical sandstone rocks, this residual saturation is of the order of 50 to 40 per cent. Because such rocks are usually considered to be water-wet, this residual saturation, denoted as \(S_{\text{or}}\), corresponds to residual oil. It also defines what is termed the microscopic displacement efficiency,

\[
E_m = \frac{1 - S_{\text{or}} - S_{\text{wi}}}{1 - S_{\text{wi}}} \tag{6}
\]

If, as may well be the case, many oil-water-reservoir rock systems are not completely water-wet, it may be possible to alter the wettability in such a way as to reduce the value of \(S_{\text{or}}\) and hence recover additional oil. In this connection, Morrow and co-workers\(^{(44,45)}\) are currently studying the dependence of both the drainage and imbibition capillary pressure versus saturation relationships on the wettability of the system, as defined by the contact angle. The model pore studies\(^{(21)}\), mentioned above, suggest that if the angle is larger than 45 degrees, a wetting phase, which has been displaced through the application of a positive capillary pressure, will not be able to reimbibe. This prediction has been borne out, at least qualitatively, by the recently reported experimental results\(^{(44,45)}\), as well as by unpublished work by Sutula and Wilson\(^{(46)}\).

Low Interfacial Tensions For Improved Recovery

Simultaneous Flow of Immiscible Fluids

When oil is displaced from a homogeneous porous solid by a waterflood process, both fluid phases undergo hydrodynamic transport through the pore space. Only when, in a given region of the porous solid, the oil-phase saturation is reduced to its residual value does the oil phase cease to flow. Under simultaneous two-phase flow conditions, the relationships between the normalized coefficients of permeability for the two phases and the water saturation are known as relative permeability curves\(^{(47)}\).
Many fundamental studies of these relationships have been reported in the literature. It is found that for so-called steady-state conditions (saturations not changing with time), such curves are closely related to the corresponding capillary pressure curves. Thus, hysteresis behaviour, as defined by differing curves for drainage and imbibition conditions, is observed.54,49. Also, the final saturations reached for both drainage (oil displacing water) and imbibition (water displacing oil) are those which are defined by the capillary pressure curves. In particular, it is found that the relative permeability relationships are independent of the flow rates employed and of the viscosities of the two fluids.50,111. This evidence suffices to prove that, on a microscopic level, the commingled fluids are substantially in mutual equilibrium as far as capillary pressure is concerned.125,133.

Studies of actual displacement processes, under non-steady-state conditions, are also revealing.109. Perkins124 has shown that when unconsolidated sand packs are waterflooded, the residual oil saturation is independent of flood rate, Loomis and Crowell152 found that for gas-oil systems under drainage conditions in homogeneous rocks, the relative permeability relationships are in good agreement with the relationships measured by steady-state methods. In the case of water-oil systems, however, these workers found that steady-state and non-steady-state methods were not in agreement, unless oil-wet conditions were maintained. Because for water displacing oil an oil-wet condition gives rise to a drainage process, it is seen that only for the non-steady-state imbibition process are departures from local capillary equilibrium significant. This strongly suggests the possibility that this type of behaviour is due to dynamic contact-angle effects. However, it is not known at present how information on the flow-rate dependence of the contact angle is actually to be applied in this context.

CRITICAL RANGE OF THE CAPILLARY NUMBER

It has been stated in the previous section that for a completely water-wet system the residual oil saturation is independent of the flood rate. This implies that, under ordinary flooding conditions, capillary forces dominate the macroscopic displacement process and that the microscopic distribution of the oil and water phases is determined by the conditions for hydrostatic equilibrium. Clearly, however, if the flood rate is made sufficiently high, this situation will no longer be maintained. Viscous forces will begin to have an effect on the magnitude of the residual oil; i.e., on the microscopic displacement efficiency as defined by Equation (6).

In order to assess the transition between a displacement process dominated by capillary forces and one dominated by viscous forces, it is convenient to consider the dependence of the microscopic displacement efficiency, on a suitable dimensionless parameter, such as the "capillary number", defined as

\[ N_{ca} = \frac{\mu_w U_w}{\varphi \gamma_{ow}} \]  

(7)

Here, \( \mu_w \) and \( U_w \) are the water phase viscosity and flow rate per unit cross-sectional area, respectively, and \( \varphi \) is the porosity of the solid. This number, or its equivalent, has been used by a number of authors.56,47,104,56. Physically, it represents the non-dimensional ratio of the magnitude of the viscous forces to the magnitude of the capillary forces.60,61. For ordinary waterflooding conditions, \( N_{ca} \) is of the order of 10\(^{-4}\).

Laboratory studies of the relationship between the capillary number and the microscopic displacement efficiency have usually been carried out by means of "tertiary" waterfloods. Such an experiment is preceded by a conventional waterflood. The resulting value of the residual oil saturation is that which corresponds to secondary recovery under field conditions. The tertiary flood then involves greatly increasing the flow rate, \( U_w \), greatly decreasing the interfacial tension, \( \gamma_{ow} \), or both. An increased wetting-phase viscosity, \( \mu_w \), may also be used. As the capillary number is substantially increased, eventually some additional oil is recovered. This increased recovery is attributed to the tertiary flood.

For packs of very coarse sand, Leverett47 reported data which showed indications of slightly improved recovery efficiency for capillary numbers as low as 10\(^{-2}\). These measurements were not extended to higher values of \( N_{ca} \). Studies on several sandstone samples were carried out by Moore and Slobod19, who found the critical value of \( N_{ca} \) for the initial reduction in residual oil saturation to be about an order of magnitude higher; i.e., about 10\(^{4}\). Results reported by Taber62,63 suggest that this lower critical value of \( N_{ca} \) is of the order of 5 \times 10\(^{-2}\), whereas values reported by Lefebre du Prey66,57 and by Foster69 are again about 10\(^{2}\). Variations in the lower critical value of \( N_{ca} \) are to be expected, as various reservoir rocks will differ widely with respect to pore structure and pore size distribution. Also, it is by no means certain that all of the reported investigations were carried out under the same contact-angle conditions.

Evidence for the magnitude of the upper critical value of \( N_{ca} \), which corresponds to complete oil recovery, has not been so extensively reported in the literature. It appears that in order to reduce the value of the residual oil saturation by a factor of about one-half, it is necessary to increase the capillary number by a factor of 10\(^{0.62,63} \) to 100 \( (66,57,58) \). Work reported by Foster69 indicates that increasing \( N_{ca} \) by a factor of 200-500 will result in microscopic displacement efficiencies which approach 100 per cent (c.f. Fig. 4). Thus, the upper critical value of the capillary number is of the order of 10\(^{5} \) to 10\(^{6}\). In a recent study by Dullien and co-workers48, the upper critical value of \( N_{ca} \) was not established. Although water-wet conditions apparently were maintained in these experiments, the techniques used to establish that such conditions existed are not specified.
Mobilization of Residual Oil

The correlation between the displacement efficiency and the capillary number, as obtained from tertiary waterflood experiments, strongly suggests that the process of mobilizing residual oil depends on a competition between viscous and capillary forces. A description of the mechanism by which this competition is brought into play would obviously be instructive. Although various authors have attempted to develop such mechanistic descriptions, these efforts are widely scattered in the literature and have not been subjected to critical examination. Clearly, a test of any such description is whether it is consistent with the observed critical range of the capillary number, \( N_{ca} \).

As pointed out by Taber\(^{62}\), the classical “Jamin effect”, discovered over 100 years ago, provides the basic concept required for the development of a mechanistic interpretation of the process of mobilizing residual oil. An early attempt in this direction is due to Gardescu\(^{63}\). This work is concerned, however, with two distinct effects, both referred to as the Jamin effect. As pointed out by Smith and Crane\(^{66}\), these two effects are associated with (a) contact-angle hysteresis, as observed in cylindrical capillary tubes, and (b) capillary-pressure hysteresis, as observed in non-cylindrical tubes, i.e. tubes in which a series of constrictions are introduced.

The resulting confusion in terminology seems to have been compounded by an insufficient appreciation of the actual basis of capillary pressure hysteresis effects\(^{69}\). As discussed above, this hysteresis is a consequence of the stability conditions applicable to the configuration of any fluid-fluid interface which is bounded by contact with a solid phase\(^{62-63}\). These stability conditions are given by Equations (3). Thus, the model calculations summarized in Equations (4) and (5) should provide a more satisfactory basis for developing the desired mechanistic interpretation of the critical range of \( N_{ca} \) than does the approach followed by Gardescu\(^{63}\).

Figure 5 is a schematic representation of an isolated segment of non-wetting-phase fluid trapped in the interstices of a porous solid by an invading wetting phase. The residual oil saturation (water-wet condition) is the sum of such trapped volumes of oil, divided by the total pore volume. Microscopic studies indicate that these oil “ganglia” usually extend over no more than about 10 neighbouring pores. If now the surrounding water phase is caused to flow at an extremely high rate, such an isolated segment will also be caused to flow. However, this flow will be accompanied by at least two individual displacement events, or rheons. One of these will be of the drainage type, in which oil moves out of the original volume occupied by the ganglion. The other will be of the imbibition type, in which water moves into the original volume. The drainage rheon (xeron) occurs at the downstream or high-pressure side of the ganglion; the imbibition rheon (hygron) occurs at the upstream or high-pressure side.

This picture of the oil mobilization process thus requires that a critical pressure gradient be exceeded in the surrounding water phase. For the simplified pore-shape model discussed above\(^{21}\), this critical gradient is given by

\[
(\Delta P_w/\Delta L)_{crit} = \gamma_{ow} \left( J_{dr} - J_{imb} \right) \frac{2}{N R} \tag{8}
\]

Here, \( J_{dr} \) and \( J_{imb} \) are the drainage and imbibition curvatures given by Equations (4a) and (4b), \( R \) again denotes the radius of the uniform spherical particles forming the porous solid, and \( N \) is the ratio of the length of the mobilized ganglion, \( \Delta L \), to the particle diameter. The quantity \( N \) thus measures the minimum number of pores comprising a particular ganglion; i.e., the number of pores encountered if the ganglion is traversed in the direction of the surrounding water-phase flow.

In order to relate the critical pressure gradient given by Equation (8) to the corresponding capillary number, \( (N_{ca})_{crit} \), it is only necessary to introduce Darcy’s law. Equation (7) can then be written as

\[
(N_{ca})_{crit} = \frac{k_w K}{\gamma_{ow}} \left( \frac{\Delta P_w}{\Delta L} \right)_{crit} \tag{9}
\]

where \( K \) is the value of the single-phase permeability and \( k_w \) is the relative permeability to water. As some authors report the results of tertiary waterflood experiments in terms of the quantity \( (\Delta P_w/\Delta L)_{crit}/\gamma_{ow} \), Equation (9) can be used to compute the corresponding values of the capillary number. In evaluating the range of capillary numbers used in the work reported by Taber\(^{62, 63}\), for instance, it is necessary to employ this relationship.

The permeability, \( K \), may also be related to the capillary pressure for the case of zero contact angle through a non-dimensional quantity, the Leverett number\(^{33}\), defined as

\[
N_{L} = J_0 \sqrt{K/\gamma} \tag{10}
\]

If now Equations (9) and (10) are combined with Equations (4) and (8), the following expression is obtained for the case of \( \theta = 0 \),

\[
(N_{ca})_{crit} = \frac{k_w (N_{L})^2 G}{4 N H_d} \tag{11}
\]

where

\[
G = 1 - (H_{imb}/H_d) \tag{12}
\]

In order to test Equation (11), the following average values of the various parameters may be used: \( k_w = 0.3, N_{L} = 1/\sqrt{5}, H_d = 2.70, G = 0.35 \) and \( N = 2 \). These values are typical for unconsolidated packs of uniform glass beads or nearly spherical sand grains. Using these values, the computed value of \( (N_{ca})_{crit} \) is approximately \( 10^5 \). Because this value falls within the critical range of capillary numbers observed experimentally, the mechanism for oil mobilization which has been described is reasonable and can be accepted as a working hypothesis.
Further consideration of Equation (11) also suggests that the observed critical range of capillary numbers ($10^4$ to $3 \times 10^5$) is associated with the expected ranges for the parameters appearing in this equation. In particular, the lower critical value of $N_{Ca}$ is seen to be related to those ganglia, formed during the original trapping processes under ordinary waterflood (imbibition) conditions, which have the largest values of the ratio $N/(N_{Le})^2$. In a similar manner, the upper critical value of $N_{Ca}$ will correspond to the mobilization of oil trapped in single pores ($N = 1$) of the smallest sizes within the pore-size distribution. Thus, the proposed mechanism easily accounts for a rather broad critical range of capillary numbers.

It should be noted that, according to Equation (11), neither the size of the spherical particles forming the porous solid nor the permeability of the solid directly influences the critical value of the capillary number. Therefore, even though reservoir rocks will differ widely with respect to these parameters, it is not expected that such variables will contribute significantly to the observed range of critical capillary numbers. On the other hand, variations in the width of the pore-size distribution and in the shapes of the pores could, as already indicated, contribute to variations in the critical capillary number.

It is clear that the picture of the oil mobilization process which leads to Equation (11) is based on the same concepts which are used to explain the occurrence of hysteresis in the capillary pressure versus fluid saturation relationship. Thus, the pressure difference in the wetting phase which appears in Equation (8) is directly related to the difference between the drainage and imbibition interfacial curvatures discussed in a previous section. It should be remarked in this connection that Dullien(67) has suggested a somewhat similar expression. However, the relationship which is proposed appears to be derived solely by considering the magnitudes of the equivalent radii of a void and of its pore entry. Thus, the mechanism of the oil mobilization process envisaged by Dullien does not explicitly, at least, involve the condition for the configurational stability of fluid interfaces. This condition, as has been pointed out above, is responsible for the occurrence of hysteresis in the capillary pressure versus saturation relationship.

The model calculations(29) on which Equation (11) is based can also be used to predict the effect of contact angle. If a normalized function expressing this effect is defined by the relationship

$$W(\theta) = \frac{(N_{Ca}(\theta)/(N_{Le}))}{\theta=0}$$

then the model leading to Equations (4) will yield the following result,

$$W(\theta) = [Z_{oil}(\theta) - (1 - G)|Z_{imb}(\theta)|(\cos \theta/G)]$$

If now Equations (5) are taken into account, it is seen that the effect of increasing $\theta$ on $Z_{oil}$ and $Z_{imb}$ may be such that $W(\theta)$ will actually increase. This is in contrast to the effect predicted by taking $W(\theta)$ to be identical with $\cos \theta$. It is found, in fact, that $W(\theta)$ may be as large as 2.2 when $\theta$ is about 45 degrees. Thus, the optimum wettability condition for tertiary waterflooding is predicted to be one of complete water-wetness ($\theta = 0$).

Having provided a satisfactory mechanistic basis for the observed range of critical capillary numbers, the problem of achieving improved oil recovery by altering the value of the interfacial tension, $\gamma_{ow}$, may be approached with added confidence, as to the magnitude of the required change. Thus, if $N_{Ca}$ is to be increased by a factor which is of the order of $10^4$, the interfacial tension must be decreased by a similar factor. In other words, the interfacial tension must be reduced to what may be called an ultra-low value. Such a value is of the order of $10^{-4}$ to $10^{-2}$ dynes/cm. Earlier estimates(66,69) of the required level suggested that 0.05 dynes/cm was an appropriate target for the purposes of tertiary oil recovery by interfacial tension alteration. These estimates, however, were based on limited evidence concerning the relationship between the capillary number and displacement efficiency.

SURFACE CHEMISTRY OF LOW-TENSION SYSTEMS

The achievement of ultra-low values of the interfacial tension between oil and water phases represents a challenge of considerable magnitude. The literature dealing with the fundamental aspects of the adsorption of surface-active chemical species at the oil-water interface offers limited guidance in this respect. The early work of Harkins and Zollman(79), who reported a single instance of a tension as low as $2 \times 10^{-3}$ dynes/cm, appears never to have been followed up by any systematic study of the composition variables suggested by this observation. Presumably, it has been believed that any such system will inevitably undergo spontaneous or self-emulsification. If this type of behaviour were of universal occurrence, the study of such interfacial states by conventional techniques based on thermodynamics would, of course, be impossible.

In a pioneering study of the interfacial behaviour of crude oil-water systems, Reisberg and Doscher(71) attributed the observed ultra-low value for $\gamma_{ow}$ by Harkins and Zollman to the in-situ formation of a highly surface-active component. Using a sample of crude oil from Ventura, California, and the pendant-drop technique for measuring interfacial tension, Reisberg and Doscher found that a tension as low as $10^{-4}$ dynes/cm could be observed when the concentration of NaOH in the aqueous phase was about 0.1 N. The tensions for such systems, however, were rather unstable, so that equilibrium values of $\gamma_{ow}$ were not obtained. Jennings(72) also used the pendant-drop method and reported an ultra-low value of $\gamma_{ow}$ for a crude oil-surfactant solution system.

More recently, studies carried out with aqueous solutions of the petroleum sulphonate class of surfactants(66,73) have also demonstrated that ultra-low values of $\gamma_{ow}$ can be achieved. It has been found that the average surfactant molecular weight, the nature of the surfactant molecular weight distribution and the electrolyte concentration of the aqueous phase are significant variables. In fact, a rather close specification of each of these parameters is essential. The interfacial compositions of such systems will be, of course, of considerable complexity. It appears, however, that the tendency for spontaneous emulsification is greatly reduced, if not eliminated, in these cases. The conditions under which instabilities of this type could arise are also complex. These conditions are the subject of an analysis recently reported by Miller and Scriven(74).

Although it seems quite likely that the basic mechanism involved in low-tension waterflooding for ter-
Summary and Conclusions

1. The distribution of commingled immiscible fluid phases, e.g., oil and water, within the interstices of a homogeneous porous solid, e.g., reservoir rock, is determined by capillary forces. When the conditions for the configurational stability of a particular fluid-fluid interface within an individual pore are not satisfied, a sudden and rapid burst of flow occurs. The ensemble of these microscopic flow events, or rheons, constitutes the macroscopic displacement process.

2. This mechanism accounts for hysteresis in the capillary pressure and relative permeability versus saturation relationships; i.e., the differences between the drainage and imbibition processes. It also accounts for the existence of residual saturations under both types of displacement processes; i.e., the minimum wetting-phase saturation for drainage and the minimum non-wetting-phase saturation for imbibition.

3. If a lower critical value of a non-dimensional quantity, the capillary number, is exceeded, the residual non-wetting-phase saturation can be reduced. When the upper critical value of the capillary number is reached, the residual non-wetting-phase saturation is eliminated. This range of critical capillary numbers can be predicted from simplified pore-shape models and a consideration of the conditions for the configurational stability of fluid interfaces.

4. In order to achieve a value of the capillary number sufficiently high that the residual oil saturation can be eliminated, an ultra-low value of the oil-water interfacial tension is required. Such a value is of the order of 10^-10 to 10^-12 dynes/cm, and it has been recently shown that aqueous solutions of petroleum sulphonates can provide tensions in this range. This finding forms the basis of several new processes for tertiary waterflooding. Model calculations indicate that a condition of complete water-wetness should provide the optimum wettability for oil recovery by this means.

Acknowledgment

Appreciation is expressed to Mobil Research and Development Corporation for permission to publish this paper.

Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>$k_r$</td>
<td>relative permeability</td>
</tr>
<tr>
<td>$K$</td>
<td>single-phase permeability</td>
</tr>
<tr>
<td>$L$</td>
<td>distance in direction of macroscopic flow</td>
</tr>
<tr>
<td>$N_{o}$</td>
<td>number of pores in trapped oil gellation</td>
</tr>
<tr>
<td>$N_{p}$</td>
<td>capillary number, non-dimensional</td>
</tr>
<tr>
<td>$P_c$</td>
<td>Leverett number, non-dimensional</td>
</tr>
<tr>
<td>$P_f$</td>
<td>fluid phase pressure</td>
</tr>
<tr>
<td>$P_{c}$</td>
<td>capillary pressure</td>
</tr>
<tr>
<td>$S_{w}$</td>
<td>grain or particle radius</td>
</tr>
<tr>
<td>$S_w$</td>
<td>saturation, fraction of void volume occupied by a fluid</td>
</tr>
<tr>
<td>$S_{f}$</td>
<td>fluid phase flux rate per unit cross-sectional area</td>
</tr>
<tr>
<td>$S_{d}$</td>
<td>fluid phase volume</td>
</tr>
<tr>
<td>$W(\theta)$</td>
<td>function expressing effect of contact angle on $a$</td>
</tr>
<tr>
<td>$Z(\theta)$</td>
<td>function expressing effect of contact angle on $r$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>interfacial or surface tension</td>
</tr>
<tr>
<td>$\theta$</td>
<td>contact angle</td>
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<tr>
<td>$\mu$</td>
<td>fluid phase viscosity</td>
</tr>
<tr>
<td>$\phi$</td>
<td>porosity, fractional void volume</td>
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Greek Letters

<table>
<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>$\rho$</td>
<td>oil phase</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>water phase</td>
</tr>
<tr>
<td>$\rho_{gw}$</td>
<td>gas-oil interface</td>
</tr>
<tr>
<td>$\rho_{gw}$</td>
<td>gas-water interface</td>
</tr>
<tr>
<td>$\rho_{gwa}$</td>
<td>oil-water interface</td>
</tr>
<tr>
<td>$\rho_{wa}$</td>
<td>oil-solid interface</td>
</tr>
<tr>
<td>$\rho_{wa}$</td>
<td>water-solid interface</td>
</tr>
<tr>
<td>$\rho_{w}$</td>
<td>oil-water-solid line of contact</td>
</tr>
<tr>
<td>$\rho_{w}$</td>
<td>drainage branch of hysteresis curve</td>
</tr>
<tr>
<td>$\rho_{w}$</td>
<td>residual wetting phase, water-wet condition</td>
</tr>
<tr>
<td>$\rho_{w}$</td>
<td>residual non-wetting phase, water-wet condition</td>
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<tr>
<td>$\rho_{w}$</td>
<td>critical value of the capillary number</td>
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Subscripts

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<tbody>
<tr>
<td>$a$</td>
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<tr>
<td>$g$</td>
<td>gas phase</td>
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<tr>
<td>$w$</td>
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</tr>
<tr>
<td>$w$</td>
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Literature Cited

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(23) Smith, W. O., Physics, 4, 184 (1933).
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(35) Leverett, M. C., Trans. AIME, 142, 152 (1941).