



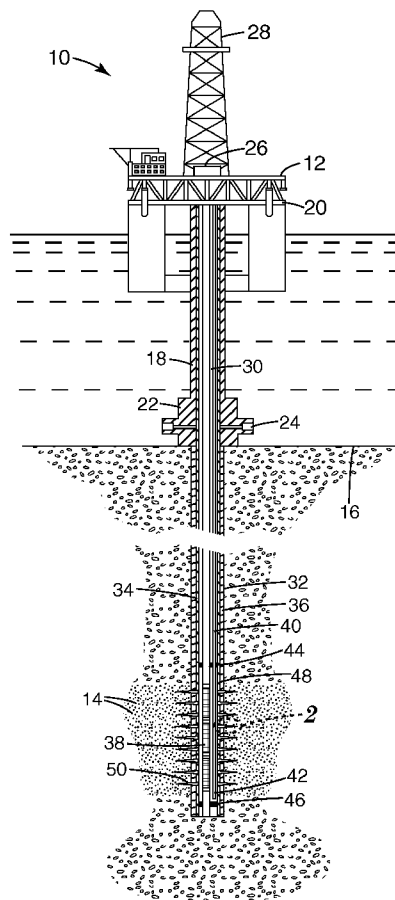
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(19) **United States**(12) **Patent Application Publication****Pope et al.**(10) **Pub. No.: US 2010/0181068 A1**(43) **Pub. Date: Jul. 22, 2010**(54) **METHOD AND SYSTEM FOR TREATING
HYDROCARBON FORMATIONS****Related U.S. Application Data**

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(75) Inventors: **Gary A. Pope**, Austin, TX (US);
Jimmie R. Baran, Jr., Prescott, WI
(US); **Vishal Bang**, Houston, TX
(US); **Mukal M. Sharma**, Austin,
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CHALKER FLORES, LLP
2711 LBJ FRWY, Suite 1036
DALLAS, TX 75234 (US)(57) **ABSTRACT**

The present invention includes compositions and methods for treating a hydrocarbon-bearing formation having brine and at least one temperature, wherein the brine has at least one first composition by obtaining first compatibility information for a first model brine and a first treatment composition at a model temperature, wherein the first model brine has a composition selected at least partially based on the first brine composition, wherein the model temperature is selected at least partially based on the formation temperature, and wherein the first treatment composition comprises at least one first surfactant and at least one first solvent; based at least partially on the first compatibility information, selecting a treatment method for the hydrocarbon-bearing formation, and treating the hydrocarbon-bearing formation with the selected treatment method.

(73) Assignees: **BOARD OF REGENTS, THE
UNIVERSITY OF TEXAS
SYSTEM**, Austin, TX (US); **3M
INNOVATION PROPERTIES
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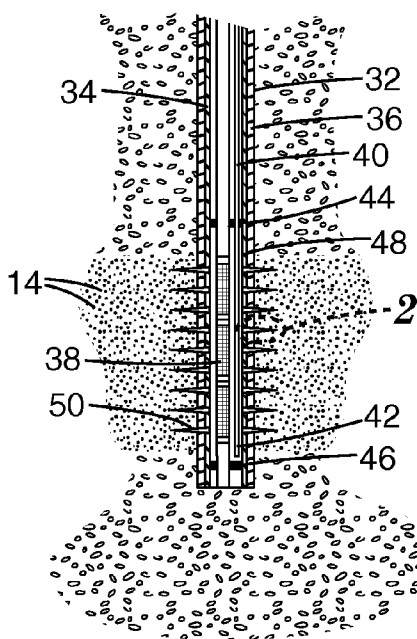
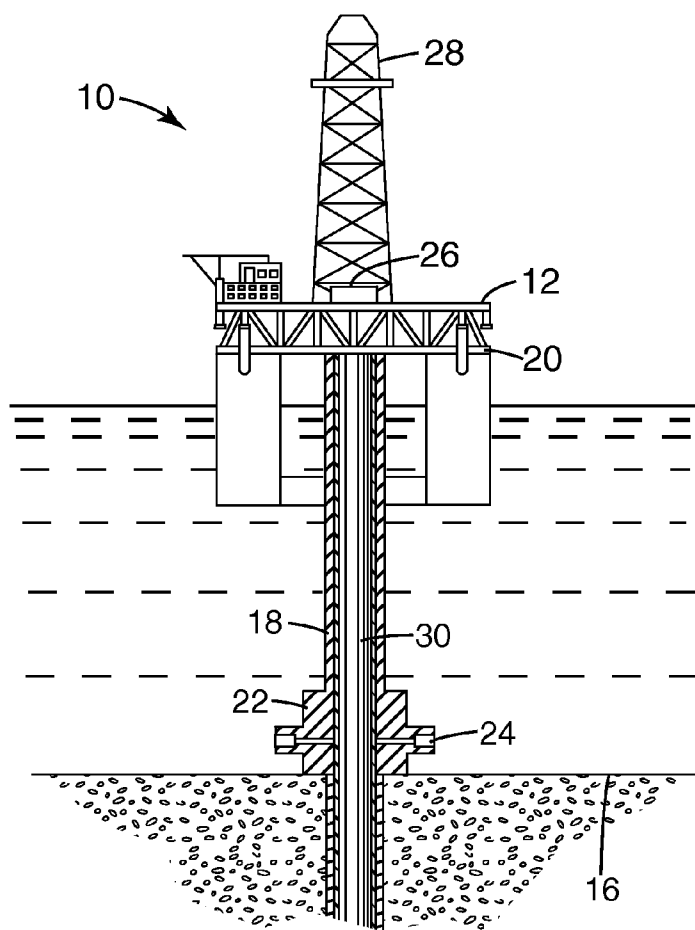


Fig. 1

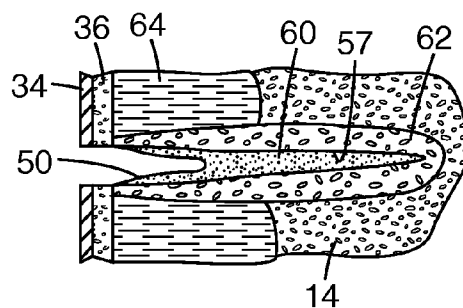


Fig. 2

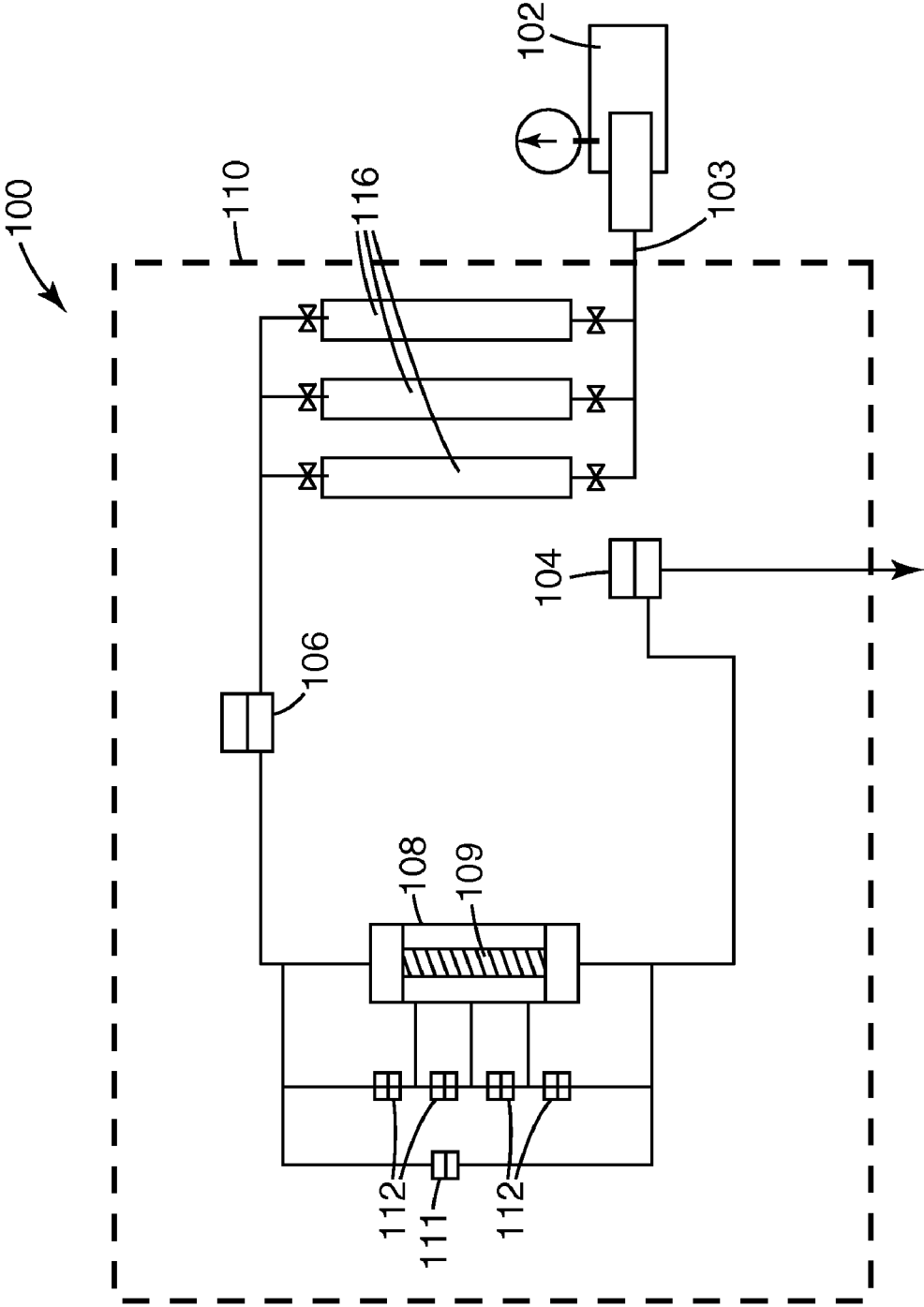


Fig. 3

METHOD AND SYSTEM FOR TREATING HYDROCARBON FORMATIONS

BACKGROUND OF THE INVENTION

[0001] It is known in the subterranean well drilling art that in some wells (e.g., some oil and/or gas wells) brine is present in hydrocarbon-bearing geological formations in the vicinity of the wellbore (also known in the art as the “near wellbore region”). The brine may be naturally occurring (e.g., connate water) and/or may be a result of operations conducted on the well.

[0002] In the case of some wells (e.g., some gas wells), liquid hydrocarbons (also known in the art as “condensate”) can form and accumulate in the near wellbore region. The presence of condensate can cause a large decrease in both the gas and condensate relative permeabilities, and thus the productivity of the well decreases.

[0003] The presence of brine and/or gas condensate in a near wellbore region of a hydrocarbon-bearing geological formation can inhibit or stop production of hydrocarbons from the well, and hence is typically undesirable.

[0004] Various approaches have been tried for increasing the hydrocarbon production of such wells. One approach, for example, involves a fracturing and propping operation (e.g., prior to, or simultaneously with, a gravel packing operation) to increase the permeability of the hydrocarbon-bearing geological formation adjacent to the wellbore. Chemical treatments (e.g., injection of methanol) have also been used to improve productivity of such oil and/or gas wells. The latter treatments are typically injected into the near wellbore region of a hydrocarbon-bearing geological formation where they interact with the brine and/or condensate to displace and/or dissolve it, thereby facilitating increased hydrocarbon production from the well.

[0005] Conventional treatments for increasing the hydrocarbon production from wells having brine and/or condensate in the near wellbore region of a hydrocarbon-bearing geological formation, however, are often relatively short-lived, and require expensive and time-consuming retreatment.

[0006] Identifying useful chemical treatments and methods that will be effective for increasing hydrocarbon productivity and be durable remains a problem, especially since well conditions such as temperature, brine content and brine composition may vary between wells and/or may even vary over time within a given well.

SUMMARY OF THE INVENTION

[0007] In one aspect, the present invention provides a method of treating a hydrocarbon-bearing formation having brine and at least one temperature, wherein the brine has at least one first composition, the method comprising:

[0008] obtaining first compatibility information for a first model brine and a first treatment composition at a model temperature, wherein the first model brine has a composition selected at least partially based on the first brine composition, wherein the model temperature is selected at least partially based on the formation temperature, and wherein the first treatment composition comprises at least one first surfactant and at least one first solvent;

[0009] based at least partially on the first compatibility information, selecting a treatment method for the hydro-

carbon-bearing formation, wherein the treatment method is Method I or Method II,

[0010] wherein Method I comprises:

[0011] contacting the hydrocarbon-bearing formation with a fluid, wherein the fluid at least one of at least partially solubilizes or at least partially displaces the brine in the hydrocarbon-bearing formation; and

[0012] subsequently contacting the hydrocarbon-bearing formation with the first treatment composition;

[0013] and wherein Method II comprises:

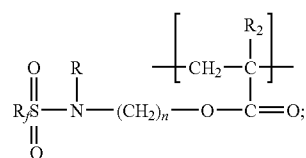
[0014] contacting the hydrocarbon-bearing formation with a second treatment composition, the second treatment composition comprising at least one second surfactant and at least one second solvent, with the proviso that after obtaining the first compatibility information, the hydrocarbon-bearing formation is not contacted with a fluid that at least one of at least partially solubilizes or at least partially displaces the brine in the hydrocarbon-bearing formation prior to contacting the hydrocarbon-bearing formation with the second treatment composition; and

[0015] treating the hydrocarbon-bearing formation with the selected treatment method.

[0016] In some embodiments, the first compatibility information indicates that the first model brine and the first treatment composition are at least partially incompatible. In some embodiments, the compatibility information indicates that the first model brine and the first treatment composition are compatible, and wherein the second treatment composition has the same composition as the first treatment composition. In some embodiments, the first compatibility information comprises information concerning the phase stability of a mixture of the first model brine and the first treatment composition. In some embodiments, the compatibility information comprises information concerning salt precipitation from a mixture of the first model brine and the first treatment composition. In some embodiments, the at least one of the first surfactant or the second surfactant is a nonionic fluorinated polymeric surfactant.

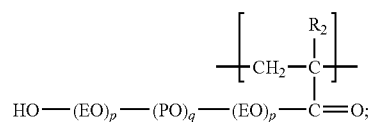
[0017] In some embodiments, the surfactant is a nonionic fluorinated polymeric surfactant comprises:

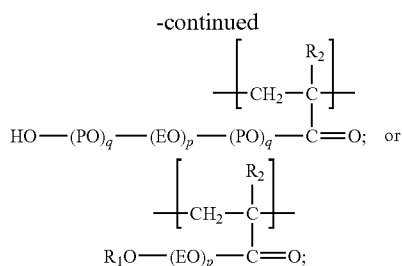
[0018] at least one divalent unit represented by formula:



and

[0019] at least one divalent unit represented by formula:





[0020] wherein

[0021] R_f represents a perfluoroalkyl group having from 1 to 8 carbon atoms;

[0022] R , R_1 , and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

[0023] n is an integer from 2 to 10;

[0024] EO represents $-\text{CH}_2\text{CH}_2\text{O}-$;

[0025] each PO independently represents $-\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-$ or $-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-$;

[0026] each p is independently an integer of from 1 to about 128; and

[0027] each q is independently an integer of from 0 to about 55.

[0028] In some embodiments, the fluid is essentially free of surfactant. In some embodiments, the fluid comprises at least one of toluene, diesel, heptane, octane, or condensate. In some embodiments, the fluid comprises at least one of a polyol or polyol ether, wherein the polyol and polyol ether independently have from 2 to 25 carbon atoms. In some embodiments, the polyol or polyol ether is at least one of 2-butoxyethanol, ethylene glycol, propylene glycol, polypropylene glycol, 1,3-propanediol, 1,8-octanediol, diethylene glycol monomethyl ether, ethylene glycol monobutyl ether, or dipropylene glycol monomethyl ether. In some embodiments, the fluid further comprises at least one monohydroxy alcohol, ether, or ketone independently having from 1 to 4 carbon atoms. In some embodiments, the fluid comprises at least one of water, methanol, ethanol, or isopropanol. In some embodiments, the fluid comprises at least one of nitrogen, carbon dioxide, or methane. In some embodiments, the at least one of the first solvent or the second solvent comprises at least one of a polyol or polyol ether, wherein the polyol and polyol ether independently have from 2 to 25 carbon atoms; and wherein the solvent comprises at least one of monohydroxy alcohol, ether, or ketone independently having from 1 to 4 carbon atoms. In some embodiments, the hydrocarbon bearing formation is clastic or nonclastic. In some embodiments, the first compatibility information is represented in a contour map that can pictorially depict the phase behavior relationships between system variables (e.g., temperature, solvent composition, and brine concentration).

[0029] In some embodiments, after the fluid contacts the hydrocarbon-bearing formation and before the first treatment composition contacts the hydrocarbon-bearing formation, the formation has a second brine composition, and Method I further comprises:

[0030] obtaining second compatibility information for a second model brine and the first treatment composition at the model temperature, wherein the second model brine has a composition selected at least partially based on the second brine composition, and wherein the sec-

ond compatibility information indicates that the first treatment composition and the second model brine are compatible.

[0031] In one aspect, the present invention provides a method of treating a hydrocarbon-bearing formation having brine and at least one temperature, wherein the brine has at least one first composition, the method comprising:

[0032] obtaining first compatibility information for a first model brine and a treatment composition at a model temperature, wherein the first model brine has a composition selected at least partially based on the first brine composition, wherein the model temperature is selected at least partially based on the formation temperature, wherein the treatment composition comprises at least one surfactant and at least one solvent, and wherein the first compatibility information indicates that the treatment composition and the first model brine are at least partially incompatible;

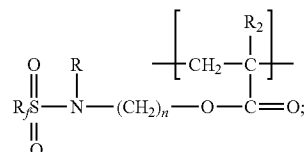
[0033] contacting the hydrocarbon-bearing formation with a fluid, wherein the fluid at least one of at least partially solubilizes or at least partially displaces the brine in the hydrocarbon-bearing formation, and wherein after the fluid contacts the hydrocarbon-bearing formation, the formation has a second brine composition;

[0034] obtaining second compatibility information for a second model brine and the treatment composition at the model temperature, wherein the second model brine has a composition selected at least partially based on the second brine composition, and wherein the second compatibility information indicates that the treatment composition and the second model brine are compatible; and

[0035] after obtaining the second compatibility information, contacting the hydrocarbon-bearing formation with the treatment composition.

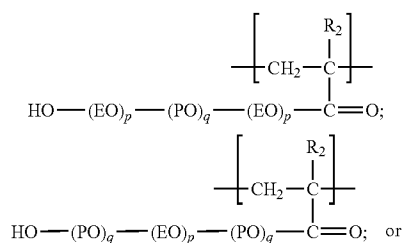
[0036] In one embodiment, the surfactant is a nonionic fluorinated polymeric surfactant, comprising:

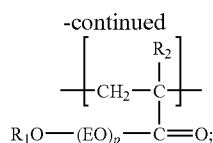
[0037] at least one divalent unit represented by formula:



and

[0038] at least one divalent unit represented by formula:





[0039] wherein

[0040] R_f represents a perfluoroalkyl group having from 1 to 8 carbon atoms;

[0041] R , R_1 , and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

[0042] n is an integer from 2 to 10;

[0043] EO represents $\text{---CH}_2\text{CH}_2\text{O---}$;

[0044] each PO independently represents $\text{---CH}(\text{CH}_3)\text{CH}_2\text{O---}$ or $\text{---CH}_2\text{CH}(\text{CH}_3)\text{O---}$;

[0045] each p is independently an integer of from 1 to about 128; and

[0046] each q is independently an integer of from 0 to about 55.

BRIEF DESCRIPTION OF THE DRAWINGS

[0047] For a more complete understanding of the features and advantages of the present invention, reference is now made to the detailed description of the invention along with the accompanying figures and in which:

[0048] FIG. 1 is a schematic illustration of an exemplary embodiment of an offshore oil and gas platform operating an apparatus for treating a near wellbore region according to the present invention,

[0049] FIG. 2 shows the near wellbore region with a fracture in greater detail (for those embodiments related to a fractured formation); and

[0050] FIG. 3 is a schematic illustration of the core flood set-up to testing cores samples and other materials using the compositions and methods of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0051] While the making and using of various embodiments of the present invention are discussed in detail below, it should be appreciated that the present invention provides many applicable inventive concepts that can be embodied in a wide variety of specific contexts. The specific embodiments discussed herein are merely illustrative of specific ways to make and use the invention and do not delimit the scope of the invention.

[0052] To facilitate the understanding of this invention, a number of terms are defined below. Terms defined herein have meanings as commonly understood by a person of ordinary skill in the areas relevant to the present invention. Terms such as “a”, “an” and “the” are not intended to refer to only a singular entity, but include the general class of which a specific example may be used for illustration. The terminology herein is used to describe specific embodiments of the invention, but their usage does not delimit the invention, except as outlined in the claims. The following definitions of terms apply throughout the specification and claims.

[0053] The term “brine” refers to water having at least one dissolved electrolyte salt therein (e.g., having any nonzero concentration, and which may be less than 1000 parts per million by weight (ppm), or greater than 1000 ppm, greater than 10,000 ppm, greater than 20,000 ppm, 30,000 ppm,

40,000 ppm, 50,000 ppm, 100,000 ppm, 150,000 ppm, or even greater than 200,000 ppm).

[0054] The term “downhole conditions” refers to the temperature, pressure, humidity, and other conditions that are commonly found in subterranean formations.

[0055] The term “brine composition” refers to the types of dissolved electrolytes and their concentrations in brine.

[0056] The term “homogeneous” means macroscopically uniform throughout and not prone to spontaneous macroscopic phase separation.

[0057] The term “hydrocarbon-bearing formation” includes both hydrocarbon-bearing formations in the field (i.e., subterranean hydrocarbon-bearing formations) and portions of such hydrocarbon-bearing formations (e.g., core samples).

[0058] The term “fracture” refers to a fracture that is man-made. In the field, for example, fractures are typically made by injecting a fracturing fluid into a subterranean geological formation at a rate and pressure sufficient to open a fracture therein (i.e., exceeding the rock strength).

[0059] The term “hydrolyzable silane group” refers to a group having at least one Si---O---Z moiety that undergoes hydrolysis with water at a pH between about 2 and about 12, wherein Z is H or substituted or unsubstituted alkyl or aryl.

[0060] The term “nonionic” refers to being free of ionic groups (e.g., salts) or groups (e.g., $\text{---CO}_2\text{H}$, $\text{---SO}_3\text{H}$, $\text{---OSO}_3\text{H}$, ---P(=O)(OH)_2) that are readily substantially ionized in water.

[0061] The term “normal boiling point” refers to the boiling point at a pressure of one atmosphere (100 kPa).

[0062] The term “polymer” refers to a molecule of molecular weight of at least 1000 grams/mole, the structure of which includes the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.

[0063] The term “polymeric” refers to including a polymer.

[0064] The term “solvent” refers to a homogenous liquid material (inclusive of any water with which it may be combined) that is capable of at least partially dissolving the non-ionic fluorinated polymeric surfactant(s) with which it is combined at 25° C.

[0065] The term “water-miscible” means soluble in water in all proportions.

[0066] The term “compatibility information” refers to information concerning the phase stability of a solution or dispersion.

[0067] The term “productivity” and “productivity information” as applied to a well refers to the capacity of a well to produce hydrocarbons; that is, the ratio of the hydrocarbon flow rate to the pressure drop, where the pressure drop is the difference between the average reservoir pressure and the flowing bottom hole well pressure (i.e., flow per unit of driving force).

[0068] The term “cloud point” of a surfactant refers to the temperature at which a nonionic surfactant becomes non-homogeneous in water. This temperature can depend on many variables (e.g., surfactant concentration, solvent concentration, solvent composition, water concentration, electrolyte composition and concentration, oil phase concentration and composition, and the presence of other surfactants).

[0069] As used herein, the term “substantially free of precipitated salt” refers to the amount of salts found in water under downhole conditions that precipitates. In one example, substantially free of precipitated salt is an amount of salt that is the less than 5% higher than the solubility product at a given

temperature and pressure. In another example, a formation becomes substantially free of precipitated salt when the amount of salt in the formation has been reduced, dissolved or displaced such that the salts do not interfere with the interaction (e.g., adsorption) of the nonionic fluorinated polymeric surfactant with the formation.

[0070] As used herein, the term “essentially free of surfactant” refers to fluid that may have a surfactant in an amount insufficient for the fluid to have a cloud point, e.g., when it is below its critical micelle concentration. A fluid that is essentially free of surfactant may be a fluid that has a surfactant but in an amount insufficient to alter the wettability of, e.g., a hydrocarbon-bearing formation under downhole conditions. A fluid that is essentially free of surfactant includes those that have a weight percent of surfactant as low as 0 weight percent.

[0071] The present invention includes the use of compatibility information to determine compositions and methods for removing water from the near-wellbore portion of a hydrocarbon-bearing formation and penetrated by a wellbore, and more particularly, to the use of treatment compositions to improve well productivity. Examples of formations that may be treated using the present invention include dry gas reservoirs, wet gas reservoirs, retrograde condensate gas reservoirs, tight gas reservoirs, gas storage reservoirs and combinations thereof.

[0072] Examples of surfactants that may be useful in methods according to the present invention include anionic surfactants, cationic surfactants, nonionic surfactants, amphoteric surfactants (e.g., zwitterionic surfactants), and combinations thereof. Many of each type of surfactant are widely available to one skilled in the art. These include fluorochemical, silicone and hydrocarbon-based surfactants. One of skill in the art, in light of the present disclosure, will recognize that the selection of surfactants will depend in the nature of the formation (clastic versus non-clastic) as well as other surfactants. Useful surfactants that may be used to treat clastic formations may include cationic, anionic, nonionic, amphoteric (e.g., zwitterionic surfactants). Non-clastic formations may be treated with anionic, amphoteric (e.g., zwitterionic surfactants).

[0073] Examples of useful anionic surfactants include alkali metal and (alkyl)ammonium salts of: alkyl sulfates and sulfonates such as sodium dodecyl sulfate and potassium dodecanesulfonate; sulfates of polyethoxylated derivatives of straight or branched chain aliphatic alcohols and carboxylic acids; alkylbenzenesulfonates, alkyl naphthalenesulfonates and sulfates (e.g., sodium laurylbenzenesulfonate); ethoxylated and polyethoxylated alkyl and aralkyl alcohol carboxylates; glycinate (e.g., alkyl sarcosinate and alkyl glycinate); sulfosuccinates including dialkyl sulfosuccinates; isethionate derivatives; N-acyltaurine derivatives (e.g., sodium N-methyl-N-oleyl taurate); and alkyl phosphate mono- or di-esters (e.g., ethoxylated dodecyl alcohol phosphate ester, sodium salt).

[0074] Examples of useful cationic surfactants include: alkylammonium salts having the formula $C_rH_{2r+1}N(CH_3)_3X$, where X is, e.g., OH, Cl, Br, HSO_4 or a combination of OH and Cl, and where r is an integer from 8 to 22, and the formula $C_sH_{s+1}N(C_2H_5)_3X$, where s is an integer from 12 to 18; gemini surfactants, for example, those having the formula: $[C_{16}H_{33}N(CH_3)_2C_4H_{2t+1}]_2X$, wherein t is an integer from 2 to 12 and X is, e.g., OH, Cl, Br, HSO_4 or a combination of OH and Cl; aralkylammonium salts (e.g., benzalkonium salts);

and cetyethylpiperidinium salts, for example, $C_{16}H_{33}N(C_2H_5)(C_5H_{10})X$, wherein X is, e.g., OH, Cl, Br, HSO_4 or a combination of OH and Cl.

[0075] Examples of useful amphoteric surfactants include alkyl dimethyl amine oxides, alkylcarboxamidoalkylenedimethyl amine oxides, aminopropionates, sulfobetaines, alkyl betaines, alkylamidobetaines, dihydroxyethyl glycinate, imidazoline acetates, imidazoline propionates, ammonium carboxylate and ammonium sulfonate amphoterics and imidazoline sulfonates.

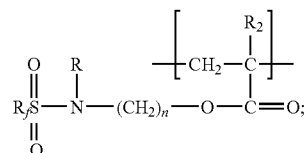
[0076] Examples of useful hydrocarbon nonionic surfactants include polyoxyethylene alkyl ethers, polyoxyethylene alkyl-phenyl ethers, polyoxyethylene acyl esters, sorbitan fatty acid esters, polyoxyethylene alkylamines, polyoxyethylene alkylamides, polyoxyethylene lauryl ethers, polyoxyethylene cetyl ethers, polyoxyethylene stearyl ethers, polyoxyethylene oleyl ether, polyoxyethylene octylphenyl ethers, polyoxyethylene nonylphenyl ethers, polyethylene glycol laurates, polyethylene glycol stearates, polyethylene glycol distearates, polyethylene glycol oleates, oxyethylene-oxypropylene block copolymer, sorbitan laurate, sorbitan stearate, sorbitan distearate, sorbitan oleate, sorbitan sesquioleate, sorbitan trioleate, polyoxyethylene sorbitan laurates, polyoxyethylene sorbitan stearates, polyoxyethylene sorbitan oleates, polyoxyethylene laurylamines, polyoxyethylene laurylamides, laurylamine acetate, ethoxylated tetramethyldecynediol, fluoroaliphatic polymeric ester, and polyether-polysiloxane copolymers.

[0077] Useful nonionic surfactants also include nonionic fluorinated surfactants. Examples include nonionic fluorinated surfactants such as those marketed under the trade designation “ZONYL” (e.g., ZONYL FSO) by E. I. du Pont de Nemours and Co., Wilmington, Del.

[0078] Nonionic fluorinated polymeric surfactants such as, may also be used.

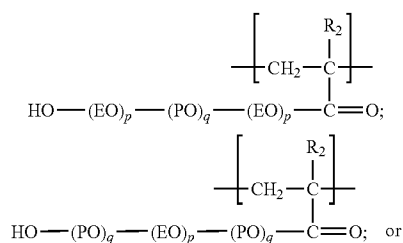
[0079] In some embodiments, the nonionic fluorinated polymeric surfactant comprises:

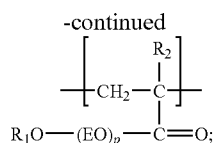
[0080] (a) at least one divalent unit represented by the formula:



and

[0081] (b) at least one divalent unit represented by a formula:





[0082] wherein:

[0083] R_f represents a perfluoroalkyl group having from 1 to 8 carbon atoms. Exemplary groups R_f include perfluoromethyl, perfluoroethyl, perfluoropropyl, perfluorobutyl (e.g., perfluoro-n-butyl or perfluoro-sec-butyl), perfluoropentyl, perfluorohexyl, perfluoroheptyl, and perfluorooctyl.

[0084] R , R_1 , and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms (e.g., methyl, ethyl, n-propyl, isopropyl, butyl, isobutyl, or t-butyl).

[0085] n is an integer from 2 to 10.

[0086] EO represents $-\text{CH}_2\text{CH}_2\text{O}-$.

[0087] PO represents $-\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-$ or $-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-$.

[0088] Each p is independently an integer of from 1 to about 128.

[0089] Each q is independently an integer of from 0 to about 55. Useful nonionic fluorinated polymeric surfactants typically have a number average molecular weight in the range of from 1,000 to 10,000 grams/mole, 20,000 grams/mole, or even 30,000 grams/mole, although higher and lower molecular weights may also be used.

[0090] Such nonionic fluorinated polymeric surfactants may be prepared by techniques known in the art, including, for example, by free radical initiated copolymerization of a nonafluorobutanesulfonamido group-containing acrylate with a poly(alkyleneoxy) acrylate (e.g., monoacrylate or diacrylate) or mixtures thereof. Adjusting the concentration and activity of the initiator, the concentration of monomers, the temperature, and the chain-transfer agents can control the molecular weight of the polyacrylate copolymer. The description of the preparation of such polyacrylates is described, for example, in U.S. Pat. No. 3,787,351 (Olson). Preparation of nonafluorobutanesulfonamido acrylate monomers are described, for example, in U.S. Pat. No. 2,803,615 (Ahlbrecht et al.), the disclosure of which is incorporated herein by reference. Examples of fluoroaliphatic polymeric esters and their preparation are described, for example, in U.S. Pat. No. 6,664,354 (Savu et al.).

[0091] Methods described above for making nonafluorobutylsulfonamido group-containing structures can be used to make heptafluoropropylsulfonamido groups by starting with heptafluoropropylsulfonyl fluoride, which can be made, for example, by the methods described in Examples 2 and 3 of U.S. Pat. No. 2,732,398 (Brice et al.), the disclosure of which is incorporated herein by reference.

[0092] In some embodiments, the hydrocarbon-bearing clastic formation has at least one fracture. In some of these embodiments, the fracture has a plurality of proppants therein. Fracture proppant materials are typically introduced into the formation as part of a hydraulic fracture treatment. Exemplary proppants known in the art include those made of sand (e.g., Ottawa, Brady or Colorado Sands, often referred to as white and brown sands having various ratios), resin-coated, sintered bauxite, ceramics (i.e., glasses, crystalline ceramics, glass-ceramics, and combinations thereof), ther-

moplastics, organic materials (e.g., ground or crushed nut shells, seed shells, fruit pits, and processed wood), and clay. Sand proppants are available, for example, from Badger Mining Corp., Berlin, Wis.; Borden Chemical, Columbus, Ohio; and Fairmont Minerals, Chardon, Ohio. Thermoplastic proppants are available, for example, from the Dow Chemical Company, Midland, Mich.; and BJ Services, Houston, Tex. Clay-based proppants are available, for example, from CarboCeramics, Irving, Tex.; and Saint-Gobain, Courbevoie, France. Sintered bauxite ceramic proppants are available, for example, from Borovichi Refractories, Borovichi, Russia; 3M Company, St. Paul, Minn.; CarboCeramics; and Saint Gobain. Glass bubble and bead proppants are available, for example, from Diversified Industries, Sidney, British Columbia, Canada; and 3M Company. In some embodiments, the proppants form packs within a formation and/or wellbore. Proppants may be selected to be chemically compatible with the fluids and compositions described herein. Particulate solids may be introduced into the formation, for example, as part of a hydraulic fracture treatment, sand control particulate introducer into the wellbore/formation as part of any sand control treatment such as a gravel pack or frac pack.

[0093] Although not wanting to be bound by theory, it is believed that, in some embodiments using proppants, surfactants useful in practicing the present invention may interact with at least a portion of the plurality of proppants, (i.e., change the wettability of the proppants). Some surfactants may interact with the plurality of proppants, for example, by adsorbing to the surfaces of the proppants (in either clastic or non-clastic formations). Methods of determining the interaction of surfactants with proppants include the measurement of the conductivity of the fracture.

[0094] In some embodiments, surfactants useful in practicing the present invention modify the wetting properties of the rock in a near wellbore region of a hydrocarbon-bearing formation (in some embodiments, in a fracture). Although not wanting to be bound by theory, it is believed the surfactants generally adsorb to formations under downhole conditions.

[0095] Again, although not wanting to be bound by theory, it is believed that surfactants generally adsorb to the surfaces of proppants and the rock surface in hydrocarbon-bearing formations and typically remain at the target site for the duration of an extraction (e.g., 1 week, 2 weeks, 1 month, or longer).

[0096] Examples of useful solvents include organic solvents, water, and combinations thereof. Examples of organic solvents include polar and/or water-miscible solvents such as monohydroxy alcohols independently having from 1 to 4 or more carbon atoms (e.g., methanol, ethanol, isopropanol, propanol, and butanol); polyols such as, for example, glycols (e.g., ethylene glycol or propylene glycol), terminal alkanediols (e.g., 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, or 1,8-octanediol), polyglycols (e.g., diethylene glycol, triethylene glycol, or dipropylene glycol) and triols (e.g., glycerol, trimethylolpropane); ethers (e.g., diethyl ether, methyl t-butyl ether, tetrahydrofuran, p-dioxane); polyol ethers (e.g., glycol ethers (e.g., ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, dipropylene glycol monomethyl ether, propylene glycol monomethyl ether, or those glycol ethers available under the trade designation "DOWANOL" from Dow Chemical Co., Midland, Mich.); ketones (e.g., acetone or 2-butanone), easily gasified fluids (e.g., ammonia, low molecular weight hydrocarbons or sub-

stituted hydrocarbons, condensate, and supercritical or liquid carbon dioxide), and mixtures thereof.

[0097] In some embodiments, component(s) of the solvent may have a normal boiling point of less than 650° F. (343° C.); for example, to facilitate removal of the solvent from a well after treatment.

[0098] The various model brines and treatment compositions (i.e., first and second treatment compositions) used herein may be prepared by any suitable method including, manually or mechanically shaking and/or stirring the various components thereof. Information concerning the temperature and brine composition of a hydrocarbon-bearing formation is typically obtained by measurement of the pertinent condition (s) in or near a wellbore located at a particular geological zone of interest in a hydrocarbon-bearing formation. Suitable measurement methods are known to the skilled artisan. In some, instances further manipulation of data (e.g., computer calculations) obtained from hydrocarbon-bearing formation may be useful, and such manipulation is within the scope of the present invention.

[0099] The compatibility information (i.e., the first and/or second compatibility information) may be generated by various methods including, computer simulation, physical measurements or a combination thereof. The compatibility information may be as small as a single set element (e.g., a measurement of compatibility between the surfactant-solvent formulation and the brine and optionally condensate at a given temperature), or it may contain any higher number of set elements. Typically, the choice of surfactant-solvent formulations and temperatures to be studied and the results included within the compatibility information will be apparent to the skilled artisan performing the method (but not a requirement) in light of the present disclosure.

[0100] One convenient method of evaluating compatibility involves combining (e.g., in a container) a model brine and optionally model condensate with a surfactant-solvent formulation (i.e., treatment composition) at a given temperature, and then mixing the model brine and optionally model condensate with the surfactant-solvent formulation (i.e., treatment composition). The mixture is evaluated over time (e.g., 5 minutes, 1 hour, 12 hours, 24 hours or longer) to see if it phase separates or becomes cloudy. By adjusting the relative amounts of model brine and optionally model condensate and the surfactant-solvent formulation, it is possible to determine the maximum brine and/or condensate uptake capacity (above which phase separation occurs) of the surfactant-solvent formulation at a given temperature. Varying the temperature at which the above procedure is carried out typically results in a more complete understanding of the suitability of surfactant solvent formulations as treatment compositions for a given well. In addition, to calculating and/or measuring interactions of the model brine and/or model condensate with a surfactant-solvent formulation, it is also contemplated that one may be able to obtain the compatibility information, in whole or in part, by simply referring to previously determined, collected, and/or tabulated information (e.g., in a handbook or a computer database). In some embodiments wherein first and second compatibility information are obtained, the first and second compatibility information may be obtained either simultaneously or sequentially and in either order.

[0101] Although not wanting to be bound by theory, it is believed that more desirable well treatment results are obtained when the treatment composition used in a particular

near wellbore region of a well is homogenous at the temperature(s) encountered in the near wellbore region. Accordingly, the treatment composition is typically selected to be homogenous at temperature(s) found in the portion of hydrocarbon-bearing formation (e.g., a near well bore region) to be treated.

[0102] Fluids (including liquids and gases) useful in practicing the present invention at least one of at least partially solubilizes or at least partially displaces the brine in the hydrocarbon-bearing clastic formation. In some embodiments, the fluid at least partially displaces the brine in the hydrocarbon-bearing clastic formation. In some embodiments, the fluid at least partially solubilizes brine in the hydrocarbon-bearing clastic formation. The brine may be connate or non-connate water, mobile (e.g., crossflow) or immobile (e.g., residual) water, naturally occurring water or water resulting from operations on the formation (e.g., water from aqueous drilling fluids or aqueous fracturing fluids). In some embodiments, the brine is connate water. Examples of useful fluids include polar and/or water-miscible solvents such as monohydroxy alcohols having from 1 to 4 or more carbon atoms (e.g., methanol, ethanol, isopropanol, propanol, or butanol); polyols such as glycols (e.g., ethylene glycol or propylene glycol), terminal alkanediols (e.g., 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, or 1,8-octanediol), polyglycols (e.g., diethylene glycol, triethylene glycol, or dipropylene glycol) and triols (e.g., glycerol, trimethylolpropane); ethers (e.g., diethyl ether, methyl t-butyl ether, tetrahydrofuran, p-dioxane); polyol ethers such as glycol ethers (e.g., ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, dipropylene glycol monomethyl ether, propylene glycol monomethyl ether, or those glycol ethers available under the trade designation "DOWANOL" from Dow Chemical Co., Midland, Mich.); and ketones (e.g., acetone or 2-butanone). Useful fluids also include liquid or gaseous hydrocarbons (e.g., toluene, diesel, heptane, octane, condensate, methane, and isoparaffinic solvents obtained from Total Fina, Paris, France, under trade designation "ISANE" and from Exxon Mobil Chemicals, Houston, Tex., under the trade designation "ISOPAR") and other gases (e.g., nitrogen and carbon dioxide).

[0103] In case the model brine and the treatment composition are at least partially incompatible, a fluid may be used to treat the formation prior to contacting the formation. In some embodiments wherein the first compatibility information indicates that the first model brine and the first treatment composition are at least partially incompatible, Method I is selected. Accordingly, the fluid amount and type is selected so that it at least one of solubilizes or displaces a sufficient amount of brine in the formation. In some embodiments of methods according to the present invention, the fluid amount and type may be selected so that it at least one of solubilizes or displaces a sufficient amount of brine in the formation such that when the composition is added to the formation, the surfactant has a cloud point that is above at least one temperature found in the formation. In some embodiments, the fluid amount and type is selected so that it at least one of solubilizes or displaces a sufficient amount of brine in the formation such that when the composition is contacting the formation, the formation is substantially free of precipitated salt.

[0104] In some embodiments wherein the compatibility information indicates that the first model brine and the first treatment composition are compatible, Method II is selected, and the second treatment composition has the same composition as the first treatment composition.

[0105] In some embodiments, a treatment method and/or composition is chosen based at least in part on the compatibility information. In general, a treatment composition is chosen that closely resembles, or is identical to, a surfactant-solvent formulation from the compatibility information set, but this is not a requirement. For example, cost, availability, regulations, flammability, and environmental concerns may influence the specific choice of treatment composition for use in testing and/or commercial production.

[0106] A contour map can be created in multiple dimensions plotting selected variables against one another. The variables to choose from can include, but are not limited to: temperature, brine concentration, total water concentration, alcohol content, condensate concentration, solvents, other chemical components, etc.

[0107] In one exemplary embodiment, a map can be created that plots brine concentration vs. total water concentration on the x and y axes, vs. temperature on the z-axis. In this instance, the user can plot the phase behavior of a particular solvent composition in three-dimensions, identifying such areas in phase space where, for example, there is a single phase system, salt precipitates and where the surfactant is insoluble. Multiple solvent combinations could be plotted on the same graph and may be done so in an automated manner depending on the data sources.

[0108] In one exemplary embodiment, the data can be to plot water concentration vs. weight percent alcohol concentration in a particular formulation on the x and y axes, then plot vs. temperature on the z-axis. In this instance, the user plots the different brine concentrations on one plot. By plotting a contour map, the skilled artisan will be able to determine whether a preflush would be needed or not, if a particular solvent combination could be used under those conditions or what the options for the composition based on additional variables, such as flashpoint. In fact, the maps also allow the user to determine if and which core tests might not be needed.

[0109] Once selected, the treatment compositions and methods may be further evaluated; for example, by injection into a specimen (e.g., a core sample) taken from a particular geological zone to be treated, or a closely similar specimen. This may be performed in a laboratory environment using conventional techniques such as, for example, those described by Kumar et al. in "Improving the Gas and Condensate Relative Permeability Using Chemical Treatments", paper SPE 100529, presented at the 2006 SPE Gas Technology Symposium held in Calgary, Alberta, Canada, 15-17 May 2006.

[0110] In some embodiments, the solvent (in a first and/or second treatment composition) is generally capable of solubilizing and/or displacing brine and/or condensate in the formation. Examples of brine include connate or non-connate water, mobile or immobile water, naturally occurring water or water resulting from operations on the well and the like. For example, the solvent may be capable of at least one of solubilizing or displacing brine in the formation. Likewise, the solvent may be, for example, capable of at least one of solubilizing or displacing condensate in the formation. In some embodiments, methods according to the present invention are typically useful for treating formations in hydrocarbon-bearing formations containing brine and optionally condensate.

[0111] The effectiveness of compositions and methods described herein for improving the permeability of a particular formation having brine (and/or condensate) therein will typically be determined by the ability of the composition

and/or fluid to dissolve the quantity of brine (and/or condensate) present in the formation. Hence, at a given temperature greater amounts of compositions and/or fluids having lower brine (and/or condensate) solubility (i.e., compositions that can dissolve a relatively lower amount of brine or condensate) will typically be needed than in the case of compositions and/or fluids having higher brine (and/or condensate) solubility and containing the same surfactant at the same concentration.

[0112] Typically, compositions useful in practicing the present invention include from at least 0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045, 0.05, 0.055, 0.06, 0.065, 0.07, 0.075, 0.08, 0.085, 0.09, 0.095, 0.1, 0.15, 0.2, 0.25, 0.5, 1, 1.5, 2, 3, 4, or 5 percent by weight, up to 5, 6, 7, 8, 9, or 10 percent by weight of the nonionic fluorinated polymeric surfactant, based on the total weight of the composition. For example, the amount of the nonionic fluorinated polymeric surfactant in the compositions may be in a range of from 0.01 to 10; 0.1 to 10, 0.1 to 5, 1 to 10, or even in a range from 1 to 5 percent by weight of the nonionic fluorinated polymeric surfactant, based on the total weight of the composition. Lower and higher amounts of the nonionic fluorinated polymeric surfactant in the compositions may also be used, and may be desirable for some applications.

[0113] The amount of solvent in the treatment composition typically varies inversely with the amount of components in compositions useful in practicing the present invention. For example, based on the total weight of the composition the solvent may be present in the composition in an amount of from at least 10, 20, 30, 40, or 50 percent by weight or more up to 60, 70, 80, 90, 95, 98, or even 99 percent by weight, or more.

[0114] In some embodiments, the treatment compositions useful in practicing the present invention may further include water (e.g., in the solvent). In some embodiments, compositions according to the present invention are essentially free of water (i.e., contains less than 0.1 percent by weight of water based on the total weight of the composition).

[0115] The ingredients for treatment compositions described herein including surfactant and solvent can be combined using techniques known in the art for combining these types of materials, including using conventional magnetic stir bars or mechanical mixer (e.g., in-line static mixer and recirculating pump).

[0116] Generally, the amount of the surfactant and solvent (and type of solvent) is dependent on the particular application since conditions typically vary between formations in hydrocarbon-bearing formations, for example, formations at different depths in the formation, and even over time in a given formation. Advantageously, methods according to the present invention can be customized for individual formations and conditions.

[0117] Methods according to the present invention may be useful, for example, for recovering hydrocarbons (e.g., at least one of methane, ethane, propane, butane, hexane, heptane, or octane) from hydrocarbon-bearing subterranean formations (in some embodiments, predominantly sandstone) or from hydrocarbon-bearing subterranean non-formations (in some embodiments, predominantly limestone). In some embodiments, the hydrocarbon-bearing formation comprises at least one of shale, conglomerate, diatomite, sand or sandstone.

[0118] The skilled artisan will be able to recognize which method to use (Method I or Method II) by first testing for

compatibility of the composition and the model brine using one treatment composition followed by a second treatment composition. Method II may be used if a second treatment composition is found that is compatible with the model brine. Typically, if a treatment composition is not found that is compatible with the model brine, Method I is selected.

[0119] Referring to FIG. 1, an exemplary offshore oil and gas platform is schematically illustrated and generally designated **10**. Semi-submersible platform **12** is centered over submerged hydrocarbon-bearing formation **14** located below sea floor **16**. Subsea conduit **18** extends from deck **20** of platform **12** to wellhead installation **22** including blowout preventers **24**. Platform **12** is shown with hoisting apparatus **26** and derrick **28** for raising and lowering pipe strings such as work string **30**.

[0120] Wellbore **32** extends through the various earth strata including hydrocarbon-bearing formation **14**. Casing **34** is cemented within wellbore **32** by cement **36**. Work string **30** may include various tools including, for example, sand control screen assembly **38** which is positioned within wellbore **32** adjacent to hydrocarbon-bearing formation **14**. Also extending from platform **12** through wellbore **32** is fluid delivery tube **40** having fluid or gas discharge section **42** positioned adjacent to hydrocarbon-bearing formation **14**, shown with production zone **48** between packers **44**, **46**. When it is desired to treat the near-wellbore region of hydrocarbon-bearing formation **14** adjacent to production zone **48**, work string **30** and fluid delivery tube **40** are lowered through casing **34** until sand control screen assembly **38** and fluid discharge section **42** are positioned adjacent to the near-wellbore region of hydrocarbon-bearing formation **14** including perforations **50**. Thereafter, a composition described herein is pumped down delivery tube **40** to progressively treat the near-wellbore region of hydrocarbon-bearing formation **14**.

[0121] Also shown in FIG. 2, a treatment zone is depicted next to casing **34**, cement **36** within perforation **50**. In the expanded view, fracture **57** is shown in which proppant **60** has been added. Fracture **57** is shown in relation to "crushed zone" **62** and regions surrounding wellbore **32** region showing virgin hydrocarbon-bearing formation **14**. Damaged zone **64** has a lower permeability and is shown between virgin hydrocarbon formation **14** and casing **34**.

[0122] While the drawing depicts an offshore operation, the skilled artisan will recognize that the compositions and methods for treating a production zone of a wellbore may also be suitable for use in onshore operations. Also, while the drawing depicts a vertical well, the skilled artisan will also recognize that methods of the present invention may also be useful, for example, for use in deviated wells, inclined wells or horizontal wells.

[0123] A schematic diagram of core flood apparatus **100** used to determine relative permeability of the substrate sample is shown in FIG. 3. Core flood apparatus **100** included positive displacement pumps (Model No. 1458; obtained from General Electric Sensing, Billerica, Mass.) **102** to inject fluid **103** at constant rate in to fluid accumulators **116**. Multiple pressure ports **112** on core holder **108** were used to measure pressure drop across four sections (2 inches (5.1 cm) in length each) of core **109**. Pressure port **111** was used to measure the pressure drop across the whole core. Two back-pressure regulators (Model No. BPR-50; obtained from Temco, Tulsa, Okla.) **104**, **106** were used to control the flowing pressure downstream and upstream, respectively, of core **109**. The flow of fluid was through a vertical core to avoid gravity segregation of the gas. High-pressure core holder (Hassler-type Model UTPT-1x8-3K-13 obtained from Phoe-

nix, Houston, Tex.) **108**, back-pressure regulators **106**, fluid accumulators **116**, and tubing were placed inside pressure-temperature-controlled oven (Model DC 1406F; maximum temperature rating of 650° F. (343° C.) obtained from SPX Corporation, Williamsport, Pa.) at the temperatures tested.

[0124] Typically, it is believed to be desirable to allow for a shut-in time after formation in the hydrocarbon-bearing formations are contacted with the compositions described herein. Exemplary set in times include a few hours (e.g., 1 to 12 hours), about 24 hours, or even a few (e.g., 2 to 10) days.

[0125] The skilled artisan, after reviewing the instant disclosure, will recognize that various factors may be taken into account in practice of the present invention including, for example, the ionic strength of the composition, pH (e.g., a range from a pH of about 4 to about 10), and the radial stress at the wellbore (e.g., about 1 bar (100 kPa) to about 1000 bars (100 MPa)).

[0126] Typically, after treatment according to the present invention hydrocarbons are then obtained from the wellbore at an increased rate, as compared the rate prior to treatment. In some embodiments wherein the formation is fractured, the fracture has at least one first conductivity prior to contacting the fracture with the composition and at least one second conductivity after contacting the fracture with the composition, and wherein the second conductivity is at least 5 (in some embodiments, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, or even 150) percent higher than the first conductivity.

[0127] Methods according to the present invention may be practiced, for example, in a laboratory environment (e.g., on a core sample (i.e., a portion) of a hydrocarbon-bearing formation) or in the field (e.g., on a subterranean hydrocarbon-bearing formation situated downhole in a well). Typically, methods according to the present invention are applicable to downhole conditions having a pressure in a range of from about 1 bar (100 kPa) to about 1000 bars (100 MPa) and a temperature in a range from about 100° F. (37.8° C.) to 400° F. (204° C.), although they may be useful to treat hydrocarbon-bearing formations under other conditions.

[0128] In addition to brine and/or condensate, other materials (e.g., asphaltene or water) may be present in the hydrocarbon-bearing formation. Methods according to the present invention may also be useful in those cases.

[0129] Various methods (e.g., pumping under pressure) known to those skilled in the oil and gas art can be used in accordance with the present invention to contact hydrocarbon-bearing subterranean formations with compositions comprising solvent and surfactant. Coil tubing, for example, may be used to deliver the treatment composition to a particular zone in a hydrocarbon-bearing formation. In some embodiments, in practicing the present invention it may be desirable to isolate a particular zone in a hydrocarbon-bearing formation (e.g., with conventional packers) to be contacted with the treatment composition.

[0130] Advantages and embodiments of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. Unless otherwise noted, all parts, percentages, ratios, etc. in the examples and the rest of the specification are by weight.

Example 1

[0131] A nonionic fluorinated polymeric surfactant ("Non-ionic Fluorinated Polymeric Surfactant A") was prepared essentially as in Example 4 of U.S. Pat. No. 6,664,354 (Savu),

except using 15.6 grams (g) of 50/50 mineral spirits/organic peroxide initiator (tert-butyl peroxy-2-ethylhexanoate obtained from Akzo Nobel, Arnheim, The Netherlands under the trade designation "TRIGONOX-21-C50") in place of 2,2'-azobisisobutyronitrile, and with 9.9 grams of 1-methyl-2-pyrrolidinone added to the charges.

[0132] A core with the dimensions specified below was cut from a source rock block. The core was dried in an oven at 100° C. for 24 hours and then was weighed. The core was then wrapped with polytetrafluoroethylene (PTFE), aluminum foil and shrink wrapped with heat shrink tubing (obtained under the trade designation "TEFLON HEAT SHRINK TUBING" from Zeus, Inc., Orangeburg, S.C.). The wrapped core was placed into a core holder inside the oven at the experimental temperature.

[0133] A preflush was conducted using a fluid pre-flush before treating a gas condensate sandstone formation that has high salinity brine and/or high water saturation. The example was performed using a Berea sandstone core at a reservoir temperature of 322° F. (161° C.).

[0134] The initial gas permeability was measured using nitrogen at 75° F. (23.9° C.). The initial brine saturation of 30% was established by injecting a measured volume of brine into the vacuumed core. The salinity of brine used was 180, 600 ppm. NaCl. The gas relative permeability at initial water saturation was measured using nitrogen at 75° F. (23.9° C.). Table 1 (below) summarizes the properties of the core and the procedure conditions.

TABLE 1

Core	Berea Sandstone
Length, inches (cm)	5.87 (14.91)
Diameter, inches (cm)	1 (2.54)
Porosity, %	20
Pore volume, cc	15.38
Swi, %	30
Temperature, ° F. (° C.)	322 (161)
k, md	311

[0135] A synthetic hydrocarbon mixture was prepared that exhibits retrograde gas condensate behavior. Table 2 (below) gives the composition of the synthetic gas mixture. A two-phase flood with the fluid mixture was done using the dynamic flashing method, which is also known as the pseudo-steady state method, by flashing the fluid through the upstream back-pressure regulator set above the dew point pressure at 5500 psig (37.91 MPa) to the core pressure set below the dew point pressure by the downstream back-pressure regulator. This experiment was done at a core pressure of 2600 psig (17.92 MPa). Table 3 summarizes the results for the pre-treatment two-phase flow.

TABLE 2

Component	Mole %
Methane	70
n-Butane	16.5
n-Heptane	7
n-Decane	3
n-Dodecane	2
n-Pentadecane	1.5

TABLE 3

	k_{rg}	k_{ro}	Improvement Factor
Pre-Treatment 2-phase flow	0.066	0.075	
Post-Treatment 2-phase flow	0.112	0.127	1.7

[0136] The core was then flushed with 20 pore volumes of fluid (described in Table 5 (below)). The pre-flush displaces the high salinity brine from the core and thus prevents the treatment solution (composition given in Table 4 (below)) from reaching the cloud point which could happen in the presence of high salinity brine or high water saturation. The core was then treated with 20 pore volumes of Composition A, described in Table 4 (below), and then shut-in for 15 hours. The steady state two-phase flow of gas and condensate was then done under the same conditions as the pre-treatment two-phase flow. Table 3 (above) summarizes the results for the post-treatment two-phase flow. The results show that the chemical treatment increased the gas and condensate relative permeability by a factor of about 1.7. Table 6 (below) shows the compatibility test results between Composition A and the brine used in Example 1 at 160° C.

TABLE 4

Composition Component	wt %
Nonionic Fluorinated Polymeric Surfactant A	2
Propylene Glycol (PG)	69
Isopropyl alcohol (IPA)	29

TABLE 5

Fluid Component	wt %
Propylene Glycol (PG)	70
Isopropyl alcohol (IPA)	30

TABLE 6

Brine, gms	Composition-A (Table-4), gms	Brine wt %	Solubility
1	4	20	Clear
1.25	3.75	25	Clear
1.5	3.5	30	Hazy
1.75	3.25	35	Cloudy

[0137] The results show that pre-flush with fluid provides an effective means of treating sandstone formations producing gas condensate fluids with high salinity brine present. The pre-flush will also be useful in treating formations that have high water saturation, as the pre-flush may solubilize or displace most of the water before the formation is treated with the surfactant. The fluid pre-flush may reduce or eliminate the possibility of the treatment solution reaching the cloud point while treating the above-mentioned formations, and thus makes the treatment more effective.

Example 2

[0138] This procedure used a fluid pre-flush before treating a low permeability gas condensate sandstone formation that

has high salinity brine (Brine 22.8% NaCl and 1.5% CaCl₂) present. The procedure was performed on a sandstone reservoir plug core having the characteristics as described in Table 7 (below) at the reservoir temperature of 279° F. (137.2° C.). Table 7 (below) summarizes properties of the core and the procedure conditions.

TABLE 7

Core	Sandstone
Length, inches (cm)	1.9
Diameter, inches (cm)	1 (2.54)
Porosity, %	13
Pore volume, cc	3.17
Swi, %	15
Temperature, ° F. (° C.)	279 (137.2)
k, md	7.3
k _g (S _{wi})	6.9

[0139] Core preparation. The core was dried in an oven at 100° C. for 24 hours and then was weighed. The core was then wrapped with polytetrafluoroethylene (PTFE), aluminum foil and shrink wrapped with “TEFLON HEAT SHRINK TUBING”. The wrapped core was placed into a core holder inside the oven at 279° F. (137.2° C.).

[0140] The initial gas permeability was measured using nitrogen at 75° F. (23.8° C.). The initial brine saturation of 15% was established by injecting a measured volume of brine into the vacuumed core. The salinity of brine used was 230,000 ppm with the brine composition of Table 8 (below). The gas relative permeability at initial water saturation was measured using nitrogen at 75° F. (23.8° C.).

[0141] Compatibility Test. Nonionic Fluorinated Polymeric Surfactant A (0.06 gram (g)) and 3 grams 70 weight % propylene glycol 30 weight % isopropanol were added to a vial. Brine (composition: Ca=2096 ppm, Sr=444 ppm, Ba=212 ppm, Mg=396 ppm, K=277 ppm, Na=21015 ppm, Fe (dissolved)=9 ppm, Fe (total)=10 ppm, counterion was chloride, remainder was water) (0.25 g) was added to the vial, and the vial was placed in a heated bath at 90° C. for one hour. The vial was removed from the bath, and then visually inspected to determine whether the sample was one phase. If the sample was one-phase, the brine addition and heating steps were repeated until the sample was no longer one-phase. The amount of brine that was added with no phase separation was 21.5% by weight. When 36.4% by weight brine was added, phase separation occurred.

TABLE 8

Chemical	g/L
NaCl	225.2
CaCl ₂	1.5
KCl	3.1

[0142] A synthetic hydrocarbon mixture was prepared that exhibits retrograde gas condensate behavior. Table 9 (below) gives the composition of the synthetic gas mixture. A two-phase flood with the fluid mixture was done using the dynamic flashing method, which is also known as the pseudo-steady state method, by flashing the fluid through the upstream back-pressure regulator set above the dew point pressure at 5500 psig (37.91 MPa) to the core pressure set below the dew point pressure by the downstream back-pressure regulator. This experiment was done at a core pressure of

2600 psig (17.92 MPa). Table 10 (below) summarizes the results for the pre-treatment two-phase flow.

TABLE 9

Component	Mole %
Methane	95
Propane	1
n-Heptane	1.25
n-Decane	1.25
n-Pentadecane	1.5

TABLE 10

	k _{rg}	k _{ro}	Improvement Factor
Pre-Treatment 2-phase flow	0.067	0.032	n/a
Post-Treatment 2-phase flow	0.091	0.043	1.36

[0143] The core was then flushed with 9 pore volumes of fluid (described in Table 11, below). The pre-flush displaces the high salinity brine from the core and thus prevents Composition B (described in Table 11, below) from reaching the cloud point which can happen in the presence of high salinity brine present in the core. The core was then treated with 20 pore volumes of the composition given in Table 11 (below) and then shut-in for 15 hours. The steady state two-phase flow of gas and condensate was then done under the same conditions as the pre-treatment two-phase flow. Table 10 (above) summarizes the results for the post-treatment two-phase flow. The results show that the chemical treatment increased the gas and condensate relative permeability by a factor of about 1.36.

TABLE 11

Component	wt %
Nonionic Fluorinated Polymeric Surfactant A	2
Propylene Glycol (PG)	69
Isopropyl alcohol (IPA)	29

TABLE 12

Component	wt %
Propylene Glycol (PG)	70
Isopropyl alcohol (IPA)	30

Example 3

[0144] This example demonstrates the benefits of using a solvent pre-flush before treating a gas condensate sandstone formation that has initial water present. The example was performed using a Berea sandstone core at a reservoir temperature of 275° F. (135° C.).

[0145] A core with the dimensions specified below was cut from a source rock block. The core was dried in an oven at 100° C. for 24 hours and then was weighed. The core was then wrapped with polytetrafluoroethylene (PTFE), aluminum foil and shrink wrapped with “TEFLON HEAT SHRINK TUBING”. The wrapped core was placed into a core holder inside the oven at 275° F. (135° C.).

[0146] The initial gas permeability was measured using nitrogen at 75° F. (23.8° C.). The initial brine saturation of 26% was established by injecting a measured volume of brine into the vacuumed core. The gas relative permeability at initial water saturation was measured using nitrogen at 75° F. (23.8° C.). Table 13 (below) summarizes the properties of the core and procedure conditions.

TABLE 13

Core	Berea Sandstone
Length, inches	8
Diameter, inches (cm)	1 (2.54)
Porosity, %	20
Pore volume, cc	20.59
Swi, %	26
Temperature, ° F.	275
k, md	231

[0147] The composition of brine is given in Table 14 (below).

TABLE 14

Salt	PPM
NaCl	59000
CaCl ₂	16000
MgCl ₂ •6H ₂ O	3500

[0148] A synthetic hydrocarbon mixture was prepared that exhibits retrograde gas condensate behavior. Table 15 (below) gives the composition of the synthetic gas mixture. A two-phase flood (condensate flood-1) with the fluid mixture was done using the dynamic flashing method, which is also known as the pseudo-steady state method, by flashing the fluid through the upstream back-pressure regulator set above the dew point pressure at 4500 (37.91 MPa) psig to the core pressure set below the dew point pressure by the downstream back-pressure regulator. This example was done at a core pressure of 1500 psig (17.92 MPa). Table 16 (below) summarizes the results for the pre-treatment two-phase flow.

TABLE 15

Component	Mole %
Methane	91.605
n-Butane	3.94
n-Decane	1.97
n-Pentadecane	0.985
Water	1.5

[0149] The core was then flushed with 16 pore volumes of methanol to displace brine. The solvent was flushed out by flowing two-phase gas condensate mixture through the core. The core was then treated with 19 pore volumes of the composition given in Table 17 (below) and then shut-in for 24 hours. The steady state two-phase flow of gas and condensate (condensate flood-2) was then done under the same conditions as the pre-treatment two-phase flow. Table 15 (below) summarizes the results for the condensate flood-2. The results show that the chemical treatment had negligible effect on the gas and condensate relative permeability.

TABLE 16

	k _{rg}	k _{ro}	Improvement Factor
Condensate flood-1 (Pre-Treatment 2-phase flow)	0.074	0.025	
Condensate flood-2	0.082	0.028	1.1
Condensate flood-3	0.121	0.042	1.64

TABLE 17

Component	wt %
Nonionic Fluorinated Polymeric Surfactant A	2
Methanol	94
Water	4

[0150] Next the core was flushed with 16 pore volumes of Toluene as a solvent. The solvent was then flushed out by flowing two-phase gas condensate mixture through the core. The core was then re-treated with 20 pore volumes of the composition given in Table 17 (above) and then shut-in for 24 hours. Finally, the steady state two-phase flow of gas and condensate (condensate flood-3) was then done under the same conditions as the pre-treatment two-phase flow. Table 16 (above) summarizes the results for the condensate flood-3. The results show that the chemical treatment improved the gas and condensate relative permeability by a factor of 1.64.

Comparative Example A

[0151] Composition. Nonionic Fluorinated Polymeric Surfactant A (2% by weight), methanol (94% by weight), and water (4% by weight) were mixed together using a magnetic stirrer and magnetic stir bar.

Core Flood Evaluation

[0152] Substrates. A Berea sandstone core plug was used in the core flood evaluation. The core had the properties shown in Table 18, below.

TABLE 18

Diameter, inch (cm)	1.0 (2.54)
Length, inch (cm)	8.0 (20.32)
Pore volume, mL	20.6
Porosity, %	20.0

[0153] The porosity was measured using either a gas expansion method or by the weight difference between a dry and a fully saturated core sample. The pore volume is the product of the bulk volume and the porosity.

[0154] Synthetic Condensate Composition. A synthetic gas-condensate fluid containing 93 mole percent methane, 4 mole percent n-butane, 2 mole percent n-decane, and 1 mole percent n-pentadecane was used for the core flood evaluation. Approximate values for various properties of the fluid are reported Table 19, below.

TABLE 19

Dewpoint, psig (Pa)	4200 (2.9 × 10 ⁷)
Core pressure, psig (Pa)	1500 (1.0 × 10 ⁷)
Liquid dropout, V/Vt %	3.2

TABLE 19-continued

Gas viscosity, cP	0.017
Oil viscosity, cP	0.22
Interfacial tension, dynes/cm	5.0

[0155] Core Preparation. The core was dried for 72 hours in a standard laboratory oven at 95° C. and then wrapped in aluminum foil and heat shrink tubing (obtained under the trade designation “TEFLON HEAT SHRINK TUBING” from Zeus, Inc., Orangeburg, S.C.). Referring to FIG. 3, the wrapped core **109** was placed in core holder **108** inside oven **110** at 75° F. (24° C.). An overburden pressure of 3400 psig (2.3×10^7 Pa) was applied. The initial single-phase gas permeability was measured using either nitrogen or methane at a flowing pressure of 1200 psig (8.3×10^6 Pa).

[0156] Brine, containing 92.25% water, 5.9% sodium chloride, 1.6% calcium chloride, 0.23% magnesium chloride hexahydrate, and 0.05% potassium chloride, was introduced into the core **109** by the following procedure. The outlet end of the core holder was connected to a vacuum pump and a full vacuum was applied for 30 minutes with the inlet closed. The inlet was connected to a burette with the brine in it. The outlet was closed and the inlet was opened to allow a known volume of brine to flow into the core. For example, a 26% water saturation (i.e., 26% of the pore volume of the core was saturated with water) was established by allowing 5.3 ml of brine to flow into the core before the inlet valve was closed. The permeability was measured at 26% water saturation by flowing nitrogen or methane gas at 1200 psig (8.3×10^6 Pa) and 75° F. (24° C.).

[0157] Core Flooding Procedure. Referring again to FIG. 3, the wrapped core **109** in the core holder **108** was placed inside oven **110** at 275° F. (135° C.) for several hours to allow it to reach reservoir temperature. The synthetic gas-condensate fluid described above was then introduced at a flow rate of about 690 mL/hr until steady state was established. Upstream back-pressure regulator **106** was set at about 4900 psig (3.38×10^7 Pa), above the dew point pressure of the fluid, and downstream back-pressure regulator **104** was set at about 1500 psig (3.38×10^7 Pa), corresponding to the bottom hole flowing well pressure. The gas relative permeability before treatment was then calculated from the steady state pressure drop. The surfactant composition was then injected into the core without first injecting a fluid into the core to attempt to solubilize or displace brine. After at least 20 pore volumes of the surfactant composition were injected, the surfactant composition was held in the core at 275° F. (135° C.) for about 15 hours. The synthetic gas condensate fluid described above was then introduced again at a flow rate of about 690 mL/hr using positive displacement pump **102** until a steady state was reached. The gas relative permeability after treatment was then calculated from the steady state pressure drop. Following the relative permeability measurements, methane gas was injected, using positive displacement pump **102**, to displace the condensate and measure the final single-phase gas permeability to demonstrate that no damage had been done to the core.

[0158] The initial single-phase gas permeability, measured prior to brine saturation, the initial capillary number, the gas relative permeability before treatment with the surfactant composition, the gas relative permeability after treatment, and the ratio of the gas relative permeabilities after and before

treatment (i.e., improvement factor) for Comparative Example A are reported in Table 20, below.

TABLE 20

Gas permeability, millidarcy (md)	231
Capillary number	1.1×10^{-5}
Gas relative permeability before treatment	0.084
Gas relative permeability after treatment	0.084
Improvement factor	1.0

[0159] It will be understood that particular embodiments described herein are shown by way of illustration and not as limitations of the invention. The principal features of this invention can be employed in various embodiments without departing from the scope of the invention. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, numerous equivalents to the specific procedures described herein. Such equivalents are considered to be within the scope of this invention and are covered by the claims.

[0160] The use of the word “a” or “an” when used in conjunction with the term “comprising” in the claims and/or the specification may mean “one,” but it is also consistent with the meaning of “one or more,” “at least one,” and “one or more than one.” The use of the term “or” in the claims is used to mean “and/or” unless explicitly indicated to refer to alternatives only or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and “and/or.” Throughout this application, the term “about” is used to indicate that a value includes the inherent variation of error for the device, the method being employed to determine the value.

[0161] The term “or combinations thereof” as used herein refers to all permutations and combinations of the listed items preceding the term. For example, “A, B, C, or combinations thereof” is intended to include at least one of: A, B, C, AB, AC, BC, or ABC, and if order is important in a particular context, also BA, CA, CB, CBA, BCA, ACB, BAC, or CAB. Continuing with this example, expressly included are combinations that contain repeats of one or more item or term, such as BB, AAA, MB, BBC, AAABCCCC, CBBAAA, CABABB, and so forth. The skilled artisan will understand that typically there is no limit on the number of items or terms in any combination, unless otherwise apparent from the context.

1. A method of treating a hydrocarbon-bearing formation having brine and at least one temperature, wherein the brine has at least one first composition, the method comprising:

obtaining first compatibility information for a first model brine and a first treatment composition at a model temperature, wherein the first model brine has a composition selected at least partially based on the first brine composition, wherein the model temperature is selected at least partially based on the formation temperature, and wherein the first treatment composition comprises at least one first surfactant and at least one first solvent;

based at least partially on the first compatibility information, selecting a treatment method for the hydrocarbon-bearing formation, wherein the treatment method is Method I or Method II,

wherein Method I comprises:

contacting the hydrocarbon-bearing formation with a fluid, wherein the fluid at least one of at least partially solubilizes or at least partially displaces the brine in the hydrocarbon-bearing formation; and subsequently contacting the hydrocarbon-bearing formation with the first treatment composition;

and wherein Method II comprises:

contacting the hydrocarbon-bearing formation with a second treatment composition, the second treatment composition comprising at least one second surfactant and at least one second solvent, with the proviso that after obtaining the first compatibility information, the hydrocarbon-bearing formation is not contacted with a fluid that at least one of at least partially solubilizes or at least partially displaces the brine in the hydrocarbon-bearing formation prior to contacting the hydrocarbon-bearing formation with the second treatment composition; and

treating the hydrocarbon-bearing formation with the selected treatment method.

2. The method of claim 1, wherein the first compatibility information indicates that the first model brine and the first treatment composition are at least partially incompatible.

3. The method of claim 1, wherein the first compatibility information indicates that the first model brine and the first treatment composition are compatible, and wherein the second treatment composition has the same composition as the first treatment composition.

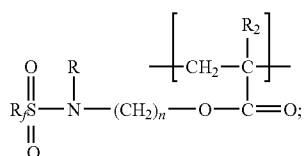
4. The method of claim 1, wherein the first compatibility information comprises information concerning the phase stability of a mixture of the first model brine and the first treatment composition, or wherein the compatibility information comprises information concerning salt precipitation from a mixture of the first model brine and the first treatment composition.

5. (canceled)

6. The method of claim 1, wherein at least one of the first surfactant or the second surfactant is a nonionic fluorinated polymeric surfactant.

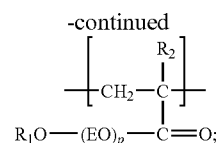
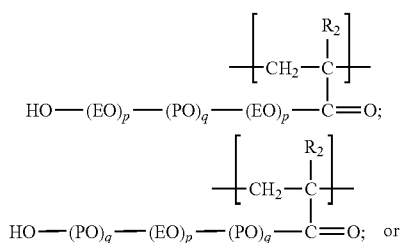
7. The method of claim 6, wherein the nonionic fluorinated polymeric surfactant comprises:

at least one divalent unit represented by formula:



and

at least one divalent unit represented by formula:



wherein

R₁ represents a perfluoroalkyl group having from 1 to 8 carbon atoms;

R, R₁, and R₂ are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

n is an integer from 2 to 10;

EO represents —CH₂CH₂O—;

each PO independently represents —CH(CH₃)CH₂O— or —CH₂CH(CH₃)O—;

each p is independently an integer of from 1 to about 128; and

each q is independently an integer of from 0 to about 55.

8. The method of claim 1, wherein the fluid is essentially free of surfactant.

9. The method of claim 1, wherein the fluid comprises at least one of toluene, diesel, heptane, octane, or condensate, or wherein the fluid comprises at least one of nitrogen, carbon dioxide, or methane.

10. The method of claim 1, wherein the fluid comprises at least one of a polyol or polyol ether, and wherein the polyol and polyol ether independently have from 2 to 25 carbon atoms.

11. (canceled)

12. The method of claim 1, wherein the fluid further comprises water or at least one monohydroxy alcohol, ether, or ketone independently having from 1 to 4 carbon atoms.

13-14. (canceled)

15. The method of claim 1, wherein at least one of the first solvent or the second solvent comprises at least one of a polyol or polyol ether, wherein the polyol and polyol ether independently have from 2 to 25 carbon atoms; and wherein at least one of the first solvent or the second solvent comprises at least one of a monohydroxy alcohol, ether, or ketone independently having from 1 to 4 carbon atoms.

16. The method of claim 1, wherein the first compatibility information is represented in a contour map.

17-18. (canceled)

19. The method of claim 1, wherein after the fluid contacts the hydrocarbon-bearing formation and before the first treatment composition contacts the hydrocarbon-bearing formation, the formation has a second brine composition, and wherein Method I further comprises:

obtaining second compatibility information for a second model brine and the first treatment composition at the model temperature, wherein the second model brine has a composition selected at least partially based on the second brine composition, and wherein the second compatibility information indicates that the first treatment composition and the second model brine are compatible.

20. The method of claim 1, wherein the formation is fractured.

21. A method of treating a hydrocarbon-bearing formation having brine and at least one temperature, wherein the brine has at least one first composition, the method comprising:

obtaining first compatibility information for a first model brine and a treatment composition at a model tempera-

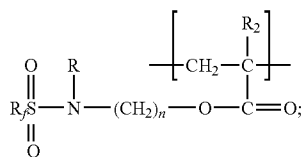
ture, wherein the first model brine has a composition selected at least partially based on the first brine composition, wherein the model temperature is selected at least partially based on the formation temperature, wherein the treatment composition comprises at least one surfactant and at least one solvent, and wherein the first compatibility information indicates that the treatment composition and the first model brine are at least partially incompatible;

contacting the hydrocarbon-bearing formation with a fluid, wherein the fluid at least one of at least partially solubilizes or at least partially displaces the brine in the hydrocarbon-bearing formation, and wherein after the fluid contacts the hydrocarbon-bearing formation, the formation has a second brine composition;

obtaining second compatibility information for a second model brine and the treatment composition at the model temperature, wherein the second model brine has a composition selected at least partially based on the second brine composition, and wherein the second compatibility information indicates that the treatment composition and the second model brine are compatible; and
after obtaining the second compatibility information, contacting the hydrocarbon-bearing formation with the treatment composition.

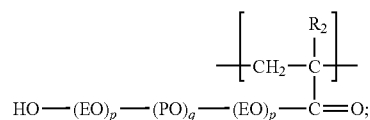
22. The method of claim **21**, wherein the at least one surfactant is a nonionic fluorinated polymeric surfactant, comprising:

at least one divalent unit represented by formula:

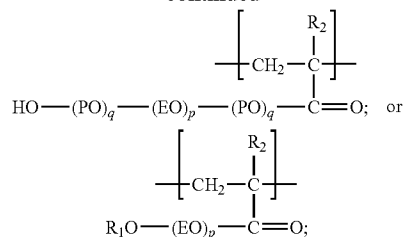


and

at least one divalent unit represented by formula:



-continued



wherein

R_f represents a perfluoroalkyl group having from 1 to 8 carbon atoms;

R , R_1 , and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

n is an integer from 2 to 10;

EO represents $-\text{CH}_2\text{CH}_2\text{O}-$;

each PO independently represents $-\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-$ or $-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-$;

each p is independently an integer of from 1 to about 128; and

each q is independently an integer of from 0 to about 55.

23. The method of claim **21**, wherein the fluid is essentially free of surfactant.

24. The method of claim **21**, wherein the fluid comprises at least one of toluene, diesel, heptane, octane, or condensate; wherein the fluid comprises at least one of nitrogen, carbon dioxide, or methane; or wherein the fluid comprises at least one of a polyol or polyol ether, and wherein the polyol and polyol ether independently have from 2 to 25 carbon atoms.

25-26. (canceled)

27. The method of claim **21**, wherein the fluid further comprises water or at least one monohydroxy alcohol, ether, or ketone independently having from 1 to 4 carbon atoms.

28-29. (canceled)

30. The method of claim **21**, wherein the at least one solvent comprises at least one of a polyol or polyol ether, wherein the polyol and polyol ether independently have from 2 to 25 carbon atoms; and wherein the at least one solvent comprises at least one of monohydroxy alcohol, ether, or ketone independently having from 1 to 4 carbon atoms.

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