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OIL RECOVERY PROCESS BY MISCIBLE DISPLACEMENT

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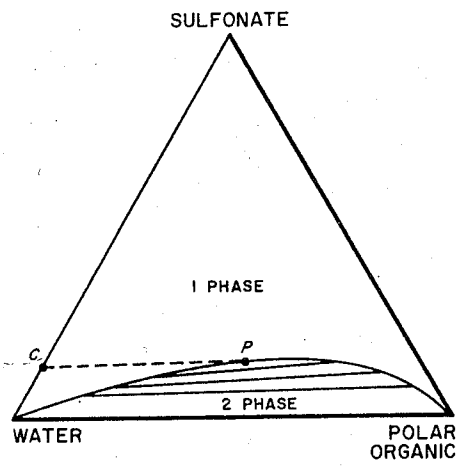


FIG. 1

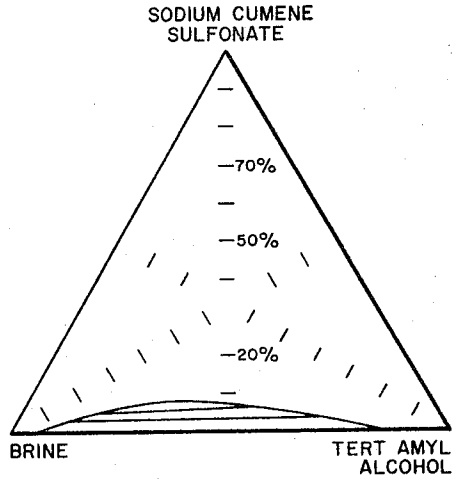


FIG. 2

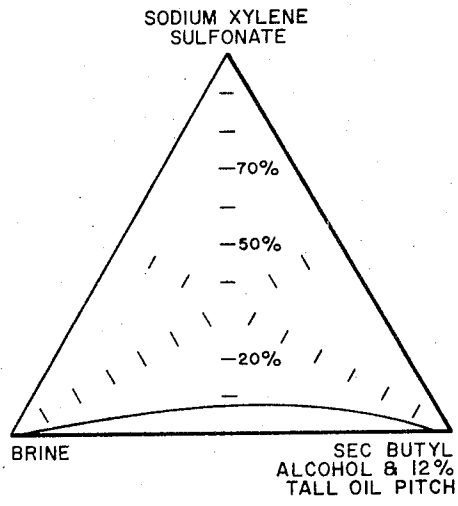


FIG. 3

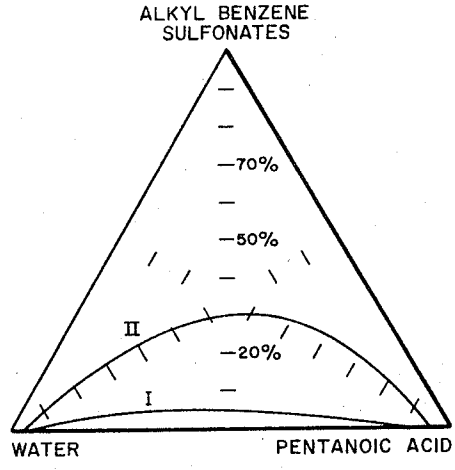


FIG. 4

ROBERT E. WILLIAMS
ROBERT C. AYERS, JR.
CLAUDE E. COOKE, JR. INVENTORS

BY Gary C. Honeycutt
ATTORNEY

United States Patent Office

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OIL RECOVERY PROCESS BY MISCIBLE DISPLACEMENT

Robert E. Williams, Robert C. Ayers, Jr., and Claude E. Cooke, Jr., Houston, Tex., assignors to Esso Production Research Company, a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

In the recovery of oil from a subsurface reservoir, a bank of polar organic solvent is injected into the reservoir followed by an aqueous detergent solution. The polar organic solvent and aqueous detergent solution are displaced into the reservoir by following flood water. The detergent employed in the aqueous detergent solution is an alkyl benzene sulfonate having one to seven alkyl carbon atoms. The volume of the injected solvent should be from about 3 to 20 percent of the flooded pore volume of the reservoir. The volume of the aqueous detergent solution injected should be about 3 percent to 20 percent of the flooded pore volume of the reservoir.

This invention relates to the recovery of oil from natural subsurface reservoirs. A method is provided for the miscible displacement of reservoir oil by injecting a bank of polar organic solvent into the reservoir, followed by injecting an aqueous solution of a low molecular weight aromatic sulfonate to displace the polar organic solvent and the oil toward one or more recovery wells.

It is generally recognized that a polar organic solvent can be readily selected which is completely miscible with crude petroleum, and that efficient recovery of the crude can be achieved by displacing such a solvent through a reservoir. It is also known, hypothetically, that if such a solvent were also miscible with water, it could be efficiently and economically displaced through a reservoir by the injection of ordinary flood water.

The concept of such an "ideal" solvent has remained hypothetical, at least for some crude oils. Recent efforts have therefore sought to provide at least two successively injected solvent banks: (1) a leading bank capable of miscibly displacing the reservoir crude, and (2) a solvent having mutual miscibility with both the leading bank and with water. For example, it has been proposed in the literature to inject a leading bank of n-amyl alcohol, selected because of its miscibility with petroleum, followed by a bank of ethyl alcohol, selected because of its miscibility with both n-amyl alcohol and with ordinary flood water. Such injection of two solvent banks would in fact permit the reservoir oil and each solvent bank to be miscibly displaced, if the process were applied to a substantially water-free reservoir, and if mixing of the solvents with the driving water were negligible. But the presence of substantial water saturations in most reservoirs, and especially in a previously waterflooded reservoir, leads to serious complications. For example, when injecting n-amyl alcohol followed by ethyl alcohol, followed by water, true miscible displacement of the n-amyl alcohol generally cannot occur because the ethyl alcohol, upon substantial dilution by water, is no longer sufficiently miscible with n-amyl alcohol.

On the other hand, if an alcohol having greater water solubility were selected to replace the n-amyl alcohol as a leading bank, in order to ensure its miscible displacement by ethyl alcohol, then water dilution of the leading bank would cause a loss of its ability to miscibly displace the reservoir oil. Perhaps if the amyl alcohol were followed by butyl alcohol, then by propyl alcohol, then by ethyl alcohol, and then by water, the reservoir oil and each alcohol bank would be miscibly displaced. However, economic considerations and mixing of the fluids in the reservoir limit the number of solvent banks that can be injected.

Prior attempts to achieve miscible displacement of the crude petroleum, followed by miscible displacement of each succeeding solvent bank, have generally contemplated true molecular dissolution of the displaced phase by the displacing medium. The present invention, however, overcomes the difficulties normally arising from dilution with reservoir water by the injection of a polar organic solvent which, in equilibrium with water, is capable of miscibly displacing the reservoir crude, followed by the injection of an aqueous solution of a low molecular weight sulfonated aromatic hydrocarbon capable of miscibly displacing the solvent bank by micellar solubilization or hydrotropy.

In accordance with a particular embodiment, the polar organic solvent injected in accordance with the invention contains a thickening agent. This embodiment is particularly useful when recovering a petroleum crude of greater viscosity than the polar organic solvent. A suitable thickening agent is selected from various natural and synthetic thickening compositions having a sufficient solubility in the polar organic bank to increase its viscosity. Any substantial increase in viscosity is beneficial; however, it is preferred to thicken the polar organic bank to a viscosity at least substantially equal to the viscosity of the reservoir oil. Examples of suitable thickened polar organic solvent banks include secondary butyl alcohol thickened with ethyl cellulose, tertiary amyl alcohol thickened with polyvinyl alcohol, tertiary octyl amine thickened with polyacrylic acid, and tertiary amyl alcohol thickened with polystyrene.

Other additives or auxiliary solvents may be blended with the polar organic bank. For example, about 5 percent to 30 percent by volume of carbon dioxide blended with an alcohol bank, or other polar organic solvent, is generally useful to increase the miscibility of the solvent with petroleum, and to reduce the cost of the solvent bank. Light hydrocarbons, such as toluene or LPG, are also useful for this purpose. The addition of tall oil pitch or other viscous bituminous or resinous substance to the polar organic bank is useful both to increase the viscosity of the bank and to increase its miscibility with oil.

In accordance with a further embodiment, the aqueous sulfonate solution injected in accordance with the invention contains a thickening agent. The use of a thickening agent in the aqueous sulfonate bank is generally useful when the mobility of the polar organic bank is less than the mobility of the sulfonate bank. (Mobility is the ratio of permeability to viscosity, and is a measure of the ease with which a fluid flows through a permeable formation.) Certain polar organic solvents have a viscosity greater than the viscosity of the typical sulfonate solutions to be injected for displacing the polar organic bank. In other instances, the polar organic bank will be more viscous than the sulfonate solution as a result of adding a thickener.

It is preferred to include a sufficient concentration of thickening agent to increase the viscosity of the sulfonate solution to a value at least substantially equal to the viscosity of the solvent bank. Suitable thickened sulfonate solutions include xylene sulfonate and a polysaccharide

polymer, xylene sulfonate and partially hydrolyzed polyacrylamide polymer, and a sulfonated light aromatic refinery stream thickened with a polysaccharide polymer.

It is also contemplated that a thickening agent will sometimes be desirable in the flood water injected to displace the sulfonate bank. Thus in some instances it may be desirable to thicken each of the various liquids injected in accordance with the invention, in order to provide a favorable mobility ratio between the reservoir oil and the solvent bank; between the solvent bank and the sulfonate bank; and between the sulfonate bank and the flood water subsequently injected to propel or displace the successive banks toward one or more recovery wells.

In accordance with a further embodiment, the mobility of the polar organic bank is reduced by the concurrent or intermittent injection of water or brine therewith. Similarly, the mobility of either the solvent bank or the sulfonate bank, or both, may be reduced by the concurrent or intermittent injection of an inert, immiscible gas.

FIGURE 1 is a ternary phase diagram illustrating the concentration of sulfonate in water required to obtain miscible displacement of a polar organic solvent bank.

FIGURE 2 is a ternary phase diagram for the tertiary amyl alcohol-brine-sodium cumene sulfonate system.

FIGURE 3 is a ternary phase diagram of a system comprising secondary butyl alcohol and tall oil pitch, brine, and sodium xylene sulfonate.

FIGURE 4 is a ternary phase diagram showing the two-phase envelopes of the pentanoic acid-water-alkyl benzene sulfonate system, and the pentanoic acid-brine-alkyl benzene sulfonate system.

The polar organic solvent injected in accordance with the invention is not mutually miscible with both water and the reservoir oil. The anhydrous solvent is completely miscible with most petroleum crudes, but has only a limited solubility in water; and is capable of dissolving only a limited amount of water. An essential characteristic of the solvent is its ability to retain substantial miscibility with petroleum, even when saturated with reservoir water. A limited amount of asphaltic material may be precipitated from the petroleum, but this occurrence is immaterial in the miscible displacement of the liquid petroleum hydrocarbons by the polar organic solvent.

Certain polar organic solvents which are initially miscible with petroleum, but which lose their abiltiy to miscibly displace the petroleum upon becoming at least partially saturated with reservoir water, can be modified to reduce the solubility of water therein, and thereby enable the solvent to retain a sufficient miscibility with the reservoir oil. For example, the addition of 20 percent toluene by weight to tertiary butyl alcohol has been found sufficient to produce a blend which retains its ability to miscibly displace reservoir oil in the presence of reservoir water, and which also retains its susceptibility of being miscibly displaced by aqueous sulfonate solutions.

It is also within the scope of the invention to inject a polar solvent which is substantially completely immiscible with water. Normal hexanol, for example, is less than 1 percent water-soluble but is far more readily solubilized by an aqueous detergent solution than is crude petroleum. A second essential characteristic of the solvent, in addition to its capability of miscibly displacing the reservoir hydrocarbons, is that it be more readily solubilized by an aqueous sulfonate solution than is the reservoir oil.

The flow behavior of a polar organic solvent bank in a porous, permeable reservoir, and the mechanism by which it miscibly displaces the reservoir oil has been the subject of several prior disclosures. Miscible displacement is generally recognized as a preferred mechanism of oil recovery, in order that on a pore volume basis much smaller, more economical banks of injected solution can be employed to obtain maximum oil recovery.

It has now been found that a polar organic solvent bank which is substantially immiscible or only partially miscible with water can itself be efficiently recovered, in a manner closely analogous to miscible displacement, by injecting an aqueous sulfonate solution, preferably followed by ordinary water or brine. The flow behavior and the mechanism by which the solvent is displaced resembles true miscible displacement. Components of the sulfonate bank may pass by mass transfer into the solvent phase, thereby increasing its volume, and components of the solvent phase may transfer into the sulfonate bank. In addition, some portions of residual solvent saturations will become mobilized because of a lowering of interfacial tension, whereby the solvent bank is driven ahead of the sulfonate solution. A substantial portion of the solvent bank is actually solubilized to form a water-continuous solution or microemulsion whereby the sulfonate solution and the solubilized solvent are transported through the reservoir at the same velocity, in a manner closely analogous to the flow behavior observed in the case of true molecular dissolution.

Suitable classes of polar organic solvents for use in accordance with the invention include the normal, secondary, tertiary, cyclo- and iso-alcohols having 4–16 carbon atoms per molecule; the normal, secondary, tertiary, cyclo- and iso-amines having 6–12 carbon atoms per molecule; phenol and substituted phenols having side chains with 1–10 carbon atoms per molecule; normal, secondary, tertiary, cyclo- and iso-mercaptans having 2–10 carbon atoms per molecule; fatty acids having 5–22 carbon atoms per molecule; ketones having 4–18 carbon atoms per molecule; ethers having 4–18 atoms per molecule; aldehydes having 4–18 carbon atoms per molecule; and mixtures of two or more of the above solvents. Each of these examples may contain saturated or unsaturated carbon-carbon bonds.

The polar organic solvent may be injected as a pure compound or as a crude mixture containing other oxygenated hydrocarbon products, or containing inert materials having no detrimental effect upon the ability of the solvent bank to displace the reservoir oil. For example, a suitable commercial source of oxygenated hydrocarbons, comprising a crude mixture of alcohols, ketones, acids and aldehydes may be obtained by the direct catalytic reaction of air or other oxygen-comprising gas with light paraffinic or olefinic hydrocarbons, such as a light petroleum distillate, in accordance with known procedures. The injected solvent may contain water or brine up to the limit of its solubility therein. Solvent recovered at production wells may be separated from the oil and reinjected elsewhere in the same reservoir, or in a separate reservoir.

The sulfonated aromatic hydrocarbon injected in aqueous solution to displace the polar solvent bank is selected from the group consisting of benzene sulfonic acid, naphthalene sulfonic acid, alkyl aryl sulfonic acids having 7–13 carbon atoms per molecule, and water-soluble salts of any of these acids, including mixtures of two or more of the acids or salts.

Preferred sulfonates are the alkyl benzene sulfonates having one to seven alkyl carbons per molecule. Specific examples include toluene sulfonate, cumene sulfonate, normal amyl benzene sulfonate, xylene sulfonate, tertiary and normal butyl benzene sulfonate, and butyl toluene sulfonate. Typically, these sulfonates are injected as alkali metal or ammonium salts; however, the sulfonic acids may be injected as such without neutralization. To some extent, the acids react with the reservoir rock to form salts in situ.

The short-chain alkyl benzene sulfonates are far superior to the well-known long-chain alkyl benzene sulfonates, primarily because of the solubility of their calcium and magnesium salts, and their much lower adsorptivity on reservoir rock or clay.

Also, the sulfonated hydrocarbons injected in accord-

ance with the invention are superior to other additives known to be useful for the purpose of solubilizing polar organic solvents in aqueous media. For example, they are compatible in aqueous solutions with polymeric thickeners used to improve the mobility ratio between the sulfonate bank and the solvent bank it displaces. Moreover, the phase diagram of the sulfonate-water-solvent system is substantially unaffected by the presence of the polymer.

The concentration of hydrocarbon sulfonate or of mixed sulfonates useful in accordance with the present invention lies in the range of about 2 percent by weight up to about 40 percent by weight, preferably from 5 percent to 25 percent by weight, based on the total weight of the injected sulfonate solution. It will be apparent that these concentrations are greater than the concentrations generally proposed in the prior art for the use of sulfonates as waterflood additives for oil recovery. The greater concentrations are essential in accordance with the present invention since the present displacement mechanism involves a solubilization of the solvent in water, to achieve miscible displacement, whereas the typical prior use of sulfonates has been to lower interfacial tension without achieving solubilization or miscible displacement.

Specific examples of suitable polar organic solvents to be injected in accordance with the invention include normal amyl alcohol, tertiary amyl alcohol, normal, secondary, or iso-butyl alcohols, valeric acid, hexanoic acid, or mixtures thereof. In selecting specific mixtures of solvents it is frequently desirable to adjust the density of the blend to substantially equal the density of the reservoir oil.

In FIGURE 1 the phase diagram of a hypothetical water-sulfonate-polar organic solvent system is shown. It can be demonstrated that a bank of the polar solvent will be miscibly displaced by the injection of an aqueous sulfonate solution having a concentration of sulfonate greater than that concentration represented by the point C in the phase diagram. The point C is defined by the intersection of a line with the water-sulfonate side of the diagram, drawn tangent to the two-phase envelope at the plait point P. The sulfonate concentration at point C is referred to herein as the minimum miscibility concentration.

Note that miscibility in all proportions between the aqueous sulfonate solution and the polar organic solvent is not a prerequisite to miscible displacement of the solvent. That is, a straight line connecting point C with the solvent vertex will usually cut across the two-phase envelope. Therefore, initial mixing of the sulfonate solution with solvent produces a two-phase composition. Further mixing, however, builds a transition zone miscible with both the sulfonate solution and the solvent, which permits true miscible displacement.

In the system represented by FIGURE 2, the brine contains about 2.3 percent sodium chloride, about 0.3 percent calcium chloride dihydrate, about 0.2 percent magnesium chloride hexahydrate, and minor amounts of other salts. As seen from the diagram, a saturated solution of brine in tertiary amyl alcohol contains only about 18 percent brine; and a saturated solution of the alcohol in brine contains only about 8 percent alcohol. But in the presence of about 8.3 percent sodium cumene sulfonate, the alcohol and brine become miscible in all proportions.

As noted earlier, however, complete miscibility is not a prerequisite to miscible displacement. The minimum concentration of sulfonate required to achieve miscible displacement of the alcohol by the brine is determined by the point at which a line intersects the brine-sulfonate base of the diagram, drawn tangent to the plait point of the two-phase envelope.

As indicated by the tie lines which dip toward the brine vertex of the diagram, the plait point of this particular envelope lies somewhat to the left of the peak which corresponds to maximum sulfonate concentration. Accordingly, the tangent line will intersect the brine-sulfonate base of the diagram at a point corresponding to substantially less than 8 percent sulfonate. In practicing the invention, however, it is generally desirable to inject a brine containing substantially more than the minimum concentration of sulfonate, in order to avoid the likelihood that dilution in situ may lower the sulfonate concentration below the minimum required to achieve miscible displacement.

In the system of FIGURE 3, the brine is the same as that represented in FIGURE 2. As indicated by the diagram, the brine and polar organic phases have substantially less mutual solubility than the corresponding phases of the system of FIGURE 2. As before, however, no more than about 8.5 percent sulfonate is required to promote total miscibility between the aqueous and organic phases. An even smaller concentration of sulfonate would be required to achieve miscible displacement, depending of course upon the exact location of the plait point as readily determinable by routine experimentation.

In the system of FIGURE 4, the effect of salt is demonstrated by comparing the two-phase envelope of a distilled water-sulfonate-pentanoic acid system (Curve I) with that of a brine-sulfonate-pentanoic acid system (Curve II), wherein the aqueous phase contains about 9.1 percent sodium chloride, about 1.1 percent calcium chloride dihydrate, about 0.09 percent magnesium chloride hexahydrate, and minor amounts of other salts. It is apparent that the salt greatly increases the amount of sulfonate required to achieved total miscibility between the aqueous and organic phases. Also, the salt greatly reduces the solubility of water in the pentanoic acid, but has substantially no effect upon the solubility of pentanoic acid in the aqueous phase.

It does not necessarily follow, however, that the amount of sulfonate required to achieve miscible displacement would be less for distilled water than for dilute brine. As seen from FIGURE 2, the plait point of a brine system falls to the left of the two-phase envelope peak, which in some instances may reduce the minimum sulfonate requirement for dilute brine compared to that of distilled water.

In each of the above systems represented by FIGURES 1 through 4, sulfonate concentrations above 25–30 percent by weight may tend to cause the formation of gels. No effort has been made to indicate the exact location of a gel envelope on the diagram, since that aspect of the system has no direct bearing upon the essential concepts of the present invention. However, it is generally advisable to test a proposed sulfonate solution, in contact with the polar organic solvent, prior to injection to determine its suitability as a displacing medium. A viscosity in excess of 100 cps., for example, is considered too great for most flooding operations, due to reduced injectivities at the input wells and the consequently excessive periods of time required to complete recovery of the oil and the polar organic bank. Preferably, the injected solutions have a viscosity no greater than 50 cps., and ordinarily no greater than 10 cps. at the temperature of injection.

It has been found convenient to approximate the phase behavior of the above systems in a ternary diagram, even though four or more components may be present. For example, in FIGURE 2 the brine contains a significant amount of sodium chloride, which is a fourth component of the system. This representation is exact only when the ratio of dissolved salt to water is the same in both phases of any two-phase composition. The error introduced by this assumption is relatively slight, however, and can readily be tolerated in preference to the complexity of a three-dimensional four-component phase model.

Water-solubility of the calcium and magnesium salts of the sulfonates injected in accordance with the invention is essential to provide compatibility with typical brines that occur naturally in most petroleum reservoirs. This compatibility was demonstrated by adding sodium amyl ben-

zene sulfonate and sodium octyl benzene sulfonate to separate portions of a brine containing the following dissolved ions:

TABLE I

Ion:	Concentration, p.p.m.
Na^+	25,970
Ca^{++}	2,972
Mg^{++}	1,061
Ba^{++}	111
Cl^-	63,825
HCO_3^-	102

The amyl benzene sulfonate dissolved readily to form a clear solution containing at least 5 percent sulfonate by weight, whereas the octyl benzene sulfonate did not dissolve.

Table II demonstrates the effectiveness of various hydrocarbon sulfonates to promote total miscibility between tertiary amyl alcohol (TAA) and distilled water. The indicated concentrations of sulfonate in percentages by weight were required to mutually solubilize equal weights of tertiary amyl alcohol and water.

TABLE II

Alkyl benzene sulfonate:	Concentration required to cause miscibility, percent
i-Propyl	3.4
t-Butyl	2.6
n-Butyl	2.3
n-Amyl	2.2
Dodecyl	2.5

It is therefore seen that the low molecular weight sulfonates of the invention are substantially equally as effective as the dodecyl benzene sulfonate in their ability to solubilize a polar organic solvent in water. Since the calcium and magnesium salts of dodecyl benzene sulfonate are insoluble in water, and since the dodecyl benzene sulfonates are strongly adsorbed on reservoir rocks and clays, the sulfonates of the invention are clearly superior for use in displacing a polar organic solvent bank through a reservoir.

The invention is further illustrated by the following example.

Example I

A petroleum reservoir is waterflooded to a residual crude oil saturation of about 30 percent of the reservoir pore volume. In accordance with the present invention, tertiary amyl alcohol is then injected at a selected number of input wells in an amount corresponding to 5 percent of the total reservoir pore volume. Thereafter, at the same input wells, an aqueous solution is injected comprising 15 percent sodium xylene sulfonate and 5 percent dissolved inorganic salts, by weight. The total amount of injected sulfonate solution corresponds to 5 percent of the reservoir pore volume. Thereafter, a 30 percent pore volume bank of thickened water is injected through the same input wells, containing 0.05 percent by weight of partially hydrolyzed polyacrylamide. The thickened water bank is then followed by water or brine until a total of about 1.2 pore volumes of cumulative flooding medium is injected, beginning with the tertiary amyl alcohol. Recovery of reservoir oil and tertiary amyl alcohol is essentially complete, from the sections of the reservoir contacted by the injected fluids, indicating miscible displacement of each.

In the practice of this invention the volume of injected solvent should be from about 3 percent to 20 percent of the flooded pore volume of the reservoir. The volume of the aqueous sulfonate solution injected should be about 3 percent to 20 percent of the flooded pore volume of the reservoir.

What is claimed is:

1. A method for the recovery of oil from a subsurface reservoir which comprises:
   (a) injecting a polar organic solvent into the reservoir, the volume of polar organic solvent being at least 3 percent of the pore volume of the reservoir to be flooded;
   (b) injecting into the reservoir an aqueous solution containing a sulfonated alkyl benzene having one to to seven alkyl carbon atoms, the volume of the aqueous solution being at least 3 percent of the pore volume of the reservoir to be flooded;
   (c) displacing the polar organic solvent and aqueous solution into the reservoir; and
   (d) recovering displacing oil from the reservoir.

2. A method as defined in a claim 1 wherein the polar organic solvent in equilibrium with water is capable of miscibly displacing the reservoir oil and the aqueous solution is capable of miscibly displacing the polar organic solvent.

3. A method as defined in claim 1 wherein the polar organic solvent is preceded by a light hydrocarbon comprising solvent, miscible with the reservoir oil.

4. A method as defined in claim 1 wherein the polar organic solvent is injected into the reservoir followed by injection of the aqueous solution, and the polar organic solvent and aqueous solution are displaced into the reservoir by injection of flood water.

5. A method as defined in claim 1 wherein the sulfonated alkyl benzene is an alkyl benzene sulfonic acid.

6. A method as defined in claim 1 wherein the sulfonated alkyl benzene is an alkyl benzene sulfonate.

7. A method as defined in claim 6 wherein the alkyl benzene sulfonate is xylene sulfonate.

8. A method as defined in claim 7 wherein the polar organic solvent is tertiary amyl alcohol.

9. A method as defined in claim 7 wherein the polar organic solvent is tertiary butyl alcohol.

10. A method as defined in claim 7 wherein the injection of the sulfonate solution is followed by the injection of thickened water.

11. A method as defined by claim 7 wherein polar organic solvent contains a thickening agent.

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STEPHEN J. NOVOSAD, *Primary Examiner.*