

RESEARCH ON ENHANCED OIL RECOVERY: PAST, PRESENT AND FUTURE

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Abstract - Past and present research on Enhanced Oil Recovery is reviewed with emphasis on the surface phenomena involved. The nature of capillary pressure phenomena in porous media has been understood for some time, and much research has been devoted towards the alteration of the surface forces which prevent the efficient displacement of oil by water. Early work often treated surface active agents as wetting agents designed to remove the oil from the solid surface by classical detergent action. More recent work has recognized the strong influence of oil-water interfacial tension on the displacement of discontinuous oil blobs or ganglia. Therefore, surfactant systems are now being developed to produce the lowest possible oil-water interfacial tensions by adjusting the various components and thus, the phase behavior in the total system. In addition to interfacial tension, the phase behavior itself can strongly influence the oil displacement. The surfactant work, current work in blob mechanics, current research in CO₂ flooding, and past results in alcohol flooding all indicate that an expanding oil phase is very important for effective oil displacement. Therefore, much current research is directed toward methods which utilize materials (including gases such as CO₂ and mobility control agents) to dislodge oil blobs, or to prevent their entrapment by maintaining a continuous oil phase and improving sweep efficiency during displacement. The general direction of future research on enhanced oil recovery is predicted.

INTRODUCTION

According to legend, the first successful attempts to force oil from underground rocks by the injection of another fluid occurred by accident. In the early oil production days in Pennsylvania, wells were often abandoned improperly, and surface water was allowed to enter the productive sand zone (1,2). Actually, the first deliberate waterflood for oil recovery may have occurred in Sweden prior to 1740 when "running water was used to produce crude oil from galleries cut into the rocks bearing strata of 'tar and sand'" (3). Early operators in America feared that water entering the productive zone would "drown" the oil wells and for years, many states had laws which prohibited the injection of water into oil-producing sands. However, the increased production from waterflooding was observed consistently and by 1940, it was considered to be "unquestionably the most efficient method ever devised for increasing oil recovery" (1).

In spite of the enormous effectiveness of waterflooding, the early engineers soon realized that waterflooding still bypassed some oil. A patent was granted in 1917 for the addition of alkali to the flooding water (4), and by 1925 (5), engineers were describing how the surface forces which were responsible for holding the oil in the rock might be altered for better oil recovery. This paper will examine some of these surface chemistry methods and comment on the "state of the art" in enhanced recovery today. Because this is a conference on surface chemistry, emphasis will be placed on methods that alter or eliminate the surface forces which exist between oil and water or between any of the fluids or the fluids and solids which are found in petroleum reservoirs. Recovery methods which depend primarily on heat will not be reviewed.

EARLY WORK ON DISTRIBUTION OF OIL, WATER AND GAS IN THE POROUS ROCKS

From the earliest times, man has recognized that the material called petroleum comes from rocks (3). Although the mechanics of the flow of petroleum, water and gas from these rocks are still being studied, the early petroleum engineers soon recognized that the oil must flow through very small passages between the sand grains, and that capillary forces must be involved wherever interfaces occur between two fluids. The earliest published work on the large resistance to flow caused by a series of bubbles in a capillary was that by Jamin (6) in 1859.

The early oil production experts were well aware of this effect. Indeed, Herold (7), in a comprehensive book dealing with mechanisms of oil production, bases his entire description of Paleozoic production (half of the book) on the fact that oil and gas are distributed uniformly as tiny droplets of oil and little bubbles of gas (he ignores water) which occur in sequence through all pore space within the rock. Just as Jamin found that a series of gas bubbles in a perfectly smooth capillary tube could build up large resistances to flow, Herold pointed out that one could visualize thousands of gas bubbles interspersed between the oil phase in either smooth or rough capillaries, and that large pressures could be built up even though the pressure across an individual gas bubble was very small. Although Jamin's original effect was observed only in smooth capillary tubes, writers now apply the name to all situations which involve resistance to flow whether it be from the hysteresis of the contact angle in smooth capillary tubes, the change in the radius of the capillary in a pore neck, or a change in interfacial tension at the forward and trailing edge of the bubble (8).

The distribution of the oil, gas and water in the porous medium was better understood when Botset and Wyckoff carried out the first experiments on relative permeability (9). They showed that either oil or gas would flow only if a specific minimum saturation of the phase in question existed in the flow region of the porous material. Some of the early workers also recognized that either the oil or gas droplets could be discontinuous, and in this condition, would be hard to displace by flowing water because of the Jamin effect. In 1927, Uren and Fahmy investigated a number of "factors" which affect the recovery of petroleum from unconsolidated sands by waterflooding (10). Table 1 lists these factors and the general results observed by Uren and Fahmy. With one exception (rate), the results observed by Uren are similar to generalizations which most experts in this field claim today after work of more than 50 years.

TABLE 1. Factors influencing recovery of petroleum (after Uren and Fahmy, 1927, Ref. 10)

Factor (Condition)	Condition for maximum recovery	Actual Value of "Variable" giving best recovery	Maximum recovery of oil at "Best Condition" % O.I.P.
1. Grain size	Largest grain size	20 to 40 mesh	41.3
2. Porosity	Highest porosity	41.1%	37.5
3. Variable grain size or texture	Most uniform	(all 40-48 mesh)	54.8
4. Coating on grains (wettability)	Smooth Carbon	Intermediate wettability	84
5. Oil viscosity	Lower oil viscosity	≈ 1 cp (gasoline)	67
6. Temperature	Highest temp.	125°F	70.5
7. Rate	Slow rates (with additives)	< 1 ft/day	59.0
8. Interfacial tension	Lowest IFT	8 dynes/cm	71
9. Salts in solution (acid or alkaline)	Highly alkaline	1.0 Normal sodium carbonate solution (also lowest IFT).	71

From Table 1, it is noted that waterflooding is more effective in coarse sand packs (therefore high permeability), in sands of high porosity, in sands with the most uniform textures, in sands which seem to have an intermediate wettability, with oils of lower rather than high viscosities, with low oil-water interfacial tensions, at high temperatures of the waterflood, and with flood waters which contain alkaline additives, especially those agents which react with sand to produce silicates. Most of Uren and Fahmy's conclusions have been borne out by the hundreds of comprehensive studies which have been conducted since that time. As one who has worked at different periods of his life in this field, it is almost embarrassing to examine Uren and Fahmy's work of 1927 and realize that we still have not answered some of the questions which Uren explored with his rather simple experiments. In any event, it is clear that Uren and other early workers recognized that the capillary forces are responsible for

holding the oil in the rock because the capillaries are so small that the surface forces far exceed the viscous forces which are available from waterflooding gradients in the reservoir. Therefore, it was logical that they should turn to materials which could modify the oil-water interfacial tension or the oil-water-rock contact angle to reduce the magnitude of the surface forces which hold the oil back during a displacement process. These attempts to change the surface forces and permit water to release or displace oil more effectively may be classed into three broad and often overlapping areas, i.e., attempts to: (1) change wettability, (2) change oil-water interfacial tension, or (3) remove the interface entirely (miscible flooding). Each of these areas will be treated separately although the interactions and overlap between them may be very strong.

WETTABILITY

Wettability must seem like the weather to most students of enhanced recovery research: until recently everyone talked about it but no one did anything about it. Now, however, professional rainmakers (using results of good surface and colloid research) do attempt to change the weather even though controversy surrounds their efforts. So it is with wettability, much has been learned in the last 50 years, but it is difficult to turn the knowledge directly into increased oil recovery.

Wettability effects in capillary action were recognized long ago. The classic Jamin effect depends, of course, on the difference between advancing and receding contact angles, and without some preferential wetting, there can be no capillary forces. (In this paper, it can be assumed that contact angles are measured through the aqueous phase unless stated otherwise. The basic concepts and equations of capillarity, including contact angles are not reviewed here, but the reader is referred to a good analysis and review of the role of capillary effects in oil recovery in the work of Melrose and Brandner [11].) The influence of wettability on oil recovery, however, has been difficult to study systematically because of the nature of the surface forces involved. Contact angles can be measured on smooth silica plates with known liquids, and various additives can be studied in these laboratory-controlled systems. However, it is extremely difficult to study contact angles inside the porous medium, particularly if it is a rock made up of scores of different minerals of many shapes and sizes.

Most early authors seemed to agree that wettability has an important effect on the recovery of oil during waterflooding. For example, Uren and Fahmy commented on wettability in 1927. As Table 1 indicates, the best oil recovery (84%) was observed by them when they treated their sand to provide a smooth carbon-like surface on the sand grains. However, they were working with large grain sizes and were flooding from the bottom up, so gravity aided the oil production.

A detailed description of the wettability effects was presented by Benner, Riches and Bartell in 1938 (12) when they described not only wettability, but other aspects of the influence of surface chemistry on oil recovery. As director of API Project 27, Bartell and co-workers (13) emphasized that there should be no controversy about whether high energy surfaces such as silica are inherently water-wet or oil-wet. From a thermodynamic point of view, silica must always be wetted by water in preference to any hydrocarbon or mixtures of hydrocarbons. According to Bartell, this is true even if the hydrocarbons are crude oils with their many different substances, some of which are known to be surface active. He examined the competition between water and crude oils for silica surfaces, and he found no crude oils (even with their many nonhydrocarbon constituents) which had greater adhesion tensions for silica than did pure water. He did point out, however, that there were large differences between the wetting properties of crude oils, and that some might be found eventually which would wet silica better than water.

Benner, Riches and Bartell (12) may also be responsible for one of the first detailed descriptions of the trapping of oil in capillaries during waterflooding, when capillary forces are much more important than the viscous forces. Using the classical pore-doublet model, they described the reasons for the advance of water in smaller capillaries (in water-wet systems), and the resultant trapping of segments of oil in larger capillaries. They carried out experiments to show conclusively that countercurrent flow of both oil and water is often observed in porous media wherein water is displacing oil under capillary control.

Bartell and coworkers (14) also presented an early analysis of the importance of advancing and receding contact angles with respect to oil recovery. Although they apparently did not recognize the saturation versus pressure differences which are always observed when fluids are allowed to imbibe into or are drained from a porous medium (i.e., capillary pressure hysteresis), they did study advancing and receding contact angles for several crude oils in packed silica powders. They found that the advancing and receding water-oil contact angles varied over a very wide range for the different crude oils. To their surprise, they found many crude oils with advancing contact angles (measured through the aqueous phase,

of course) which were considerably greater than 90° . Therefore, Bartell was forced to conclude that not all rocks behave in a water-wet fashion for every crude oil studied. However, he also found that the receding contact angle was less than 90° in every case. Thus, the hysteresis in a great many systems was often so great that advancing contact angles might indicate an oil-wet system and receding contact angles a water-wet system. With a system of this type, it is clear that neither the water nor oil can advance into a rock by capillarity alone. He concluded that spontaneous displacement of oil by water should occur only in those cases where both advancing and receding contact angles are less than 90° , and that no spontaneous movement should occur where the two angles are on opposite sides of 90° . Since that time, this non-imbibition of either oil or water has been observed by several workers (15-17).

The importance of the hysteresis of the contact angle on the oil displacement mechanism has been recognized and commented on by many other workers in the field of oil recovery. Melrose (18) has studied the problem in some detail and points out that the complexity of the geometrical shapes in the individual interconnected pores can have a very large influence on this contact angle hysteresis. His model predicts that the "pore structure in typical reservoir rock types of porous solids can lead to hysteresis effects in capillary pressures even if a zero value of the contact angle is maintained" (18). Morrow (17) studied the effect of surface roughness on hysteresis and found that the difference between advancing and receding angles could be related to the "intrinsic" angle (equilibrium angle) which is measured in the absence of roughness. In the intermediate wetting range, the difference between advancing and receding angles can exceed 100° which means that there is a very wide range over which the porous medium will not imbibe either water or oil.

Morrow conducted his experiments on polytetrafluoroethylene (PTFE) which is a low energy surface with well-studied surface characteristics. The use of this material has permitted contact angle and other wettability studies with less ambiguity than with crude oils on the high energy surfaces of reservoir rocks. With PTFE it was possible to use pure fluid pairs with reproducible contact angles and known wettabilities inside the porous medium. Using these systems, Morrow and McCaffery (19) studied immiscible displacements over a wide range of wetting conditions and found displacement behavior to be systematically related to the contact angle. They found the greatest differences between drainage and imbibition relative permeability curves in the intermediate wetting conditions. They found that the relative permeability to the wetting phase increased markedly as the advancing contact angle increased toward and through 90° . Thus, the implication is that water breakthrough occurs earlier in going from water-wet to oil-wet systems.

In the course of measuring imbibition capillary pressures, Morrow (20) also determined residual non-wetting phase saturations as a function of the intrinsic contact angle. For systems which spontaneously imbibe, he found that the residual oil values increased as the intrinsic contact angle was increased from 0° to 62° , the limit at which spontaneous imbibition occurs. Therefore, for systems which imbibe, the best recovery should be obtained from strongly water-wet systems.

The work of Morrow or Morrow and McCaffery helps to explain some of the observations of others on real reservoir fluid and rock systems, although their conclusions may appear to differ from those of earlier workers. Moore and Slobod noted that oil recovery at water breakthrough in water-wet systems is much higher than in oil-wet systems (15). Moore and Slobod also presented convincing laboratory evidence to show that the capillary forces in strongly water-wet systems were responsible for trapping oil in the larger pore spaces. Almost none of this "residual" oil could be produced after water breakthrough at any reasonable flooding rates. This "permanently trapped" residual oil varied from 37 to 45% in four different water-wet reservoir sandstones. With oil-wet systems, the oil recovery at water breakthrough was always less, the breakthrough residuals ranging from 40 to 54%. Moore and Slobod observed their best oil recoveries at intermediate wettabilities (by their definition, advancing contact angles between 30 and 90° in the water phase) where residual oil values ranging from 24 to only 29% were observed in the same sandstones. They were convinced that the best recoveries should be obtained with contact angles of exactly 90° , since they assumed that capillary forces at the oil-water interface must vanish when the $\cos \theta$ approaches zero. However, they seemed to be unaware of the increased effort required to mobilize the trapped oil because of the large hysteresis between advancing and receding contact angles in these intermediate regions. The detailed work of Morrow (21) and Melrose and Brandner (11) is in agreement that the mobilization of trapped oil should be the most difficult in this intermediate wettability region. However, Morrow also points out that the prevention of entrapment should be the easiest here, i.e., at an advancing contact angle of a little less than 90° (81° in Morrow's system) when imbibition forces do fall to zero (21). The sparse information on intermediate wetting in real oil-rock systems seems to show that lower residual oil values are indeed found in this intermediate region if sufficient pore volumes are injected (15).

Methods for improving recovery by changing wettability

The early researchers in oil recovery seemed to believe that the main function of water-flooding additives was to remove oil from the solid surface. In 1917, Squires obtained his United States patent which involved the addition of alkaline materials to floodwaters (22), and from 1925 through 1928, Nutting described his "soda process" for petroleum recovery (5, 23, 24). He showed that dissolved salts such as sodium carbonate and silicates were more effective than water for removing oil from rock surfaces. In 1956, Reissberg and Doscher (25) carried out experiments with sodium hydroxide and with strong detergents plus sodium hydroxide to show conclusively that the adhering crude oils could be removed very effectively from glass or silica by these high pH solutions. Although there continued to be some uncertainty about the quantitative aspect of the wettability of most of the world's oil reservoirs, laboratory work, especially that of Wagner and Leach in 1959, showed that drastic changes in the pH of the water would change the wettability of rocks from predominantly oil-wet to predominately water-wet, and that increased oil recovery could be obtained thereby (26). Wagner and Leach first emphasized the use of acids to reverse this wettability, but they found that the reservoir rocks consumed so much acid that it appeared to be impractical. In 1962, Leach, et al (27) demonstrated that sodium hydroxide is effective for changing rock surfaces from oil-wet to water-wet. They reported on an early field trial using this material and demonstrated improved recovery, although the economics at that time were uncertain because of the low cost of crude oil. Emery, et al (28) also reported on a field trial which used a strong solution of sodium hydroxide (2%), but they obtained an oil recovery of only 2.34% of the pore volume and also felt that the economics were uncertain.

By tradition, most of the efforts to change wettability with either strong acids or alkali have been directed toward making substances more water-wet. However, Cooke, Williams and Kolodzie (29) described a field trial wherein a water-wet reservoir was actually changed to a system which was more oil-wet with a small increase in recovery resulting from the injection of an alkaline material. In order to effect this unusual wettability reversal from water-wet to oil-wet, it was necessary to achieve the right conditions of temperature, pH and, especially, salt concentration. In this particular field trial (water-wet to oil-wet), an increased oil cut from 9 to 17% was obtained but no economic evaluation was made.

Perhaps the most successful field trial utilizing inexpensive sodium hydroxide is that reported by Graue and Johnson in 1974 (30). Although it is not considered to be a wettability reversal project, it is included here because of the use of sodium hydroxide. Graue and Johnson reported an increased oil recovery of approximately 400,000 barrels of crude oil in the Whittier Field in California by what they describe as an emulsification and entrapment mechanism. (A good review of this process along with a classification and review of all sodium hydroxide recovery processes is given by Johnson (31).) This emulsification and entrapment process is designed for very viscous oils which respond poorly to waterflooding because of the poor sweep efficiency. By converting much of the oil to a fine emulsion within the porous medium, the flow of water is partially blocked in some areas and the overall sweep efficiency of the water in the reservoir is improved. Therefore, the improved recovery comes from a more complete waterflood of the reservoir rather than from a better displacement of oil from the capillaries by sodium hydroxide.

Throughout the long history of laboratory and field experiments dealing with wettability of rock-oil-water surfaces, it has been difficult to obtain a clear consensus about the true wetting characteristics of the crude oil-water systems in contact with reservoir rock. One of the more definitive studies on this subject was the work by Treiber, et al (32) in 1972 which reported on the laboratory evaluation of the wettability of 55 different oil producing reservoirs from different parts of the world. They divided these reservoirs, which included sandstones and carbonates, into three arbitrary divisions; namely, water-wet from zero to 75° , oil-wet from 105 to 180° , and intermediate wettability from 75 to 105° , all contact angles being measured through the aqueous phase. From their careful laboratory studies, they concluded that 66% of the reservoirs were oil-wet, 27% were water-wet, and only 7% were in the intermediate range where neither oil nor water wetted the surface very strongly. From this study, it would appear that the search for agents to change the wettability from oil-wet to water-wet might be a fruitful avenue for research to improve oil recovery. Morrow (20) has pointed out that it would be better to classify intermediate wettability as systems which do not spontaneously imbibe either phase. This increases the range from 62° (advancing) to 133° (receding) according to his work on well-characterized surfaces. Based on the contact angle measurements of Treiber et al, this would put 47% of the reservoirs into the intermediate category with 26% classified as water-wet and only 27% as oil-wet.

One of the significant aspects of wettability information related to oil recovery is the fact that nature may be providing the best possible wettability conditions for optimum recovery in some of the reservoirs. For example, Richardson, et al (33) studied a large number of "fresh" and aged cores taken from the Woodbine Reservoir of the East Texas field. If they cleaned these Woodbine cores and resaturated them with oil to carry out a normal water-flood for residual oil determination, they observed the usual laboratory residual oil values

of about 30% of pore volume. However, if they conducted their waterfloods on fresh cores, they observed much lower residuals of only 15-18% of pore volume. In some parts of the reservoir, the residual oil values were reduced to less than 10% of the pore volume. These residual oil values are lower than those obtainable by most recovery methods even with good laboratory formulations unless very high combinations of flooding rate and low interfacial tensions are used (see the next section).

In an attempt to understand how nature is able to achieve such low residual oil saturations without help of engineers or laboratory specialists, Salathiel in 1973 (34) described a method for changing the wettability of rock surfaces in an unusual way. By treating cores which were saturated with typical values of oil and water, he was able to generate a mixed-wettability condition in the laboratory wherein surfaces in the larger pores were primarily oil-wet and rock surfaces in the smaller pores remained water-wet. With this special mixed wettability condition, it appears that the oil relative permeability can remain finite to very low saturations, with the oil apparently draining or flowing in very small rivulets until extremely low values of residual oil saturation can be obtained. With this laboratory-generated system, he feels he has reproduced the situation which nature may have providently provided in the East Texas field.

This is not to be taken as a concluding note that all should be left to nature and that those of us engaged in enhanced oil recovery should cease to search for methods where we can alter wettability to improve oil recovery, but it does suggest that our knowledge is far from complete and that our task remains a difficult one. The author of this paper is reminded of his first meeting many years ago with his new research director, an experienced oil recovery expert in one of the world's major oil corporations. He was a powerful man, and he shook the room with the demand that "we need to be struck by lightning with wettability." It is the opinion of this author that the lightning bolt has yet to strike.

OIL-WATER INTERFACIAL TENSION AND SURFACTANTS FOR OIL RECOVERY

Early work with surface active agents

In the early days of chemical flooding, surface active agents were thought of primarily as detergents and the term "wetting-agent" was often used by the companies or salesmen attempting to promote the use of these materials in waterflooding. In much of the early work, these materials were assumed to be effective primarily for releasing oil from the solid surface of the rock (25). The laboratory experimenters were alert to the need for interfacial tension reduction and some correlations were attempted in this area, but the laboratory results were not consistent. Some of the early workers even reasoned that since water displaces oil largely by capillary action, better displacement would occur if the interfacial tension could be increased to increase the capillary driving force. Some of the early experimenters also reported that very little improvement in oil recovery could be expected with many of the surface active materials (35). One detailed study indicated that oil recovery actually decreased slightly when the oil-water interfacial tension was decreased in the experiments (36).

Although there was no consensus on the effectiveness of detergents for oil displacement, it was clear in the early work that a very serious problem was the adsorption of the materials on the large surface area of the rock. Not only was a large amount of the detergent lost to the rock, but this adsorption prevented the advance of detergent through the formation along with the bank of water in the waterflood. In 1968, Taber pointed out that very high concentrations of detergent (about 10%) would permit an advance of the detergent front at a rate which was only a little less than that of the advancing flood water (37). These high concentrations also appeared to recover oil more effectively than the low concentrations, but the actual recovery varied with conditions of the laboratory test. It appeared to Taber that the most sensitive variable in detergent flooding, at least in laboratory experiments, was the rate of flooding. As long as effective detergents with or without sodium hydroxide were used, additional oil could be produced whenever the rate of flooding was increased. Therefore, in his early work citing possibilities of the use of detergents in waterfloods, he restricted recovery predictions to situations where the laboratory flooding rates were close to field rates with the result that predicted oil recovery by surfactants was rather low (37).

Taber also observed that the widely different responses for oil recovery with various detergents and at various rates could be understood if the experiments were carried out at equivalent values of the ratio of viscous to interfacial forces. For the displacement of presumed, non-wetting residual oil, he observed that no oil could be displaced until a critical value of $\Delta P/L\sigma$ had been reached, where ΔP is the pressure drop over the distance L and σ is the oil-water interfacial tension (38). This value in English engineering units for Berea sandstone was about 2-5 psi ft/dyne cm, or approximately 45-113 kPa/mN (kiloPascal/milliNewton) in SI units. Taber observed this ratio with several fluids and under a number of different conditions, varying interfacial tension, length and pressure gradient

independently. In every case, after the critical gradient had been exceeded, additional oil could be recovered as long as the value of $\Delta P/L\sigma$ was raised even further. Although it was difficult to accomplish, essentially all of the oil could be displaced from the Berea sandstone if the value of $\Delta P/L\sigma$ was made large enough. However, the rates and the resulting pressure gradients were more than 1,000 times those experienced in the field.

TABLE 2. Capillary number or "displacement ratio" correlating groups

Reference	Author(s)	Year Published	Porous Media	Correlating Group
39	Fairbrother and Stubbs	1935	Capillary	$\sqrt{\frac{v\mu}{\sigma}}$
40	Leverett	1939	Sandstone	$\frac{LP_c}{\Delta P}$
41	Brownell and Katz	1947	Sandstone	$\frac{K}{g \cos\theta} \frac{\Delta P}{L\sigma}$
42	Ojeda, Preston and Calhoun	1953	Sandstone	$\frac{\sigma}{\Delta P}$
15	Moore and Slobod	1956	Sandstone	$\frac{v\mu}{\sigma \cos\theta}$
43	Saffman and Taylor	1958	Hele-Shaw Cell	$\frac{v\mu}{\sigma}$
38	Taber	1969	(Berea) Sandstone	$\frac{\Delta P}{L\sigma}$
44	Foster	1973	(Berea) Sandstone	$\frac{v\mu}{\phi\sigma}$
45	Lefebvre duPrey	1973	Teflon, Steel, and Aluminum	$\frac{\sigma}{v\mu}$
11	Melrose and Brandner	1974	Unconsolidated Glass Beads	$\frac{Kk_{rw} \Delta P}{\phi L\sigma} \text{ or } \frac{v\mu}{\phi\sigma}$
46	Ehrlich, Hasiba and Raimondi	1974	Sandstone	$\frac{K\Delta P}{\phi L\sigma}$
47	Abrams	1975	Sandstone Limestone	$\frac{v\mu_w}{\sigma} \left(\frac{\mu_w}{\mu_o} \right)^{0.4}$
48	MacDonald and Dullien	1976	Sandstone	$\frac{\bar{\epsilon}}{(1/\bar{D}_e - 1/\bar{D})L\sigma} \Delta P$
49	Reed and Healy	1977	Various	$\frac{K}{\cos\theta} \frac{\Delta P}{L\sigma}$
50	Stegemeier	1977	Analysis of Various	$\frac{\phi L^2 k_{rw} \psi^2}{2f}$
21	Morrow	1978	Teflon	$\frac{v\mu}{\sigma Z_{imb} \cos\theta_A}$
51	Oh and Slattery	1979	Model Pore	$\frac{r}{n} \frac{\Delta P}{2\sigma}$

The capillary number concept

A number of authors have studied the ratio of viscous to capillary forces and the effect of the ratio or dimensionless group on oil recovery. Table 2 lists several of these groups which have been described by various authors (11,15,21,38-51). Many are dimensionless and are often referred to collectively as either the "capillary number" or the "critical displacement ratio" by workers dealing with surface phenomena and oil recovery. Although the experimental data are still rather limited as far as capillary number results are concerned for different types of rocks, the consensus by the various workers is good. Different authors have examined the pore dimensions and geometry in both synthetic and real systems to calculate the critical value of the capillary number at which either residual oil will be displaced or at which better oil displacement will occur during waterflooding. For example, Melrose and Brandner (11) have calculated these values and estimated the results for three different

types of porous media, generalizing them as those with large, intermediate, and small differences in the capillary constrictions. The displacement efficiencies predicted for each of these media are given by Fig. 1. MacDonald and Dullien (48), Oh and Slattery (51), and Stegemeier (50) have made calculations and have compared them with experimental data of their own or from the literature. In general, the calculations agree with experimental data. For example, Fig. 2 shows that Stegemeier's calculated results for the remaining oil saturations at various capillary number values agree rather well with the data presented by Taber as long as the advancing contact angle of the displacing phase is taken as 60°.

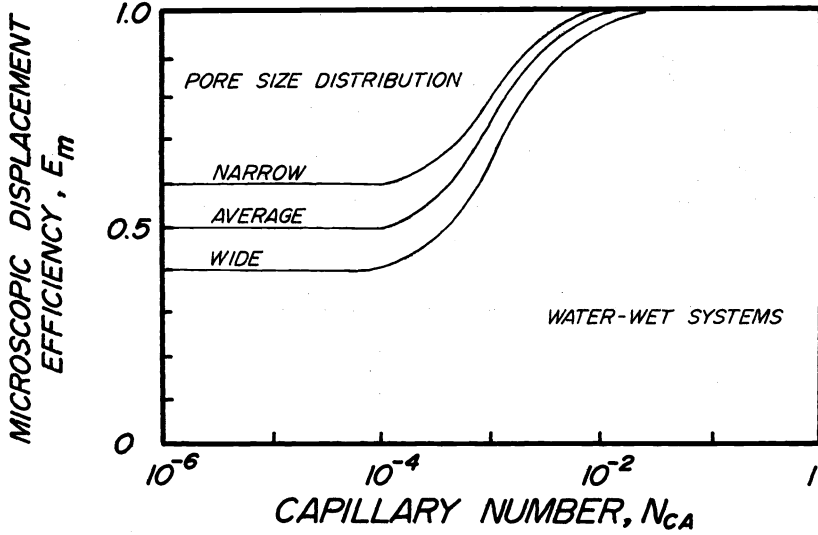


Fig. 1. Correlation of microscopic displacement with capillary number. (After Melrose & Brandner, Ref. 11).

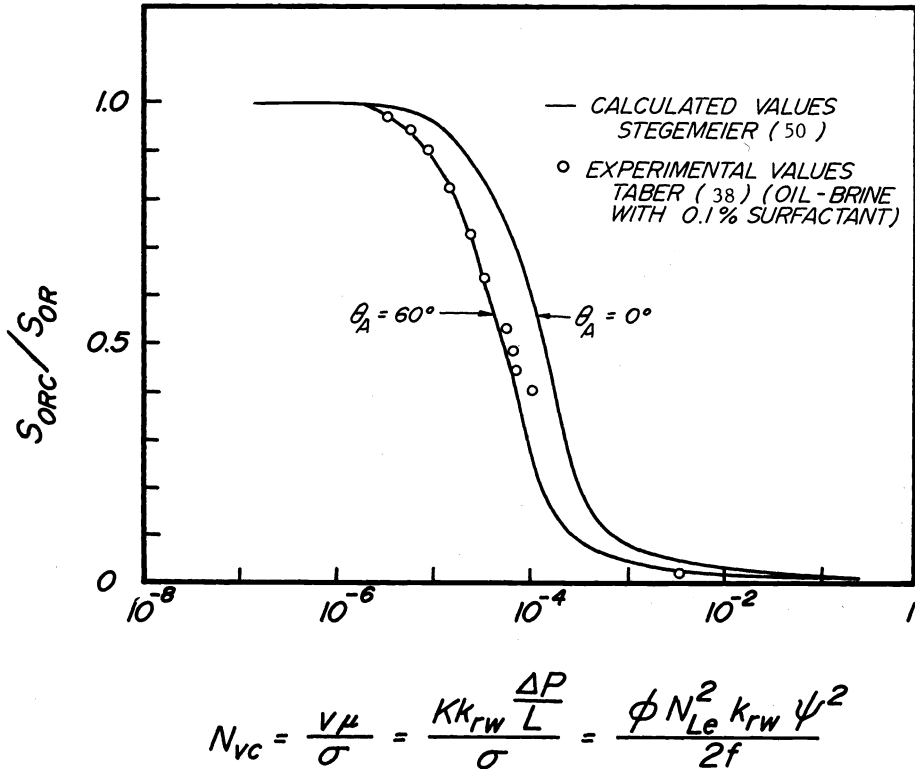


Fig. 2. Calculated and experimental residual oil. (After Stegemeier, Ref. 50).

The results of several other studies to illustrate the desaturation of either the residual non-wetting (usually oil) phase or the wetting phase at various capillary numbers were compared by Stegemeier and are reproduced here as Fig. 3. In general, the results show that the initial desaturation of the non-wetting phase occurs over several orders of magnitudes of the capillary number and at lower viscous to capillary ratios than reported by Melrose and Brandner (Fig. 1). However, the results of the displacements of discontinuous non-wetting fluid (oil, for Taber (38) and Foster (44), gas for Wagner and Leach (52)), from similar sandstones are fairly close with significant removal of the fluid starting at capillary numbers from 10^{-6} to 10^{-5} . The work of Wagner and Leach is noteworthy because they achieved very low interfacial tensions with no additives in their gas-liquid systems near the critical point. In addition, they carried out their studies at slow rates which were close to flooding rates in the field, and their work is often cited as direct evidence for the need for low interfacial tensions for effective displacement at field rates. For the desaturation of continuous or at least partially connected oil, the work of Abrams (47), Lefebvre duPrey (45), as well as Moore and Slobod (15), shows that desaturation of the continuous oil starts at a much lower ratio of the viscous to capillary forces, i.e., a capillary number of about 10^{-7} . However, after the initial oil displacement in their experiments, the oil must become discontinuous at the lower saturations and Fig. 3 shows that their values are then closer to those of Foster or Taber.

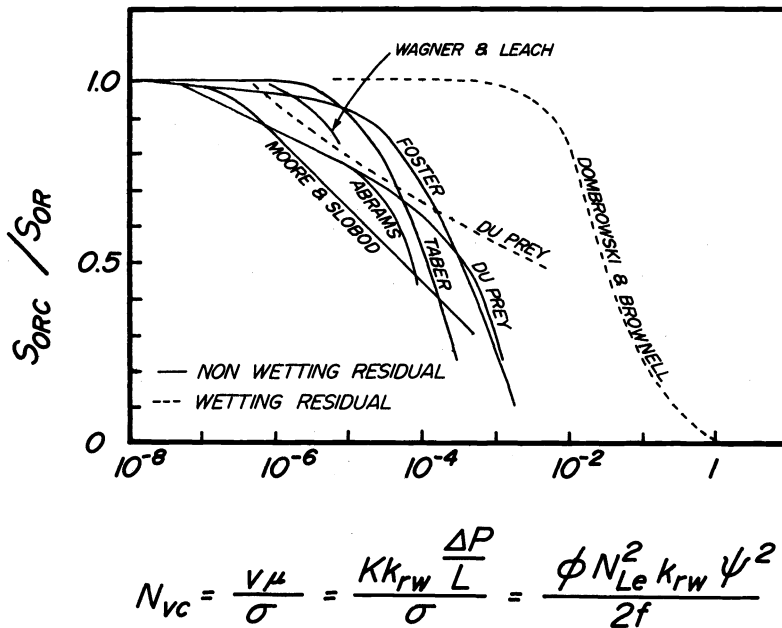


Fig. 3. Average experimental recoveries of residual phases. (After Stegemeier, Ref. 50).

The work of Dombrowski and Brownell (53) shows that it is much harder to displace the residual wetting phase from a porous medium (in this case, small glass beads). Fig. 3 indicates that the capillary number required for their displacement of the wetting phase is two orders of magnitude higher than that required for the displacement of most non-wetting phases. Jenks, et al (54) also presented a clear picture of the increased ratio of viscous to capillary forces which are required for the displacement of the wetting (water) phase compared to the oil phase in Berea sandstone. At a pressure gradient of 2,000 psi/ft, they observed that only 4% of the residual water was displaced by oil, but about 40% of the residual oil was produced by a waterflood on a similar Berea core at the same conditions.

Other than the information summarized and compared in Fig. 3, the experimental data on displacement of residual oil at supercritical values of the capillary number are not extensive. Taber, Kirby and Schroeder (55) carried out experiments to determine the critical values of $\Delta P/L\sigma$ for several sandstones which had permeabilities ranging from 40.8 to 2,190 millidarcies. Prior to the critical displacement test, all rock samples were waterflooded at slow (subcritical) rates until each sample contained its normal residual oil value. The flooding

rate was then increased until measurable quantities of residual oil were produced, i.e., until the critical value of $\Delta P/L\sigma$ was attained.

The results which are given in Fig. 4 indicate a definite trend towards higher $\Delta P/L\sigma$ critical values at lower permeabilities. Since the experiments were done on different rocks from several formations (55), a precise correlation between permeability and the critical displacement ratio should not be expected. However, where data are available in the literature, the values do appear to fit the general trend in Fig. 4. For example, Jenks, et al (54,56) observed that a critical $\Delta P/L\sigma$ value of 8.9 (psi/ft)/(dyne/cm) (201 kPa/mN) was required for the displacement of residual oil from their Berea sandstone. Although this is higher than the critical values observed for Berea by Taber, et al, the Jenks, et al value fits the trend because their Berea had a permeability of only 150 to 180 md compared to Berea permeabilities of 300 to 900 md for the other Berea data points in Fig. 4. (Sandstones other than Berea are also plotted on Fig. 4.)

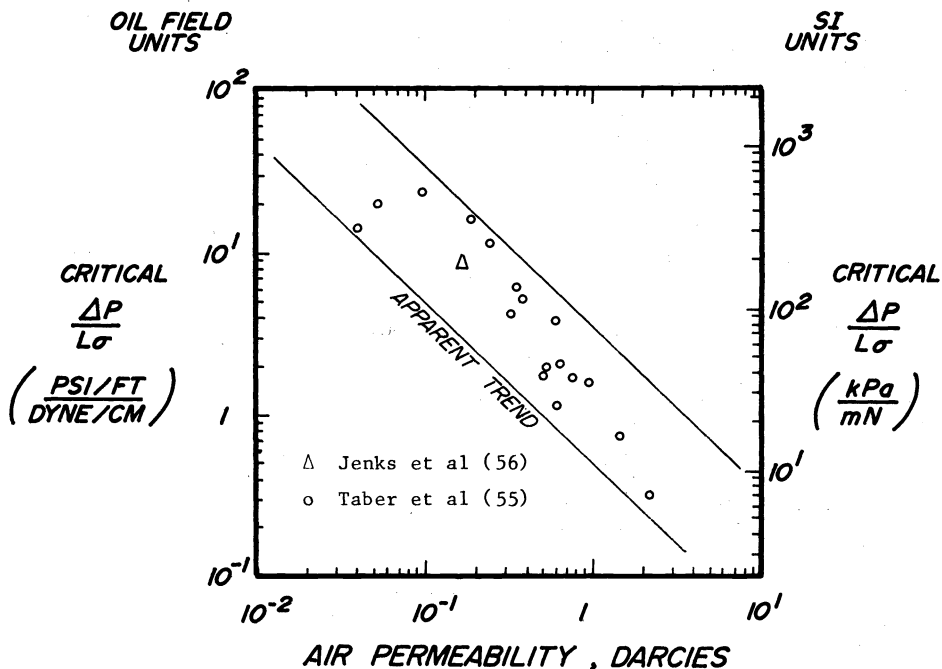


Fig. 4. Relationship between permeability and the critical value of $\Delta P/L\sigma$. (After Taber, et al, Ref. 55).

As pointed out above, most authors have preferred to use a dimensionless form of the capillary number. However, it is often more convenient in laboratory and field calculations to use the simple critical displacement ratio $\Delta P/L\sigma$ which has the units of L^{-2} . For example, by using methods outlined by Stosur and Taber (57), it is possible to calculate the critical displacement ratio at points close to the wellbore or deeper in the reservoir. Their work indicates that this may be important when certain logging methods are used to estimate the in situ residual oil saturation remaining after a waterflood. From Fig. 4, it appears that the critical displacement ratio is a property of the rock, and it is hoped that more values will be determined for future work in enhanced oil recovery.

Some laboratory experiments may be easier to interpret in terms of quantitative $\Delta P/L\sigma$ values instead of a dimensionless capillary number. For example, when experiments with surfactants are carried out at constant rates, (and thus a constant $v\mu/\sigma$) on rocks of different permeabilities, it appears that the oil recovery actually increases for those rocks with lower permeabilities. Clearly, the better recovery is not a "reverse permeability effect" but it comes about because the $\Delta P/L\sigma$ is much higher in tighter rocks when all experiments are carried out at a constant rate. In general, almost all of the experimental and theoretical work indicates that the displacement of oil increases with higher values of the ratio of viscous to interfacial forces. An exception is the recent work by Sayyoun, et al (58) which indicates that at very slow rates (less than 1 ft/day), the recovery appears to increase slightly with a further decrease in rate. Therefore, the complex nature of the oil displacement process still warrants the continuing research emphasis which it is receiving. In addition to the work cited above, current progress is being made by the investigation of

gravity forces along with the viscous forces for the mobilization of trapped oil. Morrow (21) reports that gravity alone may dislodge oil when interfacial tensions are low enough to bring the system into the critical capillary number region at reservoir rates. In addition, the current work by Larson and Scriven (59), who are applying certain facets of percolation theory to the mechanics of oil displacement, is bringing new insight into the whole process.

Micellar-polymer fluids

The evidence that low oil-water interfacial tensions will enhance oil recovery has led to an enormous effort by many experts to prepare surfactant formulations which will be effective in underground reservoirs. In contrast to the early work with low concentrations, between 1957 and 1968 several workers proposed the use of somewhat higher concentrations in special formulations to overcome adsorption problems and to provide the optimum interfacial tension conditions (37,60-64). These high surfactant concentrations could be dissolved in either oil or water and normally contained other additives to improve the stability or overall effectiveness. In 1968 Gogarty, Tosch (65), Davis and Jones (66) published their first papers dealing with "Oil Recovery and Displacement Mechanisms with Micellar Solutions." They described their surfactant fluids as microemulsions which are effective with either oil or water as the external phase. In addition to the three main components (surfactant, hydrocarbon and water), a "cosurfactant" (usually an alcohol) and an inorganic salt are normally added to provide the optimum formulation for oil displacement. Similar oil external fluids called "soluble oils" which were developed by Holm, et al (60,67,68) also have proved to be effective oil recovery formulations. These micellar fluids, or microemulsions as defined by Schulman (69), are not only excellent recovery agents, but they appear to reduce the adsorption loss to the reservoir under certain conditions. However, the adsorption problem is far from solved though good work by a number of investigators is continuing (70-74). A review of the surfactant adsorption literature is beyond the scope of this paper.

Good recovery with microemulsions also requires good mobility control, i.e., to prevent viscous fingering of the drive water into the surfactant bank or of the surfactant into the reservoir oil-water bank, the viscosities of the injected fluids must be increased in most cases (75,76). The microemulsion viscosity can be controlled by adjusting the components in the formulation, and the drive water or "mobility buffer" is normally thickened by adding a natural or synthetic, water-soluble polymer (77). However, the polymer mobility control agents present additional problems for the surface chemists. Several authors have shown that the large polymer molecules will not penetrate the smallest pores of typical rocks and, thus, move faster in the larger pores than the average advance of the waterfront (78-81). Because of this "inaccessible pore volume," the polymer solution invades the microemulsion fluid to bring about a phase separation of the surfactant-rich phase, according to Trushenski (82). If the interfacial tension is high enough, the surfactant-rich phase can be trapped in the pores much like residual oil. Trushenski describes various methods for reducing this adverse surfactant-polymer interaction including the use of more surfactant solubilizers, i.e., cosolvents such as alcohols (82).

The never-ending quest for ultralow oil-water interfacial tensions in these oil recovery systems was given a big boost by the pioneering development of the spinning drop apparatus by Cayias, Schechter and Wade (83) at the University of Texas for interfacial tension measurement (first suggested by Vonnegut (84)). When measuring the interfacial tension of pure hydrocarbons against an aqueous surfactant solution, Cayias, et al (85) showed that the minimum interfacial tension was found against only one of the hydrocarbons in a homologous series. This minimum interfacial tension was very specific, not only for normal alkanes but for branched, cyclic and aromatic hydrocarbons as well. From these correlations, and by using a series of surfactants, Cayias, et al (86,87) were able to assign an "equivalent alkane carbon number" (EACN) to any hydrocarbon or mixture of hydrocarbons including crude oils. Their work indicates that most crude oils appear to have an EACN ranging from 6.2 to 8.6, i.e., from the point of view of interfacial tension, crude oils behave as if they were comprised primarily of hydrocarbons in the range of hexane to nonane. This information has permitted many surfactant investigators to work with pure hydrocarbons such as octane (or specific hydrocarbon mixtures) with more confidence that their laboratory hydrocarbon is not an unrealistic model for crude oils. To determine the surfactant molecular weight or other property most effective for interfacial tension lowering, the University of Texas group also developed the concept of n_{\min} , i.e., the specific EACN which produces the lowest interfacial tension for a given surfactant or mixture of surfactants (88,89). This n_{\min} concept proved to be useful for studying the variables, such as temperature, age of system, and the concentrations of added electrolyte or cosurfactant. For example, they noted that the n_{\min} increases with electrolyte concentration; also, n_{\min} decreases with increasing temperature for anionic surfactants and increases for nonionic surfactants. Temperature effects have also been reported by Burkowsky and Marx (90) who observed consistent minima in interfacial tension at the relatively high temperatures of 60 and 76°C for surfactant-crude oil systems for two German oil fields. The best oil recoveries were also obtained when displacement experiments were conducted at the temperatures of lowest interfacial tensions.

The urgent need for the preparation of the very best formulations and, therefore, for understanding microemulsions has led to an upsurge of basic and applied work in the area of micellar fluids. Since this subject will be reviewed thoroughly by others, only applied aspects related to oil recovery can be touched on here. Although the oil-water-surfactant systems are very complex, especially after cosolvents and electrolytes have been added, a number of workers have been able to describe the systems and adjust the required properties to provide the best oil recovery. The work of Reed, Healy (49,91-94) and their co-workers is noteworthy for providing a clearer picture of the physical nature of the system, especially the gross phase behavior under the influence of many variables. Their studies on the addition of electrolytes to the surfactant systems has brought a sense of order into what had been a rather confusing picture. Ever since Harkins (95) showed that extremely low interfacial tensions can be obtained by, in effect, salting out the surfactant so that it goes to the oil-water interface, others (38, 96-98) have utilized this added salt concentration to lower the oil-water interfacial tension. Reed, Healy and their co-workers developed a system of "optimal salinity" for maximizing the desired property by the judicious addition of the electrolyte. In general, optimal salinity is usually thought of as that specific salt concentration in an oil-water-surfactant system which produces the lowest interfacial tension, and Reed, et al showed that this optimal salinity affects several of the interrelated properties of the microemulsion system. It can be measured in at least four different ways; namely, the salt concentration at which the lowest interfacial tension is observed, the salt concentration which provides the most favorable phase behavior for oil recovery, the salt concentration which provides equal solubility parameters (as defined by Healy and Reed), and the salt concentration at which contact angles between each liquid phase and the solid reach similar equilibrium values. The optimal salinity measured by any one of the four methods on a particular system agrees reasonably well with that obtained with the other methods. Perhaps more important than the measurement of the exact quantity of electrolyte which maximizes a particular sought-after property, the work by Reed and Healy also demonstrated that oil recovery was, in general, a function of these expected properties, and that oil recovery correlated well with the capillary number.

The concept of optimal salinity has aided many other workers as they have pursued a better understanding of these microemulsions through various types of fundamental studies. Miller, et al (99) presented a model for the phase separation which occurs as the salinity is increased until the middle or surfactant phase is observed. Miller's model indicates that the repulsive forces shift sufficiently with the addition of salt until the aggregates come close enough together to force an actual phase separation at the optimal salinity. His studies indicate that this middle or surfactant phase is water continuous (99). With careful studies using the polarizing microscope, Benton, Fort and Miller (100) showed that there are two distinct structures, i.e., one, at low salinities, and one at the high salinity values. In the intermediate region near optimal salinity, both structures were observed. Hwan, et al (101) observed the effect of salinity on the actual drop sizes in the microemulsions. By studies with an ultracentrifuge they found that drop sizes increased in a regular way with salinity, reaching a maximum in the region of the so-called optimal salinity and then decreasing at the higher salinity values. Their studies also confirmed the existence of oil in water microemulsions at low salinities and water in oil microemulsions at high salinities. Between these two regions the ultracentrifuge work indicates that the drops are characteristic of both oil-continuous behavior and water-continuous behavior, thus adding additional evidence to the dual nature of these micellar fluids in the intermediate salinity ranges. As early as 1976, Scriven (102) had also presented an interesting model for an equilibrium bi-continuous structure of the microemulsion systems, i.e., his analysis showed that both oil and water may be continuous in these intermediate salinity regions of greatest interest.

Chan and Shah (103) have also studied microemulsions as a function of optimal salinity as well as several other variables which can bring about the phase transition from lower to middle to upper phase in these systems. In general, their work indicates that the surfactant partition coefficient between the oil phase and the excess brine phase is unity at the optimal parameter value. Their work indicates that there is a strong similarity between the interfacial tension behavior of low concentration systems and those of high concentration systems. Bansal and Shah (104) also showed that the salt tolerance of surfactant systems can be extended to rather high salt concentrations by mixing ethoxylated sulfonates with the usual petroleum sulfonate materials. An optimal salinity as high as 32% sodium chloride was observed in one of the mixed systems which was also characterized by very low oil-water interfacial tensions.

This section started with a discussion of the need for low interfacial tensions between oil and water for good oil recovery. It is clear that this sense of urgency in finding low interfacial tensions has contributed to a much clearer understanding of complex systems containing surface-active materials plus oil, water and other additives. It is also clear that systems which achieve low interfacial tensions may exhibit very complicated phase behavior characteristics, and that the combination of interfacial tension and the phase behavior of the fluids should be important for maximum oil recovery. The connection between phase behavior and oil recovery will be discussed more fully in the next section.

MISCIBLE FLOODING AND EFFECT OF PHASE BEHAVIOR ON OIL RECOVERY

Introduction to miscible processes

The allure of miscible displacement for complete oil recovery is obvious; it is the only method which permits 100% recovery, even in theory. As long as two phases exist in small capillaries, some trapping of the oil phase will normally occur even under the best conditions. However, if the two fluids are truly miscible, and no other fluid phase is present, (seldom true in oil reservoirs) there can be no capillary forces to trap off segments of oil. If the "miscible slug" is large enough, all of the oil can be displaced to achieve a theoretical recovery of 100%. However, to date no practical method has been devised which can provide complete miscibility in real reservoirs (where both oil and water are present) so 100% recovery remains a distant goal.

The common miscible processes can be generalized very loosely by the three-component phase diagram in Fig. 5. The fluid which is miscible with both oil and water (or oil and gas) at the prescribed conditions is shown at the apex of the ternary diagram. As long as the percentage of this "miscibilizing fluid" (or amphipathic solvent) is high enough, the three-component mixture will be single phase and no interfaces should exist between the displaced and displacing fluid. Below this concentration, two phases exist and capillarity will return to interfere with the efficient displacement of the oil. It will be shown that the normal presence of both oil and water flowing in advance of a miscible driving fluid apparently prevents the attainment of true miscibility in large segments of the rock because of the capillary trapping of oil.

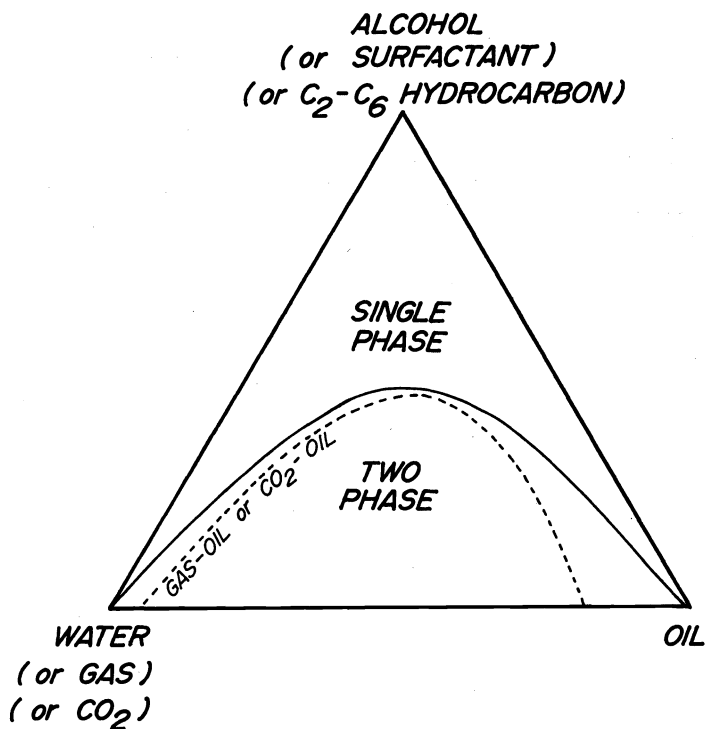


Fig. 5. General phase behavior to illustrate miscible type processes for enhanced oil recovery.

Figure 5 illustrates the conventional diagram normally used for oil-water-alcohol (or surfactant) processes. For CO_2 or hydrocarbon-miscible processes, authors conventionally rotate the ternary diagram 120° clockwise, but the illustrated principle is the same. The binodal curve is normally higher for alcohol and lower for surfactants than the curve shown in Fig. 5. Although no real reservoir process can be completely miscible in the exact sense, the following are often referred to as miscible: (the names refer to the displacing phase)

- Hydrocarbon miscible processes
- CO_2 processes
- Miscible slug or alcohol processes
- Micellar processes (certain segments of some processes)

These will be discussed briefly with some comments on the surface chemistry involved. This is an apparent contradiction since in true miscible systems there are no interfaces.

Hydrocarbon miscible processes

The original efforts to conduct miscible displacements made use of gaseous or liquid hydrocarbons in the low molecular range. At one time, methane and liquefied petroleum gas (LPG) were readily available and inexpensive compared to crude oil. In the 50s, several published papers presented research results which indicated that these low molecular weight hydrocarbons could be miscible with the crude oil and a driving gas under the proper conditions in the reservoir (105-109). The techniques may be classified broadly as High Pressure Gas Drive (105-107), Enriched Gas Drive (110,111) and Miscible (Hydrocarbon) Slug Flooding (108,109). The miscible hydrocarbon slug process is the easiest to visualize--a quantity of propane or LPG is injected into the reservoir and followed by dry gas. At most common reservoir temperatures and pressures, the propane will be miscible with both the reservoir oil and the driving gas. The enriched gas process develops miscibility by adding some C_2-C_6 hydrocarbons to the injected dry gas (methane) to bring the three-component system closer to the single phase region in Fig. 5. The high pressure gas drive achieves miscibility by vaporizing enough of the C_2-C_6 (or higher intermediates) to bring the two phase system up into the single phase region. This "vaporizing gas drive" mechanism is explained by Hutchinson and Braun (112).

All of these hydrocarbon-miscible processes can recover oil, but there are many difficulties. Mobility control is a very serious problem, although techniques such as alternate water and gas injection (WAG) can be used to reduce the mobility of the lighter, driving fluids (113). In the United States, the intermediate hydrocarbons as well as methane are in short supply and are valuable as fuel or chemical feedstocks. Therefore, much attention in the United States is now focused on materials such as CO_2 or other inert gases which have no fuel value but which can provide some miscible displacement under certain conditions. In parts of the world where light hydrocarbons and methane are available, the hydrocarbon-miscible process and various modes of gas injection should increase oil recovery for many years.

Carbon dioxide processes

Carbon dioxide (CO_2) processes are usually listed with miscible processes even though much of the research which is now underway is directed toward finding an answer to the question: What are the conditions required for miscibility (if it can be attained), and what is the nature of the phase behavior of the CO_2 -crude oil system? Normally, CO_2 is not completely miscible with crude oils, but it is very soluble in most oils at reservoir conditions.

Early work with carbon dioxide for enhanced recovery was divided between carbonated waterflooding and " CO_2 slug" flooding, the latter often being called " CO_2 miscible flooding" or by now just CO_2 flooding. In 1963, Holm (114) showed that a CO_2 slug, injected at reservoir pressures was much more effective than carbonated waterflooding if equivalent quantities of CO_2 were used in the displacements. Therefore, the emphasis has swung away from carbonated water to the injection of very large quantities of CO_2 at reservoir pressures to attempt a miscible or "partially miscible" displacement.

The CO_2 flooding process has been described by several authors (115-119). A good review of the process (including laboratory and field work) with estimates of the future recovery potential has been given by Stalkup (120). While not normally miscible at reservoir conditions, the CO_2 has a high solubility in the oil, and it does do an effective job of displacing oil, at least in laboratory experiments. Investigators have suggested several factors which aid in this improved recovery:

1. Swelling of oil. For tertiary recovery, this may be one of the most important effects because oil cannot flow until it is continuous and has finite relative permeability (118,119).
2. Viscosity reduction. The viscosity of the "swollen oil" will be much less than that of the original crude oil at reservoir temperatures if large quantities of CO_2 are dissolved in the oil.
3. Vaporization of crude oil. The lighter hydrocarbons are vaporized by the high pressure CO_2 in a process analogous to a high pressure vaporizing gas drive. In this way, miscibility can be generated in the reservoir to provide an effective displacement of the crude oil. This vaporizing mechanism may be the key to whole processes.
4. Blowdown recovery. At the end of high pressure laboratory experiments, additional oil is recovered when the pressure is lowered, and a similar effect should be noted toward the end of a field displacement, but this production will, of course, only be realized in the final stages of the process.

5. Interfacial effects. Although early published reports claimed that CO₂ can form detergents or alter the wettability of the rock-oil system (121), there is no hard evidence that this was a major effect in the carbonated water case for which it was claimed. However, interfacial effects may be very important when the system is close to miscibility which is a goal of the process design for most fields' (122).

In general, CO₂ flooding is a very complicated process. The phase behavior is difficult to pin down; at times 3 phases appear in the CO₂-hydrocarbon system, and the actual flow mechanisms in these complicated, near-miscible regions are not well understood. Laboratory studies have indicated that full miscibility is not necessarily required in displacements because good recovery can be obtained when several phases are flowing (116,117,122,123).

It can be presumed that interfacial effects must be very important in these near miscible regions, and at least one study has shown that oil recovery from CO₂ injection decreased markedly in lower permeability sandpicks, presumably because the critical capillary number requirements for displacement are higher in low permeability media (124).

In conclusion, it appears that CO₂ flooding requires the same types of conditions which are required for alcohol or micellar processes, i.e., a high oil saturation to provide good oil permeability and less trapping of the oil phase, along with near miscibility and low interfacial tensions between the displaced and displacing phases. The complete experimental evidence for these "requirements" is still lacking for CO₂ flooding. The good evidence for the controlling factors in alcohol-miscible and micellar-polymer flooding will be examined in the next sections.

Alcohol-water-oil miscible processes

Alcohol flooding is discussed here in some detail because it provides a basis for understanding the relationship between phase behavior, interfacial tension, and oil recovery. It is recognized that no successful field trial of the alcohol process has ever been carried out.

The use of alcohol as a miscible driving fluid for the displacement of oil has a number of advantages over other materials. Certain low molecular weight alcohols are miscible in all proportions with both the driving water and with some reservoir oils. If not miscible with oils of high molecular weights, miscible displacement of the oil can be still achieved by the injection of a segment of an intermediate hydrocarbon such as a gasoline fraction. By choosing the proper alcohol, and if necessary, an advance slug of hydrocarbon, it is possible to be in the single phase region in Fig. 5 for essentially any combination of water, oil, and alcohol. Another big advantage of alcohol is that it can be driven through the reservoir with water and the water can be thickened with a polymer. Therefore, it is possible to choose a system which has a much more favorable mobility ratio than the previous systems which used methane, light hydrocarbon slugs, or carbon dioxide.

Since the use of alcohol provides the possibility of a true miscible system, 100% oil recovery is theoretically possible and the early work in this area indicated that some of these theoretical promises would be borne out (125-127). The early interest led to a field trial which failed because the required hydrocarbons of low to intermediate molecular weight were not injected in advance of the alcohol slug and the required phase behavior characteristics were not met (128, 129).

In 1960, Gatlin and Slobod (130), by utilizing concepts developed by Wilson, et al (131), proposed their "piston-like" displacement theory which explained that the oil and water flowing simultaneously in front of the miscible alcohol piston would adjust their saturations to form stabilized banks whose saturations could be calculated from the relative permeability and viscosity of the fluids. They carried out a number of experiments which initially appeared to agree quite well with this straightforward theory.

Taber, Kamath and Reed (132) attempted to confirm the piston-like theory on relatively long, single pieces of consolidated sandstone (Torpedo and Berea), and in addition, they attempted to determine if the slug deterioration did follow the miscible mixing theories, i.e., did it deteriorate (lose miscibility) in proportion to the square root of the distance travelled by the slug. They found that the displacement was not at all piston-like, and it appeared that oil but not water was leaking into the alcohol piston. The reason for this inefficient and non-piston-like displacement is found in the ternary phase diagram for isopropyl alcohol, oil and water used in the initial system (Fig. 6-A). Because of the slope of the tie lines, the oil phase diminishes as the alcohol concentration increases at the leading edge of the alcohol slug. Therefore, the oil saturation in the bank falls below the normal residual oil saturation and much of this oil becomes trapped in a fashion similar to regular waterflooding. As alcohol of higher concentration continues to flow past these trapped ganglia of oil, the oil is extracted so that 100% recovery is still possible eventually, but the displacement is no longer piston-like because the average forward velocity of the oil mass is now much less than that of the water and alcohol. To overcome the poor recovery caused by shrinking of the oil phase in the alcohol transition zone, Taber, et al chose an alcohol system such as

the one using tertiary butyl alcohol illustrated in Fig. 6-B which permits an expanding oil phase in the region of increasing alcohol concentration as the system approaches the region of miscibility. By convention, these two different phase diagrams are referred to as plait point-right and plait point-left, or, rather loosely, as a shrinking oil phase and an expanding oil phase during the displacement process.

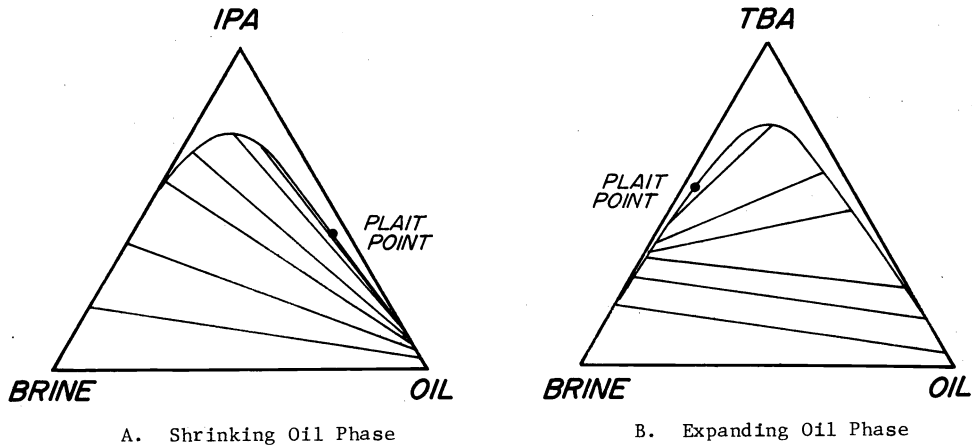


Fig. 6. Typical phase behavior of alcohol (or surfactant)-oil-water systems. (After Taber, Kamath and Reed, Ref. 132).

The recovery with this expanding oil phase was much better; the oil recovery per unit of alcohol injected increased by a factor of seven by moving the plait point of the ternary phase diagram from the right to the left side to permit an expanding oil phase. This effectiveness of displacements with an expanding oil phase (which keeps the oil phase continuous) was confirmed quickly by several others (133-135), and, more recently, by researchers working with surfactants (see below).

Gatlin and Slobod's displacement appeared to be piston-like because they had a very low residual oil saturation to ordinary waterflooding, and they used high flooding rates. Contrary to the assumption by some experts that there should be no interfacial tension or capillary number effects in alcohol displacements because the system is miscible, experiments show that rate effects are extremely important. Taber and Meyer (136) showed that the deviation from piston-like displacement is at a maximum at rates from about 1 to 12 ft/day. When the rate of displacement was increased beyond 12 ft/day, the recovery improved steadily with ever increasing rates until at the limit of their experiment at 70 ft/day, their displacements were almost piston-like. Gatlin and Slobod carried out their experiments at even higher rates of 120 to 144 ft/day in their unconsolidated sandpack inside a steel pipe. At these conditions, the value of $\Delta P/L\sigma$ at most alcohol concentrations, would be well above the critical value. Therefore, in Gatlin and Slobod's experiments, there was no oil trapping (or oil leaking into the alcohol piston) and the piston-like theory appeared to be confirmed by experiment. Additional situations wherein oil trapping occurs even with an expanding oil phase will be discussed along with the relationship between phase behavior and surfactants in the next section.

Phase behavior and micellar-polymer fluids

The importance of phase behavior on oil recovery was mentioned in the section on micellar polymer fluids. Healy, Reed and Stenmark (93) showed that most common types of phase behavior for these complicated surfactant-oil-water systems can be classified as lower, middle and upper phase microemulsions. Their lower phase microemulsion corresponds to the alcohol-oil-water phase behavior in Fig. 6-A while the upper phase corresponds to the slope of the tie lines and the phase behavior in Fig. 6-B. The phase diagram for a surfactant system which has a middle phase microemulsion as described by Healy, Reed and Stenmark is not illustrated here. Nelson and Pope (137) have also investigated the relationship between phase behavior and oil recovery. They prefer to call the phase behavior exhibited in Figure 6-A as Type II-(the slope of the tie lines is negative) and Figure 6-B as Type II+ (slope of the tie lines is positive for expanding oil phase). For microemulsions with a prominent middle phase, they used the same designation as Winsor (138) and Healy, et al, i.e.,

Type III to illustrate the three phases.

In general, Nelson and Pope agree with the observations of Reed and Healy (49) that the best oil recovery should be obtained with microemulsions exhibiting the Type III behavior because this is normally near the optimal salinity with interfacial tensions at a minimum between both the oil and water phases in contact with the middle microemulsion phase. However, all of the data reported by Nelson and Pope indicate that the recovery from the Type II+ surfactant system (expanding oil phase) was equally good. They observed an oil recovery of 89% of the residual oil in both the Type III and the Type II+ displacement experiments.

Larson (139) also carried out a detailed analysis of the influence of phase behavior on surfactant flooding. He constructed mathematical models to account for phase behavior, low interfacial tension, dispersion and other mechanisms to determine conditions under which good oil recovery can be obtained. He also found that the best recovery should come from Type II+, that is an expanding oil phase with the plait point on the left. Larson goes even further in his analysis to claim that good recovery can be achieved from phase behavior alone without the requirement for low interfacial tensions. However, without the aid of low interfacial tension, the good recovery is delayed according to Larson.

Therefore, it appears that this section could be concluded with the summary that the best oil recovery with fluids which bring about low interfacial tension can come either from fluids which are at their optimal salinity so that a fluid of very low interfacial tension is interposed between the oil phase and the brine phase, or, in the event that the surfactant-oil-water system is a two-phase mixture, it is essential that the displacement process occur with the Type II+ mechanism as described by Nelson or Larson, i.e., an expanding oil phase should be part of the displacement process in the region where surfactant or alcohol concentration is increasing.

Unfortunately, when it comes to multi-phase flow in porous media, nature does not permit us to come to such straightforward conclusions. Taber and Meyer (136) observed what might be termed an "inverse viscosity effect." During a long series of experiments in which they were able to provide an expanding oil phase throughout the displacement process (simply by adding oil to the injected alcohol), they noted that oil recovery actually decreased in some cases when their target oil in the Berea sandstone had a low viscosity. This adverse displacement of a low viscosity oil with a very favorable mobility ratio, in a presumed miscible displacement, was contrary to all information on miscible displacement at that time. They noted that even though phase behavior was much more favorable, as, for example with pentane, the recovery was actually somewhat less than the recovery of soltrol (a C_{10} - C_{12} hydrocarbon) because the heavier and more viscous hydrocarbon was trapped less in the oil-water bank which was being displaced by the alcohol piston. This increased trapping of less viscous oil is observed only when oil and water banks are flowing simultaneously as they must when they are being displaced with a fluid miscible with each of them. According to the stabilized bank theory, an oil of a high viscosity will automatically flow with a much higher saturation in the stabilized bank than an oil of lower viscosity. Raimondi and Torcaso (140) have shown that the trapping of the oil phase when both oil and water are flowing simultaneously is a function of the saturation of that oil phase in the bank. Therefore, oils with high viscosities will have high oil saturations in the stabilized bank ahead of the alcohol piston and relatively little capillary trapping of this viscous oil will take place. On the other hand, oils with low viscosities, such as isooctane or pentane will be flowing at oil saturations much closer to the normal residual saturation. Therefore, the amount of oil trapped is somewhat higher for the low-viscosity oils. This means that the alcohol is unable to produce all of the oil in this stabilized bank except by extraction even for systems with an expanding oil phase. The data of Taber and Meyer indicates that the optimum oil recovery for normal hydrocarbons should come with an oil having a viscosity of about 2 or 3 centipoises. For oils which are more viscous than this, the phase diagram becomes less favorable, and with oils having viscosities somewhat less than 3 centipoises, the "Raimondi and Torcaso" type trapping in simultaneously flowing banks takes over and displacement becomes inefficient regardless of the favorable phase diagram employed. Therefore, it appears that any displacement, wherein oil and water are both pushed ahead of a miscible solvent, will be aided by low interfacial tensions because of the difficulty of avoiding oil trapping at some point in the displacement process.

It appears that a miscible displacement can approach the theoretical value (in which the slug deteriorates in proportion to the square root of the distance travelled) only in those cases where there is no water (or 2nd phase) in advance of the miscible slug.

FUTURE DIRECTIONS FOR ENHANCED OIL RECOVERY

As hydrocarbons become more valuable and also less available in the United States and Canada, it is clear that the increased use of inert gases such as carbon dioxide, nitrogen and waste flue gases will be emphasized. Laboratory research will continue to try to understand the mechanisms and researchers will try to devise better techniques for using these

inexpensive low-viscosity fluids more effectively. Research on efforts to use that almost incompressible fluid, water, to drive the special gases through the reservoir will undoubtedly receive more emphasis.

For those tertiary oil recovery processes where thickened water must serve as the efficient driving fluid, the direction of the future research emerges from the discussions in the previous sections. The engineers and surface chemists will continue to try to find formulations which not only provide very low interfacial tensions between the oil and water but which will function to keep the oil phase expanding or flowing at a high saturation during the displacement process. Recent work with microwave techniques indicate that the transitory high oil saturations at the leading edge of the oil-water bank during micellar flooding come from hysteresis in the fractional flow curve (141). This work may provide insight into possible new methods for optimizing this oil bank saturation at the bank-micellar (or solvent) interface to minimize deleterious capillary trapping in near-miscible systems.

New experimental work on oil-water interfacial viscosities and the coalescence of oil droplets will also be carried out because some authors have shown that these phenomena can affect oil recovery, especially in some oil-water-surfactant systems (142-145). However, to date it has been difficult to separate the net contributions of coalescence or interfacial viscosity from the well-documented influence of interfacial tension on oil recovery.

There already is a tendency to use higher quantities of certain alcohols as cosurfactants in these formulations, and it is anticipated that the use of these materials will increase. Although alcohols are expensive, the potential advantages for oil recovery are so great that future research may continue to examine the possibility of using alcohols as the main slug material for some processes.

There will also be efforts to improve the effectiveness of recovery processes by changing the geometry of the standard injection well-production well system. With these recovery fluids becoming more expensive, it is anticipated that there will be efforts to drill long lateral drain holes to put the fluids more precisely where they are needed in the reservoir. Drilling technology is improving and strides are being made which permit horizontal drilling with a shorter turning radius at the bottom of the well. Some of this emphasis has come with the increased need for in situ processes for coal gasification, but there are good reasons to use this technology to convert the inefficient radial, 5-spot pattern into a flood which may approach a linear drive. In addition to the marked improvement in efficiency for placing the fluids, horizontal drain holes can increase the flooding rate and the resultant $\Delta P/L\sigma$ ratio by a factor of 2 to 4 compared to the ordinary 5-spot patterns (38).

There will be new attempts to recover the valuable fluids which are injected in recovery processes. Most field operations with micellar-polymer fluids are designed with the understanding that all of the surfactant and other chemicals are sacrificed to the reservoir. The cost of the lost chemicals must be made up by a very large increase in oil production. As hydrocarbons become more valuable, it appears that a system of alcohols may become practical if a large portion of these alcohols can be recovered by continuing the waterflooding beyond the point at which most of the oil has been produced. Economic recovery of the injected solvents will be difficult because there will be large quantities of single phase fluids composed of oil plus alcohol dissolved in large amounts of water and complete separation of these fluids (by distillation, etc.) might take more energy than that contained in the solvents and hydrocarbons recovered. Therefore, it has been suggested that solar energy (which is too expensive today) might provide some non-hydrocarbon energy for at least partial separation of the alcohol and water produced. Not all of the alcohol, oil and water mixture would need to be separated; some of it could be reinjected as a field process is expanded.

In conclusion, much has been learned since Uren, Fahmy and others started investigating the possibility of improving oil recovery by using materials to alter the surface properties of the oil-water-solid system. An ideal displacement process for displacing oil should include good mobility control and a method for keeping the oil phase continuous while low oil-water interfacial tension is maintained.

Present formulations and methods are designed now to provide just these conditions economically, but the difficulty of propelling the recovery fluids through the formation while maintaining these optimum conditions will keep surface chemists occupied for many years to come.

SYMBOLS

- D average pore diameter [L] (Leverett)
- \bar{D} median pore diameter [L] (MacDonald and Dullien)
- \bar{D}_e mean pore entry diameter [L] (MacDonald and Dullien)
- E_m microscopic displacement efficiency [Dimensionless]
- f multiple oil filament length to radius ratio $\equiv \frac{\Delta L}{a}$ [Dimensionless], where
 ΔL = length of multipore oil mass [L] and a = average radius of
trapped oil mass [L] (Stegemeier)
- g gravitational constant $\equiv 32.2$ (ft/sec)/sec [LT^{-2}]
- K total (absolute) permeability [L^2]
- k_{rw} relative permeability to displacing wetting phase (usually water)
[Dimensionless]
- L length over which pressure drop occurs [L]
- \bar{l} mean length of an oil ganglion [L] (MacDonald and Dullien)
- N_{ca} capillary number $\equiv \frac{v\mu}{\phi\sigma} = \frac{Kk_{rw}\Delta P}{\phi L\sigma}$ [Dimensionless] (Foster; Melrose and
Brandner)
- N_{Le} Leverett number $\equiv J_d K/\phi$ [Dimensionless], where J_d = drainage curvature,
reciprocal of sum of interface radii [L^{-1}] (Stegemeier)
- N_{vc} viscous/capillary number $\equiv \frac{v\mu}{\sigma} = \frac{Kk_{rw}\Delta P}{L\sigma}$ [Dimensionless] (Stegemeier)
- P_c capillary pressure ("displacement" pressure as used by Leverett),
normally $P_c = \frac{2\sigma\cos\theta}{r}$ [$ML^{-1}T^{-2}$], where r = pore radius
- ΔP pressure drop [$ML^{-1}T^{-2}$]
- r_n pore neck radius [L] (Oh and Slattery)
- v Darcy velocity of displacing wetting phase (usually water) [LT^{-1}]
- Z_{imb} curvature correction factor for imbibition [Dimensionless] (Morrow)
- Greek
- θ contact angle at phase boundary between wetting and non-wetting
phase (usually oil and water), normally measured through wetting
phase (usually water) [Dimensionless]
- μ effective viscosity of displacing wetting phase (usually water) $\equiv \mu_w$
[$ML^{-1}T^{-1}$]
- μ_w same as μ [$ML^{-1}T^{-1}$]
- μ_o effective viscosity of displaced non-wetting phase (usually oil) [$ML^{-1}T^{-1}$]

- σ interfacial tension between wetting and non-wetting phase (usually oil and water) [MT^{-2}]
- ϕ porosity of medium [Dimensionless]
- ψ geometrical factor for curvature of front and back of trapped oil mass [Dimensionless]

REFERENCES

1. DeGolyer, E. (editor), Elements of the Petroleum Industry, AIME, New York, 289 (1940).
2. Smith, R.C., Mechanics of Secondary Oil Recovery, R. E. Kreiger, Huntington, New York (1975).
3. Forbes, R.J., Studies in Early Petroleum History, E.J.Brill, Leiden, Netherlands, 52 (1958).
4. Squires, F., U.S. Patent No. 1,238,355.
5. Nutting, P.G., Ind. Eng. Chem. 17, 1035 (1925).
6. Jamin, J.M., Compt. Rend. 50, 172-176, 311-314, 385-389 (1860).
7. Herold, S.C., Oil Well Drainage, Stanford University Press, Stanford, California (1941).
8. Calhoun, J.C., Jr., Fundamentals of Reservoir Engineering, University of Oklahoma Press, Norman, Oklahoma, 123-126 (1953).
9. Wyckoff, R.D. and Botset, G.H., Physics 7, 325 (1936).
10. Uren, L.D. and Fahmy, E.H., Trans. AIME 77, 318-335 (1927).
11. Melrose, J.C. and Brandner, C.F., J. Can. Pet. Tech. 13, 54-62 (1974).
12. Benner, F.C., Riches, W.W. and Bartell, F.E., API Drilling and Production Practice, 442 (1938).
13. Benner, F.C. and Bartell, F.E., API Drilling and Production Practice, 341-346 (1941).
14. Benner, F.C., Dodd, C.G. and Bartell, F.E., API Drilling and Production Practice, 169-177 (1942).
15. Moore, T.F. and Slobod, R.L., Prod. Monthly 20, 20-30 (Aug. 1956).
16. Ammot, E., Trans. AIME 216, 156-162 (1959).
17. Morrow, N.R., J. Can Pet. Tech. 14, 42 (1975).
18. Melrose, J.D., Soc. Pet. Eng. J. 5, 259 (1965).
19. Morrow, N.R. and McCaffery, F.G., Wetting, Spreading and Adhesion, J. J. Padday, ed., Academic Press, Inc., London, 289-319 (1978).
20. Morrow, N.R., J. Can. Pet. Tech. 15, 49 (1976).
21. Morrow, N.R., Paper No. 78-29-24, presented at the 29th meeting of the Pet. Soc. of CIM, Calgary, June 13 (1978).
22. Nutting, P.G., Oil Gas J. 25 45, 76, 150 (1927).
23. Nutting, P. G., Oil Gas J. 25 50, 32, 106 (1927).
24. Nutting, P.G., Oil Gas J. 27 22, 146, 238 (1928).
25. Reisberg, J. and Doscher, T.M., Prod. Monthly 21 1, 43-50 (Nov. 1956).
26. Wagner, O.R. and Leach, R.O., Trans. AIME 216, 65-72 (1959).
27. Leach, R.O., Wagner, O.R., Wood, H.W. and Harpke, C.F., J. Pet. Tech. 206-212 (Feb. 1962); Trans. AIME 225, 206-212 (1962).
28. Emery, L.W., Mungan, N. and Nicholson, R.W., J. Pet. Tech., 1569-1576 (Dec. 1970).
29. Cooke, C.E., Jr., Williams, R.E. and Kolodzie, P.A., J. Pet. Tech. 1365-1374 (Dec. 1974).
30. Graue, D.J. and Johnson, C.E., Jr., J. Pet. Tech., 1353-1358 (Dec. 1974).

31. Johnson, C.E., Jr., J. Pet. Tech., 85-92 (Jan. 1976).
32. Treiber, L.E., Archer, D.L. and Owens, W.W., Soc. Pet. Eng. J. 12, 531-540 (1972).
33. Richardson, J.G., Perkins, F.M. and Osoba, J.S., Trans. AIME 204, 89-91 (1955).
34. Salathiel, R.A., J. Pet. Tech., 1216-1224 (Oct. 1973).
35. Guereca, R.A. and Butler, H.S., Prod. Monthly 19, 21 (1955).
36. Kennedy, H.T. and Guerrero, G.T., Trans. AIME 201, 124-131 (1954).
37. Taber, J. J., Trans. AIME 213, 186-192 (1959).
38. Taber, J.J., Soc. Pet. Eng. J. 9, 3-12 (1969).
39. Fairbrother, F. and Stubbs, A.E., J. Chem. Soc., 527-529 (1935).
40. Leverett, M.C., Trans. AIME 132, 149-169 (1939).
41. Brownell, L. E. and Katz, D. L., Chem. Eng. Progr. 42, 601 (1947).
42. Ojeda, E., Preston, F. and Calhoun, J.C., Prod. Monthly 18, 20-29 (Dec. 1953).
43. Saffman, P.G. and Taylor, G., Proc. Royal Soc. London, Ser. A 245, 312-329 (1958).
44. Foster, W.R., J. Pet. Tech. 205-210 (1973).
45. Lefebvre duPrey, E.G., Soc. Pet. Eng. J. 13, 39-47 (1973).
46. Ehrlich, R., Hasiba, H.H. and Raimondi, P., J. Pet. Tech. 1335-1343 (Dec. 1974).
47. Abrams, A., Soc. Pet. Eng. J. 15, 437-447 (1975).
48. MacDonald, I.F. and Dullien, F.A.L., J. Pet. Tech., 7-9 (Feb. 1976).
49. Reed, R. L. and Healy, R.N., Improved Oil Recovery by Surfactant and Polymer Flooding, D. O. Shah and R. S. Schechter, ed., Academic Press, Inc., New York, 383-437 (1977).
50. Stegemeier, G. L., Improved Oil Recovery by Surfactant and Polymer Flooding, D. O. Shah and R. S. Schechter, ed., Academic Press, Inc., New York, 55-91 (1977).
51. Oh, S. G. and Slattery, J. C., Soc. Pet. Eng. J. 19, 83-96 (1979).
52. Wagner, O.R. and Leach, R.O., Soc. Pet. Eng. J. 6, 335-344 (1966).
53. Dombrowski, H.S. and Brownell, L.E., Ind. Eng. Chem. 46, 1207-1219 (1954).
54. Jenks, L.H., Huppler, J.D., Morrow, N.R. and Salathiel, R.A., J. Pet. Tech., 932 (Aug. 1969).
55. Taber, J.J., Kirby, J.C. and Schroeder, F.U., AIChE Symp. Ser. No. 127, 53-56 (1973).
56. Jenks, L.H., Huppler, J.D., Morrow, N.R. and Salathiel, R.A., J. Can. Pet. Tech. 7, 172-180 (July 1968).
57. Stosur, J.J. and Taber, J.J., J. Pet. Tech., 865-868 (Aug. 1976).
58. Sayyoub, M.H.M., Farouq Ali, S.M. and Stahl, C.D., paper SPE 7639, presented at the SPE-AIME Eastern Regional Meeting, Washington, D.C., Nov. 1-3 (1978).
59. Larson, R.G., Scriven, L.E. and Davis, H.T., Nature 268, 409-413 (1977).
60. Holm, L. W. and Bernard, G. G., U. S. Patent No. 3,006,411 (1958).
61. Csaszar, A.K., U. S. Patent No. 2,356,205 (1942).

62. Gogarty, W.B. and Olson, R.W., U. S. Patent No. 3,254,714 (1962).
63. Jones, S.C., U.S. Patent No. 3,497,006 (1967).
64. Jones, S.C., U. S. Patent No. 3,506,070 (1967).
65. Gogarty, W.B. and Tosch, W.C., J. Pet. Tech., 1407-1414 (Dec. 1968); Trans. AIME 243, 1407-1414 (1968).
66. Davis, J.A., Jr. and Jones, S.C., J. Pet. Tech., 1415-1428 (Feb. 1973); Trans. AIME 243, 1415-1928 (1968).
67. Holm, L.W., U.S. Patent No. 3,537,520 (1970).
68. Holm, L.W., J. Pet. Tech. 1475-1483, (Dec. 1971); Trans. AIME 251, 1475-1483 (1971).
69. Schulman, J.H., Stoeckenius, W. and Prince, L.M., J. Phys. Chem. 63, 1677 (1959).
70. Somasundaran, P. and Hanna, H.S., Improved Oil Recovery by Surfactant and Polymer Flooding, D. O. Shah and R. S. Schechter, ed., Academic Press, Inc., New York, New York, 205-251 (1977).
71. Hanna, H.S. and Somasundaran, P., Improved Oil Recovery by Surfactant and Polymer Flooding, D. O. Shah and R. S. Schechter, ed., Academic Press, Inc., New York, New York, 253-274 (1977).
72. Malmberg, E.W. and Smith, L., Improved Oil Recovery by Surfactant and Polymer Flooding, D. O. Shah and R. S. Schechter, ed., Academic Press, Inc., New York, New York, 275-291 (1977).
73. Gale, W.W. and Sandvik, E. I., Soc. Pet. Eng. J. 13, 191-199 (1973).
74. Trogus, F. J., Schechter, R.S., Pope, G.A. and Wade, W.H., J. Pet. Tech., 769-778 (June 1979)
75. Gogarty, W.B., Meabon, H.P. and Milton, H.W., Jr., J. Pet. Tech., 141-147 (Feb. 1970).
76. Gogarty, W.B. and Davis, J.A., Jr., paper SPE 3806, presented at the SPE-AIME Improved Oil Recovery Symposium, Tulsa, Oklahoma, April 16-19, 1972.
77. Sandiford, B. B., Improved Oil Recovery by Surfactant and Polymer Flooding, D. O. Shah and R. S. Schechter, ed., 487-5109, Academic Press, Inc., New York, New York (1977).
78. Dawson, R. and Lantz, R. B., Soc. Pet. Eng. J. 12, 448 (1972).
79. Trushenski, S. P., Dauben, D. C. and Parrish, D.R., Soc. Pet. Eng. J. 14, 633 (1974).
80. Vela, S., Peaceman, D.W. and Sandvik, E.I., paper SPE 5102, presented at the SPE-AIME 49th Annual Fall Meeting, Houston, Texas (1974).
81. Dominguez, J.G. and Willhite, G.P., paper SPE 5835, presented at the SPE-AIME Improved Oil Recovery Symposium, Tulsa, Oklahoma, March 22-24 (1976).
82. Trushenski, S. P., Improved Oil Recovery by Surfactant and Polymer Flooding, D.O. Shah and R.S. Schechter, ed., 555-575, Academic Press, Inc., New York, New York (1977).
83. Cayias, J. L., Schechter, R.S. and Wade, W.H., Am. Chem. Soc. Symp. Ser. No. 9, 235 (1975).
84. Vonnegut, B., Rev. Sci. Instrum. 13, 6 (1942).
85. Cayias, J.L., Schechter, R.S. and Wade, W.H., J. Coll. Interface Sci. 59, 31-38 (1977).
86. Cash, R.L., Cayias, J.L., Fournier, G., MacAllister, D.J., Schares, T., Schechter, R.S. and Wade, W.H., J. Coll. Interface Sci. 59, 39-44 (1977).
87. Cash, R.L., Cayias, J.L., Fournier, G., Jacobson, J.K., Schares, T., Schechter, R.S. and Wade, W.H., paper SPE 5813, presented at the SPE-AIME Improved Oil Recovery Symposium, Tulsa, Oklahoma, March 22-24 (1976).

88. Jacobson, J.K., Morgan, J.C., Schechter, R.S. and Wade, W.H., paper SPE 6002, presented at the SPE-AIME 51st Annual Fall Meeting, New Orleans, Louisiana, Oct. 3-6 (1976).
89. Cash, R.L., Cayias, J.L., Fournier, G., Jacobson, K.J., LeGear, C.A., Schares, T., Schechter, R.S. and Wade, W.H., Oil Chemists Soc., Short Course at Hershey, Pennsylvania, June (1975).
90. Burkowsky, M. and Marx, C., Erdoel-Erdgas Zeitschrift (Int'l Edition) 93, 33-38, Nov. (1977).
91. Healy, R. N. and Reed, R.L., Soc. Pet. Eng. J. 14, 491-501 (1974); Trans. AIME 257.
92. Healy, R.N., Reed, R.L. and Carpenter, C.W., Soc. Pet. Eng. J. 15, 87-103 (1975); Trans. AIME 259, 87-103 (1975).
93. Healy, R.N., Reed, R.L. and Stenmark, D.G., Soc. Pet. Eng. J. 16, 147-160 (1976); Trans. AIME 261, 147-160 (1976).
94. Healy, R.N. and Reed, R.L., paper SPE 5817, presented at SPE-AIME Improved Oil Recovery Symposium, Tulsa, Oklahoma, Mar. 22-24 (1976).
95. Harkins, W.D. and Zollman, H., J. Am. Chem. Soc. 48, 69 (1926).
96. Henderson, J.H. and Taber, J. J., U.S. Patent No. 3,199,586 (1965).
97. Wilson, P.M., Murphy, L.C. and Foster, W.R., paper SPE 5812, presented at the SPE-AIME Improved Oil Recovery Symposium, Tulsa, Oklahoma, Mar. 22-24 (1976).
98. Puerto, M.C. and Gale, W.W., paper SPE 5814, presented at the SPE-AIME Improved Oil Recovery Symposium, Tulsa, Oklahoma, Mar. 22-24 (1976).
99. Miller, C.A., Hwan, R., Benton, W.J. and Fort, T., Jr., J. Coll. Interface Sci. 61, 554 (1977).
100. Benton, W.J., Fort, T., Jr. and Miller, C.A., paper SPE 7579, presented at the SPE-AIME 53rd Annual Fall Meeting, Houston, Texas, Oct. 1-3 (1978).
101. Hwan, R.N., Miller, C.A. and Fort, T., Jr., J. Coll. Interface Sci. 68, 221-234 (1979).
102. Scriven, L.E., Nature 263, 123 (1976).
103. Chan, K.S. and Shah, D.O., paper SPE 7896, presented at the 1979 SPE-AIME Int'l Symp. on Oilfield and Geothermal Chemistry, Houston, Texas, Jan. 22-24 (1979).
104. Bansal, V.K. and Shah, D.O., Soc. Pet. Eng. J. 18, 167-172 (1978).
105. Slobod, R. L. and Koch, H.A., Jr., Oil Gas J. 51 48, 85-88, 115-117 (April 16, 1953).
106. Brownscombe, E.R., Oil Gas J. 53 6, 133 (June 14, 1954).
107. Kern, L.R., Kimbler, O.K. and Wilson, R., J. Pet. Tech. 16 (May 1958).
108. Kennedy, H.T., Oil Gas J. 51 8, 58-61, 69. (June 30, 1952).
109. Koch, H.A., Jr. and Slobod, R. L., Trans. AIME 210, 40 (1957).
110. Kehn, D.M., Pyndus, G.T. and Gaskell, M.G., J. Pet. Tech., 45 (June 1958).
111. Welge, H.J., Johnson, E.J., Dwing, S.P., Jr. and Brinkman, F.H., paper SPE 1525-G, presented at SPE-AIME Annual Fall Meeting, Denver, Colorado, Oct. (1960).
112. Hutchinson, C.A., Jr. and Braun, P.H., Trans. AIME 219, 229-237. (1960).
113. Caudle, B.H. and Dyes, A.B., Trans. AIME 213, 281-284 (1958).
114. Holm, L.W., Prod. Monthly 27, 6 (Sept. 1963).
115. Beeson, D.M. and Ortloff, H.D., Trans. AIME 216, 388-391 (1959).

116. Holm, L.W., Trans. AIME 216, 225 (1959).
117. Rathmell, J.J., Stalkup, F.I. and Hassinger, R.C., paper SPE 3483, SPE-AIME, Dallas, Texas (1971).
118. Holm, L.W. and Josendal, V.A., J.Pet. Tech., 1427-1438, Dec. (1974).
119. Huang, E.T.S. and Tracht, J.H., paper SPE 4735, presented at the SPE-AIME Improved Oil Recovery Symposium, Tulsa, Oklahoma, April (1974).
120. Stalkup, F.I., paper SPE 7042, presented at SPE-AIME Improved Oil Recovery Symposium, Tulsa, Oklahoma, April 16-19, (1972).
121. Martin, J.W., Prod. Monthly 16, 13 (1951).
122. Rosman, A. and Zana, E., paper SPE 6723, presented at the 52nd Annual Fall Meeting, Denver, Colorado, Oct. 9-12 (1977).
123. Metcalfe, R.S. and Yarborough, L., paper SPE 7061, presented at the SPE-AIME Improved Oil Recovery Symposium, Tulsa, Oklahoma, April 16-19 (1972).
124. Sarhosh, H., M. S. Thesis, Texas A & M University (1977).
125. Morse, R. A., German Patent No. 849,534, July (1952).
126. Sievert, J.A., Dew, J.M. and Conley, F.R., Trans. AIME 213, 228 (1958).
127. Slobod, R.L., Prod. Monthly 22, 4, 24, Feb. (1958).
128. Breston, N., Prod. Monthly 24, 11, 22 (1960).
129. Slobod, R.L., Prod. Monthly 26, 3, 2 (1962).
130. Gatlin, C. and Slobod, R.L., Trans. AIME 219, 46 (1960).
131. Wilson, L.A., Wygal, R.J., Reed, D.W., Gergins, R.L. and Henderson, J.H., Trans AIME 213, 146 (1958).
132. Taber, J.J., Kamath, I.S.K. and Reed, R.L., Soc. Pet. Eng. J. 1, 195-212 (1961).
133. Holm, L.W. and Csaszar, A.K., Soc. Pet. Eng. J. 2, 129 (1962).
134. Farouq Ali, S.M. and Stahl, C.D., Prod. Monthly 27, 1, 2 (1963).
135. Burcik, E.J., Prod. Monthly 26, 3, 2 (1962).
136. Taber, J.J. and Meyer, W.K., Soc. Pet. Eng. J. 4, 37-48 (1964).
137. Nelson, R.C. and Pope, G.A., Soc. Pet. Eng. J. 18, 325 (1978).
138. Winsor, P.A., Solvent Properties of Amphiphillic Compounds, Butterworth's Scientific Publications, London (1954).
139. Larson, R.G., paper SPE 6744, presented at the SPE-AIME 52nd Annual Fall Meeting, Denver, Colorado, Oct. 9-12 (1977).
140. Raimondi, P. and Torcaso, M.A., Trans AIME 231, 49-55 (1964).
141. Gladfelter, R.E. and Gupta, S.P., paper SPE 7577, presented at the SPE-AIME 53rd Annual Fall Meeting, Houston, Texas, Oct. 1-3 (1978).
142. Mannheimer, R.J. and Schechter, R.S., J. Coll. Interface Sci. 32, 195-211 (1970).
143. Slattery, J.C., AIChE J. 20, 1145, (1974).
144. Wasson, D.T. and Mohan, V., Improved Oil Recovery by Surfactant and Polymer Flooding, D. O. Shah and R. S. Schechter, ed., Academic Press, Inc., New York, 161-203 (1977).
145. Flumerfelt, R.W. and Payatakes, A.C., Enhanced Oil Recovery and Improved Drilling Technology, Progress Review No. 19, USDOE, BETC - 79/3, 59, (Sept. 1979).