

TABLE VII
End-Use Patterns of Selected Surfactants

	AAS	FAS	APE	PS
Commercial laundry.....	4
Cosmetics.....	6
Formulated detergents.....	6	19
Household.....	(85)	(80)	(14)
Laundry.....	64	65	14
Dishwashing.....	16	20 ^a
Scouring powder.....	5	35
Intermediate..... ^a
Metal cutting.....	11
Petroleum.....	2	82
Textile.....	13
Miscellaneous.....	7	5	19	7

^a Combined as the uses are alternate.

Conclusions

This study emphasizes the differences in properties required of surfactants for various application, the large and growing number of uses requiring more than 500,000 pounds per year, and the constantly changing pattern of use, making most of the recent estimates of volume distribution obsolete.

For some time it has been customary to estimate the household market as 75-80% of the total. This study shows that this estimate is certainly high as household use is now probably only 50-55% of the total. This fact may be important in releasing our energies for the creative development of markets in the industrial fields. There is a rich potential market in such applications as ore flotation, agriculture, road building, and petroleum processing.

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[Received September 26, 1956]

Evaluation of Surfactants for Oil Field Flooding

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CRUDE OIL IN PETROLEUM RESERVOIRS occurs as a liquid distributed in the pore spaces of fine-grained sedimentary rock. Water is always present in the pores as a second liquid phase. On the average the pores are from 10 to 20 microns in diameter. Oil contained in an undeveloped field is usually saturated with hydrocarbon gas and is under considerable pressure. The first production obtained from wells in a new field is therefore the result of the release and expansion of dissolved gas. When this natural source of energy is depleted, flow of oil into the producing wells declines to a low rate or ceases altogether until finally continued operation becomes uneconomical. At this point in many fields it is not uncommon to find more than two-thirds of the original oil content still remaining within the pores of the reservoir rock. Unless some external source of energy is applied, this oil will remain uncovered.

One of the most common and most efficient external sources of energy used to supplement the natural reservoir energy and prolong oil production is water under pressure. Water may be injected into part of the existing wells, and the oil driven ahead of it may be collected in those remaining. The process of ap-

plying energy from external sources to increase oil production is known as secondary recovery. When water under pressure is the external source, the process is called water-flooding. Under ideal conditions, water flooding can about double the volume of oil produced. Nevertheless about one-third of the original oil in place still remains within the reservoir, unrecoverable by presently practical methods. It is estimated (1) that there are 194 billion barrels of oil in U. S. reservoirs which is not now economically recoverable. This is about five times the known recoverable reserves.

Surfactant Flooding

Aside from occasional gross inhomogeneities in oil reservoir rocks, the failure of water flooding to displace a larger fraction of the oil present can be blamed on capillary forces operating within the rock pores. These capillary forces are generally described in terms of the energies of the phase boundaries present, *e.g.*, the oil-water, rock-water, and rock-oil interfaces. The relationship between these energies controls such important factors as the degree to which water tends to displace oil from the rock surface and

the ease with which small bubbles of oil surrounded by water deform in passing from one pore to another.

Although the exact relationship between water-flood efficiency and capillary forces is not well understood, their importance in water flooding has long been recognized. Thus it is not surprising that the possibility of improving water-flood efficiency by the addition of capillary-active substances, *i.e.*, surfactants, to the injected water was being discussed as early as 1927 (2). The idea was simply that, through their profound effects on capillary forces, surfactants might alter the capillary balance within the reservoir in such a way as to allow the water to displace a greater part of the oil present.

Our own experience, and that of the others (3), indicates that these early hopes were justified. Surfactants in moderate concentration can often increase water-flood efficiency by 50% or more under conditions closely approaching those encountered in field practice. On the other hand, not all surfactants are effective, and no one surfactant seems to be effective in all water-rock-crude oil systems. The reasons for this high degree of specificity are not known in detail. In fact, the mechanism of oil release by surfactant is itself still a subject of controversy. Despite this however the technical feasibility of increasing water-flood oil-recovery through the use of surfactants may be regarded as an accomplished fact. The problem which remains is that of placing surfactant flooding on an economic basis.

Surfactant Slug Flooding

Until 1952 most of those engaged in studying the surfactant-flooding problem tacitly assumed that it was necessary to add surfactant to all of the water injected. Their results were generally discouraging in terms of the quantities of surfactant required per barrel of additional oil recovered. This was caused partly by the fact that very small concentrations were usually ineffective and partly by the fact that loss of surfactant through adsorption on the internal rock surfaces was excessively high.

In 1952 Preston and Calhoun (4) suggested that perhaps only part of the injected water need be treated with surfactant. Their idea was to establish a relatively narrow zone of surfactant solution within the reservoir by injecting a batch, or slug, of treated water and to move this zone of partially adsorbed surfactant through the reservoir by continued injection of untreated water. It was anticipated that such a process might require substantially less surfactant than previous thinking had indicated. They showed how DeVault's (5) equations for the chromatographic process could be applied to the problem and how these equations could be used to calculate the size of the surfactant slug required and its rate of travel through the reservoir.

While it is reasonable to suppose that a relatively narrow zone of surfactant might be established and moved through a reservoir, Preston and Calhoun presented no evidence to show that such a zone could bring about increases in recovery comparable with those obtained by continuous surfactant injection. Two assumptions are implicit in the suggestion that a narrow zone of surfactant can perform as well as the same surfactant continuously injected. The first is that the time required for the oil release process is not longer than the time it takes the zone to pass

a given point within the reservoir. If it is, oil will be left behind by the moving zone and will not be released. The second is that oil, once released, must be able to move ahead faster than the surfactant zone. This is theoretically possible since the partially adsorbed surfactant always moves more slowly than the water which is eluting it. If the released oil moves at a velocity between that of the surfactant zone and that of the water, this requirement will be satisfied. If it does not, then oil will be left behind the moving zone and will revert to its former equilibrium state of immobility.

Our own laboratory experiments, although not reported here in detail, have shown that, for at least two natural rock-water-oil systems, these two requirements are satisfied. They show that almost all of the extra oil obtained is produced ahead of the surfactant zone. They also show that, at rates of flow approximating those used in field practice, a surfactant zone a few tenths of an inch thick is sufficient to complete the oil release process. Thus we believe that the slug flooding method is technically feasible, that for practical purposes the calculation of slug size can be based on the adsorptive properties of the reservoir material, and that, from an economic point of view, the slug method of application is the most promising yet conceived.

The Maximum Economic Slug Volume

Because the slug method appears attractive from a practical standpoint, it is important to obtain a clear formulation of the economics of the process. This should be stated in terms of variables whose values can be easily determined, either experimentally or through the use of readily available information. In developing such a formulation, it is most convenient to start by considering a surfactant flood in a field which has already been water flooded to the point where no more oil can be produced. It will be shown later however that the economics are more favorable when the surfactant is injected at the beginning of a conventional water-flood.

The important costs to be considered are the cost of surfactant required to make up the slug and the cost of continuing water injection long enough to drive the surfactant zone through the reservoir. The first of these is given by 1,

$$v C D_a \quad (1)$$

in which v is the volume of the surfactant slug in barrels, C is the concentration of surfactant in the slug in pounds per barrel, and D_a is the cost of surfactant in dollars per pound. The cost of continuing water injection is given by 2,

$$n D_w \quad (2)$$

in which n is the total number of barrels of water required to drive the surfactant zone through the reservoir and D_w is the cost of continuing the injection and lifting of water with existing equipment, expressed in dollars per barrel. The value of D_w is sometimes difficult for one not directly involved in water-flooding activities to estimate because so many subsidiary variables enter into its computation. However an upper limit for any particular water-flood location may be assigned to it. For example, wherever water flooding is in progress there will be some maximum ratio of water to oil which a well may

produce before its operation is considered unprofitable and it is shut in. This figure can be obtained from the engineering staff and is usually of the order of 25 to 100 barrels of water per barrel of oil. If the sale price of the produced oil is known, then the upper limit of D_w is given by Equation 3,

$$D_w = D_o / \text{WOR}_m \quad (3)$$

where D_o is the sale price of the crude oil in dollars per barrel and WOR_m is the maximum value of the producing water-oil ratio which will still allow an acceptable profit on the produced oil. Among the costs included in D_w as defined by Equation 3 are such items as royalty, mineral and property tax, operating cost, overhead, depreciation on plant investment, and income tax. Moreover D_w includes, in addition to the costs involved, a small amount which represents the minimum acceptable profit per barrel of injected water.

The return on the surfactant flood is represented by Expression 4,

$$f D_o \quad (4)$$

where f is the number of barrels of additional oil recovered ahead of a surfactant zone at concentration C .

Equating total costs and return on the operation gives Equation 5,

$$v C D_d + n D_o / \text{WOR}_m = f D_o \quad (5)$$

which defines the conditions under which a surfactant-slug flood, in a previously water-flood depleted field, will result in a minimum acceptable profit. The use of Equation 5 can be made more convenient by dividing through by V_p , the pore volume in barrels of the reservoir to be flooded. This yields Equation 6,

$$V C D_d + N D_o / \text{WOR}_m = F D_o \quad (6)$$

in which V is the volume of the surfactant slug expressed in pore volumes (dimensionless), N is the number of pore volumes of water required to drive the surfactant zone through the reservoir, and F is the additional oil recovered, expressed as a fraction of the pore volume of the reservoir being flooded. Since D_o and WOR_m can be obtained from engineering and field data in locations where surfactant flooding might be contemplated, D_d is available from the surfactant manufacturer, and C , N , and F can be determined by experimental flooding of small rock samples in the laboratory, the utility of Equation 6 lies in the fact that it can be used to find V in terms of the other variables.

Obtained in this way, V represents the maximum volume which the surfactant slug may possess if a minimum acceptable profit is to be realized. Because of this special meaning which attaches to V when it is determined by the other variables, it will hereafter be written with the subscript max. A convenient expression for V_{\max} is obtained by rearrangement of Equation 6 to give Equation 7.

$$V_{\max} = \frac{F D_o}{C D_d} \left[1 - \frac{N}{F (\text{WOR}_m)} \right] \quad (7)$$

It should be noted that if N is greater than $F(\text{WOR}_m)$, a negative value will be obtained for V_{\max} . This means simply that the cost of injecting enough water to drive the surfactant zone through the reservoir is itself too large to allow attainment of a minimum acceptable profit, regardless of how little surfactant may be required.

The economics of surfactant flooding can be improved by injecting the surfactant slug at the beginning of the conventional water-flood operation rather than waiting until it has reached its economic limit. The advantage gained is not because of any increase in recovery efficiency but because of the fact that the water injected in the conventional flood can be used to move the surfactant zone at least part way through the reservoir. As a rule of thumb, the total water injected over the life of a conventional flood is about two and one-half pore volumes. The cost of these first two and one-half pore volumes should not be regarded as one of the expenses of surfactant flooding, if surfactant is injected at the beginning of a flood which would otherwise have been carried out in a conventional manner. Using the rule of thumb stated above, Equation 7 can be modified to apply to injection of surfactant at the beginning of a normal flood. This is done by substituting $(N - 2.5)$ for N to yield Equation 8.

$$V_{\max} = \frac{F D_o}{C D_d} \left[1 - \frac{(N - 2.5)}{F (\text{WOR}_m)} \right] \quad (8)$$

The Minimum Effective Slug-Volume

In order to measure the degree to which a surfactant satisfies the requirements for economic application, the minimum slug volume, V_{\min} , which will be fully effective must be determined. If this is less than V_{\max} , the largest volume which can be injected profitably, then use of the surfactant is practical. If V_{\min} is greater than V_{\max} , then the difference between them can be regarded as a measure of the degree by which the surfactant fails to meet minimum requirements for profitable water-flood application.

As already mentioned, experimental indications are that V_{\min} is dictated by the adsorptive characteristics of the reservoir material. If this is so, its calculation can be based on the theories developed by DeVault (5) to explain the movement of partially adsorbed solute through porous adsorbents in chromatographic columns. The equations describing zone movement are, in turn, based on a description of the adsorptive characteristics of the reservoir material in terms of an adsorption isotherm, $f(C)$. Here C is the concentration of dissolved surfactant in equilibrium with surfactant adsorbed on the surface. The function $f(C)$ is usually defined by Equation 9.

$$f(C) = Q/M \quad (9)$$

There Q is the total mass of surfactant adsorbed and M the total mass of adsorbent. For the purpose of this discussion, however, it is more convenient to define $f(C)$ by means of Equation 10.

$$f(C) = Q/V_p \quad (10)$$

There Q is the total mass of surfactant adsorbed and V_p is the total pore volume of the system. It is possible to use this definition because the pore volume per unit mass is a characteristic property of each reservoir rock. If Q is in pounds and V_p in barrels, then $f(C)$ will be the weight of surfactant adsorbed in pounds per barrel of pore space. These units will be used in subsequent discussion. A typical surfactant-adsorption isotherm plotted in these units is shown in Figure 1. Nearly all surfactant-adsorption isotherms are concave toward the concentration axis as is that of Figure 1.

A moving zone of surfactant, whose adsorption

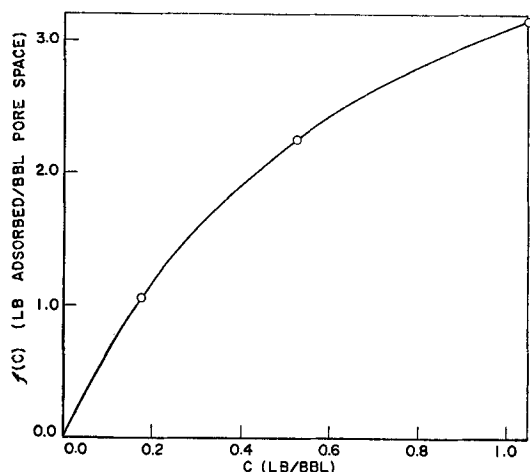


FIG. 1. Typical surfactant-adsorption isotherm.

isotherm is concave toward the concentration axis, will exhibit a concentration profile of the general shape shown in Figure 2 (4). The zone consists of two parts separated by the point X_2 . The one to the right of X_2 is of constant concentration equal to the concentration at which it was injected. The one to the left of X_2 is of variable concentration. As the whole zone is moved to the right by continued injection of untreated water, the point X_1 moves ahead more slowly than X_2 . This causes the zone of variable concentration, the trailing edge, to lengthen. At the same time the point X_2 moves ahead more rapidly than X_3 , the sharp leading edge. This results in a gradual narrowing of the zone of constant concentration. For any given volume of surfactant solution, a volume of injected water will eventually be reached at which X_2 overtakes X_3 . When X_2 equals X_3 and X_3 is the total length of the system, then the volume of the surfactant slug is the minimum necessary to maintain the injection concentration through a complete traverse of the system. This we regard as the minimum effective slug volume, V_{\min} . DeVault's (5) equations show that V_{\min} at any particular surfactant concentration, C_0 , will be given by Equation 11.

$$V_{\min} = f(C_0)/C_0 - f'(C_0) \quad (11)$$

Here $f(C_0)$ is simply the weight of surfactant adsorbed in pounds per barrel of pore space when the equilibrium concentration of surfactant in the water is C_0 . The quantity $f'(C_0)$ is the concentration derivative of $f(C)$ evaluated at concentration C_0 . Thus V_{\min} can be calculated at any concentration for comparison with V_{\max} if $f(C)$, the adsorption iso-

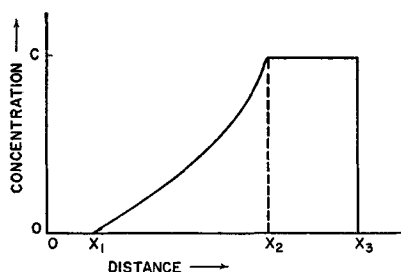


FIG. 2. Generalized concentration-distance profile for a moving zone of surfactant whose adsorption isotherm is concave toward the concentration axis.

therm, is known. Equation 11 is valid for solutes composed of a single molecular species. While most commercial surfactants are mixtures of isomers, their adsorption on sand surfaces often resembles that of a single compound. The equation applies to both radial and linear flow. How well it predicts behavior in some of the other geometric patterns used in water flooding has not been tested.

Experimental Measurements

It is necessary to determine three quantities experimentally in order to calculate V_{\max} and V_{\min} . These are $f(C)$, N , and F . All three should be evaluated over a reasonable range of surfactant concentration. If N is known, $f(C)$ can be calculated, using Equation 12.

$$f(C) = (N - 1) C \quad (12)$$

N is most easily measured on a sample of reservoir rock by injecting surfactant at a given concentration and measuring the number of pore volumes (N) injected before the sharp surfactant front emerges from the outflow face of the sample. This procedure should be repeated at a sufficient number of different concentrations so that a reasonable plot of N versus C can be constructed. The smoothed data from this plot can then be used to find $f(C)$. This method of frontal analysis is valid as long as the adsorption is rapid and reversible. The results could be checked by injecting water after the surfactant front has emerged and analyzing for surfactant as the diffuse trailing edge appears. In principle this procedure could give V_{\min} directly. In practice however inhomogeneity of the small rock samples available makes determination of the trailing edge more uncertain than location of the front. In addition, the low rates of flow used make analysis of the trailing edge a time-consuming procedure. Usually surfactant adsorption is assumed to be rapid and reversible, and both $f(C)$ and V_{\min} are calculated, using Equations 12 and 11.

The surfactant oil recovery, F , may be measured by saturating a sample of reservoir rock with water and oil, flooding it with water until no more oil is produced, and then flooding with surfactant solution. The effluent from the surfactant flood is sampled regularly, and both the oil cut, that is the fraction of total effluent which is oil, and the surfactant concentration are measured. F is the total oil produced by the surfactant front. It is expressed as a fraction of the total pore volume.

Our experience has shown that the presence of oil in the reservoir rock tends to reduce the N values somewhat. For this reason measurement of the N values while oil recovery is taking place is probably the best procedure. If this practice is followed, N can be obtained from the same experiments in which F is measured. To illustrate, Figure 3 shows a typical set of experimental results. Estimates of N at the three different concentrations are indicated on the figure. F is given in pore volumes by the area under the oil cut curve, bounded on the right by the N value. Values for C , N , and F obtained from Figure 3 are listed in Table I. Figure 4 shows these N values plotted versus surfactant concentration. The adsorption isotherm of Figure 1, presented earlier, was constructed, using these N values and Equation 12. Finally Figure 5 shows F plotted versus surf-

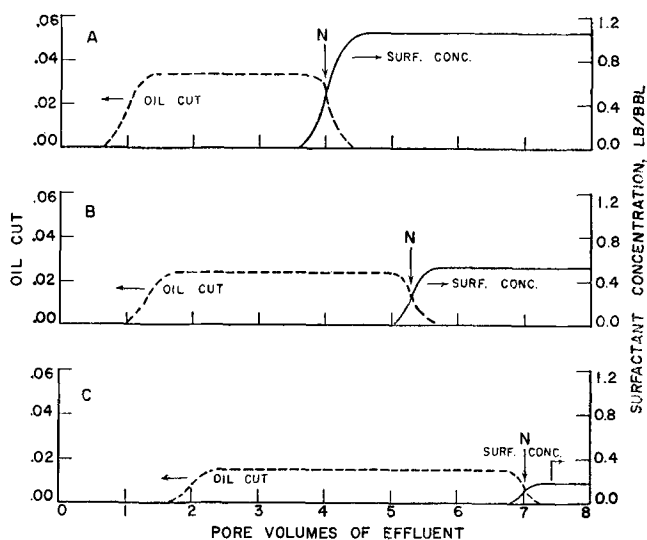


FIG. 3. Typical experimental data from which N and F can be obtained. A. Surfactant injected at a concentration of 1.05 lb./bbl. B. At 0.525 lb./bbl. C. At 0.175 lb./bbl.

TABLE I
(C , N , and F Values Taken from Figure 3)

C , ppb	N , pore vols.	F , pore vols.
1.05	4.0	0.100
0.525	5.8	0.099
0.175	7.0	0.075

actant concentration. The dotted portion of the curve is an extrapolation, which illustrates typical behavior of F at low concentrations.

A Sample Calculation

Having experimentally obtained $f(C)$, N , and F as functions of concentration, curves showing V_{max} and V_{min} as functions of concentration can be constructed, using Equations 7, 8, and 11. The slope of the adsorption isotherm, $f'(C)$, which is required in Equation 11, may be obtained graphically. If the isotherm is one of the common types, such as the Langmuir, the appropriate constants can be calculated and $f'(C)$ determined numerically. Figure 6 is a plot of V_{min} , and V_{max} for two possible situations. To complete the construction of Figure 6 we have assumed the limiting produced water-oil ratio (WOR_m) to be 100 barrels of water per barrel of

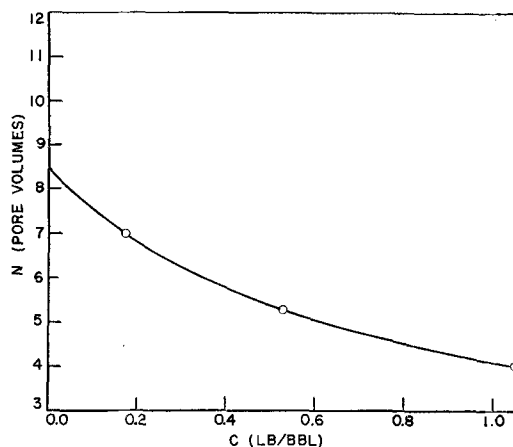


FIG. 4. Plot of N versus C based on data from Figure 3 (Table I). Circles represent the measured values.

oil, the sale price of the oil (D_o) to be \$2.50 per barrel, and the cost of surfactant (D_a) to be 25¢ per lb. Figure 6 shows that, under these conditions, when surfactant is injected after depletion by conventional water-flooding, V_{max} is never greater than V_{min} . This process falls short of economic feasibility. If surfactant is injected at the beginning of water flooding, V_{max} is greater than V_{min} at concentrations ranging between about 0.15 and 0.40 pound per barrel. If the concentration of the surfactant slug is within this range, additional oil should be recovered profitably. It is also obvious that an optimum slug

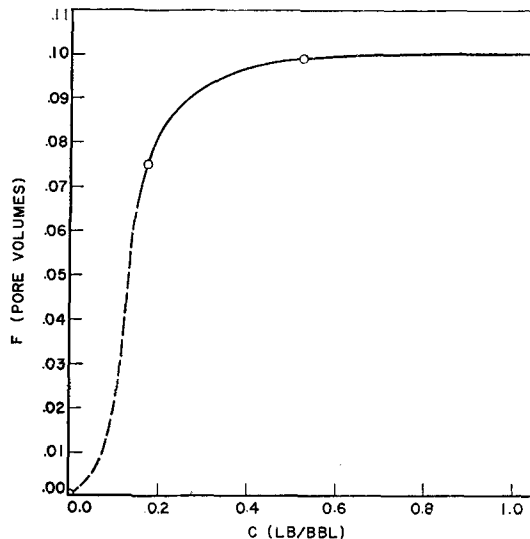


FIG. 5. Plot of F versus C based on data from Figure 3 (Table I). Circles represent the measured values.

concentration lies somewhere between 0.2 and 0.3 pound per barrel.

The method used in making these predictions is based upon well established chromatographic theory and upon experimental laboratory measurements on appropriate small samples of reservoir materials. A certain degree of confidence in the results is therefore justified. It must be admitted however that such predictions have not yet been tested in actual oil field practice.

Economic Limitations on Adsorption

Some idea of the nature and extent of adsorption which a surfactant may exhibit without exceeding economic limitations can be gained by considering average values for the important variables and the approximate ranges of values encountered in practice. Table II lists approximate ranges and averages for some of the variables. If the average values are substituted in Equation 8, it is seen that if N is higher than 7.5, the cost of injecting enough water to drive the surfactant zone through the reservoir

TABLE II
Estimated Ranges and Average Values of Some Variables Involved in Surfactant Flooding

Variable	Range	Average Value
F	0.05-0.20	0.10 pore volumes
C	0.20-1.00	0.35 lb./bbl.
WOR_m	25-100	50 dimensionless
D_o	2.00-4.00	3.00 \$/bbl.
D_a	0.20-0.50	0.30 \$/lb.

will be prohibitive. An N value of 4.5 would allow injection of 1.7 pore volumes of surfactant solution (V_{\max}). Now in order that V_{\min} be equal to or less than 1.7, the adsorption isotherm must be such that $f(C)/C - f'(C)$ is equal to or less than 1.7, where C is 0.35 pound per barrel. Rearrangement of Equation 12 shows that $f(C)/C$ is equal to $(N - 1)$ or 3.5. The slope of the isotherm must therefore be at least 1.8 where the concentration is 0.35 pound per barrel.

In addition, the best information available shows that the surface areas of porous sandstone reservoir rocks generally lie between 1 and 40 square meters per cubic centimeter of pore volume (6). However the surface areas available for adsorption of larger molecules like stearic acid (7) and methylene blue (8) are usually six or seven times smaller. An average value for the area available for surfactant adsorption might be close to 2 square meters per cubic centimeter of pore volume. Equation 12 gives 1.225 pounds for $f(C)$, the weight of surfactant adsorbed per barrel of pore space. If the surfactant molecular weight is 350 and N cannot be greater than 4.5, then adsorption on the average rock surface cannot be greater than one molecule per 117 square Angstrom units of surface area. This amounts to less than complete monolayer coverage for surfactants of this molecular weight. This raises a question as to the mechanism of oil release by surfactant. The process may well involve adsorption of surfactant in order to alter the wetting properties of the rock surface.

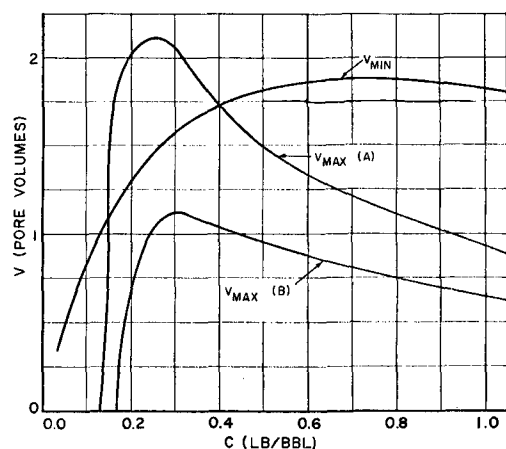


FIG. 6. Comparison of maximum economic slug volumes with the minimum effective slug volume, each shown as a function of surfactant concentration. (A) For surfactant injected at the beginning of water flooding. (B) For surfactant injected after prior depletion by conventional water flooding.

If so, can the surfactant do its work at coverages substantially less than a complete monolayer? In place of a direct answer, two facts can be mentioned. First, evidence is available showing that as little as 40% coverage is sufficient to cause large changes in

the wetting properties of some metal surfaces (9). Second, DeBruyn (10) has shown that only 5% of a monolayer of dodecylammonium acetate is sufficient fully to float quartz powder. Furthermore it should be kept in mind that the numbers used here for illustration are averages. A lower than average specific surface area, or a higher than average F or WOR_m , would all result in less stringent restrictions on adsorption.

Summary

The problem of placing surfactant flooding on an economic basis should be of interest to both the oil producer and the surfactant manufacturer. To oil producers it could mean an increase of as much as 6 billion barrels in the recoverable reserves of the United States alone. This figure is based on application in areas where conventional water flooding is at present economically feasible (1). To surfactant manufacturers it could mean a market for as much as 20 billion pounds which amounts to 10 years of sales at current rates (11). If the process were developed to the point that it could make water flooding attractive in areas where it is now technically, but not economically feasible, another 20 billion barrels of oil might be recovered and perhaps 30 billion pounds of surfactant utilized.

It is hoped that others interested in the problem of surfactant flooding will find the analysis and calculations presented here helpful. Adsorption has been emphasized because it is probably the most difficult of the many subsidiary problems involved. Those who have studied surfactant adsorption in relation to oil field flooding have consistently reported unfavorable results (4). Unfortunately not much is known about structural changes in surfactant molecules which might be used to control adsorption onto mineral surfaces. Neither is there much information available on the effective surface-areas of reservoir rocks with respect to adsorption of surfactant-size molecules. Both of these subjects require intensive study if surfactants are to be used successfully in water flooding.

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[Received September 26, 1956]