SURFACTANT ADDITIVES FOR STIMULATING SUBTERRANEAN FORMATION DURING FRACTURING OPERATIONS

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ABSTRACT

The present invention relates to surfactant additives useful for restoring permeability of a subterranean formation and methods of use thereof. One embodiment of the present invention provides a method that includes providing a fracturing fluid having an aqueous fluid, and a microemulsion surfactant, wherein the fracturing fluid is substantially free of an organic solvent; and placing the fracturing fluid into a subterranean formation at a rate sufficient to create or enhance at least one fracture in the subterranean formation.
SURFACTANT ADDITIVES FOR STIMULATING SUBTERRANEAN FORMATION DURING FRACTURING OPERATIONS

BACKGROUND

[0001] The present invention relates to hydrocarbon production, and more particularly, to surfactant additives useful for restoring permeability of a subterranean formation and methods of use thereof.

[0002] Formation damage is typically the result of unwanted side effects from exposing a producing formation with subterranean treatment fluids. Examples of subterranean treatment fluids that may cause formation damage include, for example, drilling fluids, completion fluids, fracturing fluids, work-over fluids, and the like. As used herein, “formation damage” and its related terms (e.g., damaged formation) generally refer to a reduction in the capability of a reservoir to produce its fluids (e.g., oil and gas), such as a decrease in porosity or permeability or both.

[0003] There are several mechanisms that can lead to formation damage. These mechanisms may include, among other things, physical plugging of pores, alteration of reservoir rock wettability, precipitation of insoluble materials in pore spaces, clay swelling, and blocking by water (i.e., water blocks). In particular, a water block is often caused by an increase in water saturation in the near-wellbore area, which results in a decrease in relative permeability to hydrocarbons.

[0004] As used herein, the term “water block” generally refers to a condition caused by an increase in water saturation in the near-wellbore area. The increased presence of water may cause any clay present in the formation to swell and cause a reduction in permeability and/or the water may collect in the pore throats, resulting in a decreased permeability due to increased capillary pressures and cohesive forces.

[0005] Water blocks can be especially problematic in certain fracturing operations where a large volume of aqueous fracturing fluid leaks off into the formation through the fracture face, which can lead to a decrease in the rate at which oil or gas can be produced. Because water is immiscible with hydrocarbons, the leaked off fluid can be slow to return to the surface due to the formation being preferentially water-wet. This problem becomes increasingly serious with decreasing natural permeability of a formation because pore sizes are often smaller and capillary action is typically stronger.

[0006] Clean up or removal of water blocking is often difficult, expensive, and/or environmentally unfriendly. For example, one common remedial approach is to treat a formation with surfactants that are capable of reducing interfacial tension and/or altering wettability properties. However, these treatments typically require a surfactant/solvent system that uses harsh organic solvents that may be environmentally unfriendly and/or expensive.

SUMMARY OF THE INVENTION

[0007] The present invention relates to hydrocarbon production, and more particularly to surfactant additives useful for restoring permeability of a subterranean formation and methods of use thereof.

[0008] In some embodiments, the present invention provides methods comprising: providing a fracturing fluid comprising: an aqueous fluid, and a microemulsion surfactant, wherein the fracturing fluid is substantially free of an organic solvent; and placing the fracturing fluid into a subterranean formation at a rate sufficient to create or enhance at least one fracture in the subterranean formation.

[0009] In other embodiments, the present invention provides methods comprising: providing a fracturing fluid comprising: an aqueous fluid, a microemulsion surfactant, and a co-surfactant, wherein the fracturing fluid is substantially free of an organic solvent; and placing the fracturing fluid into a subterranean formation at a rate sufficient to create or enhance at least one fracture in the subterranean formation.

[0010] In still other embodiments, the present invention provides methods comprising: providing a composition comprising: a microemulsion surfactant, wherein the composition is substantially free of an organic solvent; placing the composition into at least a portion of a fracture in a subterranean formation having a first permeability; and allowing the composition to remove a water block from the subterranean formation to increase permeability of the subterranean formation to a second permeability.

[0011] The features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The following FIGURE is included to illustrate certain aspects of the present invention, and should not be viewed as an exclusive embodiment. The subject matter disclosed is capable of considerable modifications, alterations, combinations, and equivalents in form and function, as will occur to those skilled in the art and having the benefit of this disclosure.

[0013] FIG. 1 shows a plot illustrating regain permeability resulting from surfactant treatments as described in Example 1.

DETAILED DESCRIPTION

[0014] The present invention relates to hydrocarbon production, and more particularly to surfactant additives useful for restoring permeability of a subterranean formation and methods of use thereof.

[0015] The present invention provides a number of advantages. In some embodiments, the compositions and methods of the present invention are able to at least partially remediate and/or reverse some of the effects of formation damage often caused by the invasion of aqueous or aqueous-based fracturing fluids into a subterranean formation. In one or more embodiments, the present invention is able to remove water blocks by using microemulsion surfactants without the use of organic solvents, which is common in conventional surfactant-based remedial treatments. In some embodiments, the present invention is able to remediate and/or reverse some of the effects of formation damage better than conventional surfactant-based remedial treatments that contain organic solvents (see Example 1). The elimination of organic solvents from the fracturing fluids of the present invention is a key advantage, which may provide efficacy, cost, and/or environmental benefits.

[0016] It has been discovered that the use of a fracturing fluid capable of forming a microemulsion without organic solvents in-situ can at least partially restore the permeability of a damaged formation. In some embodiments, the use of a fracturing fluid of the present invention can result in a retained...
producibility or regain permeability that is higher than that obtained by using conventional fracturing fluids containing surfactants and organic solvents. Without being limited by theory, it is believed that the present invention can form microemulsions in-situ and water wet the surface of a reservoir which can eliminate water blocks that often reduce production of oil and gas.

[0017] As used herein, “retained producibility” or “regain permeability” refers to the relative permeability of a formation after exposure to a fracturing fluid divided by the permeability of the formation prior to exposure to the fracturing fluid. Permeability may be determined by flowing, for example, oil, gas, or water through a base disk or natural core and recording the differential pressure required to flow at a specific rate. The disk or core is then exposed to the fracturing fluid and a return permeability is obtained by again flowing oil/gas/water. The ability to increase the permeability of the formation, or in a sense stimulate the formation using the fracturing fluid of the present invention, may be considered advantageous.

[0018] In some embodiments, the present invention provides methods comprising: providing a fracturing fluid comprising: an aqueous fluid, and a microemulsion surfactant, wherein the fracturing fluid is substantially free of an organic solvent; and placing the fracturing fluid into a subterranean formation at a rate sufficient to create or enhance at least one fracture in the subterranean formation. Examples of organic solvents found in conventional surfactant-based remedial treatments (but excluded from the fracturing fluids of the present invention) include, but are not limited to, terpene-based solvent, an alkyl acid ester of a short chain alcohol, an aryl acid ester of a short chain alcohol, benzene, toluene, xylene, or any other solvents known to one of ordinary skill in the art for use in a wellbore. The fracturing fluid (and/or the separate components thereof) may be introduced into a portion of a subterranean formation by any means known in the art.

[0019] As used herein, the term “fracturing fluid” generally refers to a subterranean treatment fluid placed into a well as part of a stimulation process, oftentimes at a pressure that is sufficient to overcome pressures within the formation so as to create or enhance fractures therein. Stimulation is typically achieved by injecting the fracturing fluid at a flow rate sufficient to increase pressure downhole to exceed the fracture gradient of the rock. A fracturing fluid is often a water-based fluid containing various additives. A common additive found in fracturing fluids is a gelling agent that increases the viscosity of the fluid. The gelling agent is commonly a polymeric material that absorbs water and forms a gel as it undergoes hydration. A fracturing fluid may contain additional additives such as, but not limited to, acids, biocides, friction reducers, iron control agents, crosslinking agents, breakers, surfactants, proppants, and the like. Suitable examples of these additives are well-known by those of ordinary skill in the art.

[0020] The aqueous fluid used in the fracturing fluids of the present invention can comprise any suitable aqueous fluid known to one of ordinary skill in the art. Suitable aqueous fluids may include, but are not limited to, fresh water, saltwater (e.g., water containing one or more salts dissolved therein), glycol, brine (e.g., saturated saltwater), brine (e.g., an aqueous solution of sodium bromide, calcium bromide, zinc bromide and the like), and any combination thereof. Generally, the aqueous fluid may be from any source, provided that it does not contain components that might adversely affect the stability and/or performance of the fracturing fluids of the present invention. In certain embodiments, the density of the aqueous fluid can be increased, among other purposes, to provide additional particle transport and suspension in the fracturing fluids of the present invention using, for example, one or more salts. In some embodiments, the aqueous fluid is present in the fracturing fluid in an amount ranging from about 40% to about 99.9% by weight of the fracturing fluid.

[0021] In general, the methods and compositions of the present invention are capable of forming microemulsions in a fracturing fluid. The term “microemulsions” as used herein refers to liquid dispersions of water and oil that are made thermodynamically stable by the mixture of three or more components: a polar phase (e.g., water), a nonpolar phase (e.g., oil), and a microemulsion surfactant. In some embodiments, the microemulsion may include other surfactants (e.g., a cosurfactant such as an alcohol, glycol or phenol, or their ethoxy derivatives). In some embodiments, the microemulsion surfactant may form the microemulsion within a subterranean formation. The use of a fracturing fluid comprising a microemulsion surfactant can be used to alter the wettability of the formation surface, remove oil and/or water blocks, and alter the wettability of a filter cake or other fluid loss additive placed into the subterranean formation during a fracturing operation. In some embodiments, the fracturing fluids and methods described herein may be used to remove a water block by removing at least a portion of the water in the near wellbore area, and/or altering the wettability of the subterranean formation. This may directly or indirectly lead to reduced capillary pressure in the porosity of the formation. Reduced capillary pressure may lead to increased water and/or oil drainage rates. As will be appreciated, improved water-drainage rates should allow a reduction in existing water blocks, as well as a reduction in the formation of water blocks.

[0022] As used herein, the term “microemulsion surfactant” can include any surfactant capable of forming a microemulsion in a fracturing fluid that comprises a polar phase and a non-polar phase and/or an oleaginous fluid, alone or in combination with a co-surfactant. As used herein, a “co-surfactant” refers to a compound that participates in aggregation of molecules into a microemulsion but does not aggregate on its own.

[0023] The phase equilibria of microemulsions may be classified by Winsor types. These types are generally described as one of the following: a Winsor I which describes a microemulsion in equilibrium with an excess oil phase; a Winsor II which describes a microemulsion in equilibrium with excess water; and a Winsor III which describes a middle phase microemulsion in equilibrium with excess water and excess oil (e.g., as a part of a three-phase system). In addition, a Winsor IV is a single-phase microemulsion, with no excess oil or excess water. The thermodynamically stable single phase Winsor IV microemulsion could evolve by a change in formulation or composition into the formation of a miniemulsion or nano-emulsion, which is a two-phase system with submieron size droplets which could be stable for long periods of time, but not permanently stable as a microemulsion.

[0024] The fracturing fluids of the present invention may comprise one or more microemulsion surfactants. Suitable microemulsion surfactants include, but are not limited to, polymeric surfactants, block copolymer surfactants, di-block polymer surfactants, hydrophobically modified surfactants,
fluoro-surfactants, non-ionic surfactants, anionic surfactants, cationic surfactants, zwitterionic surfactants, derivatives thereof, and combinations thereof. Suitable non-ionic surfactants include, but are not limited to, alkyl polyglycosides, sorbitan esters, methyl glucose esters, amine ethoxylates, diamine ethoxylates, polyglycerol esters, alkyl ethoxylates, alcohols that have been polypropoxylated and/or polyethoxylated or both, derivatives thereof, and combinations thereof. Suitable cationic surfactants include, but are not limited to, arginine methyl esters, alkylanilines, alkylbenzylimidazoles, alkyl ether sulfonates, alkyl ether sulfates, alkyl metal alkyl sulfates, alkyl or alkylaryl sulfonates, sulfo succinates, alkyl or alkylaryl disulfonates, alkyl disulfates, alcohol polypropoxylated and/or polyethoxylated sulfates, taurates, amine oxides, alkylamine oxides, ethoxylated amides, alkoxylated fatty acids, alkoxylated alcohols, ethoxylated fatty amines, ethoxylated alkyl amines, betaines, modified betaines, alkylamidobetaines, quaternary ammonium compounds, alkyl propoxy-ethoxysulfonate, alkyl propoxy-ethoxysulfate, alkylaryl-propoxy-ethoxysulfonate, derivatives thereof, and combinations thereof. Specific microemulsion surfactants may also include, but are not limited to, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate, polyoxyethylene sorbitan monolaurate, linear alcohol alkoxylates, alkyl ether sulfates, dodecylbenzene sulfonic acid, linear nonyl-phenols, dioctane, ethylene oxide, polyethylene glycol, ethoxylated castor oils, dipalmitoylethanolamine chloride, sodium 4-1 heptyl nonyl benzenesulfonate, polystyrene nonyl phenyl ether, sodium dioctyl sulfosuccinate, tetraethyleneglycoldecylether, sodium octylbenzenesulfonate, sodium hexadecyl sulfate, sodium laureth sulfate, ethylene oxide, decylamine oxide, dodecylamine betaine, decylamine oxide, any derivative thereof, and any combination thereof. In one or more non-limiting embodiments, at least two surfactants in a blend may be used to create single phase microemulsion in-situ. Suitable microemulsion surfactants may also include surfactants containing a non-ionic spacer-arm central extension and an ionic or non-ionic polar group. The non-ionic spacer-arm central extension may be the result of polypropylation, polyethoxylation, or a mixture of the two, in non-limiting embodiments.

The term “derivative,” as used herein refers to any compound that is made from one of the identified compounds, for example, by replacing one atom in the listed compound with another atom or group of atoms, or rearranging two or more atoms in the listed compound.

The amount of microemulsion surfactant included in the fracturing fluid of the present invention may be based on a number of factors including, but not limited to, the type of aqueous fluid, the temperature of the formation, the particular surfactant or surfactant blend used, the type of optional additives included, and the like. In some embodiments, the microemulsion surfactant is present in the fracturing fluid in an amount of from about 0.001% to about 50% by weight of the fracturing fluid. In some embodiments, the microemulsion surfactant is present in the fracturing fluid in an amount of from about 0.01% to about 20% by weight of the fracturing fluid.

In some embodiments, the fracturing fluid may comprise a microemulsion surfactant or a surfactant blend or a surfactant-co-surfactant mixture. Suitable co-surfactants useful with the fracturing fluids of the present invention include, but are not limited to, alcohols (e.g., propanol, butanol, pentanol in their different isomerization structures, ethoxylated and propoxylated alcohols), glycols, phenols, thiols, carboxylates, sulfonates, ketones, acrylamides, sulfonates, pyridolines, derivatives thereof, and combinations thereof. In some embodiments, an alcohol useful as a co-surfactant may have from about 3 to about 10 carbon atoms. In an embodiment, suitable alcohols can include, but are not limited to, t-butanol, n-butanol, n-pentanol, n-hexanol, 2-ethyl-hexanol, propanol, and sec-butanol. Suitable glycols can include, but are not limited to, ethylene glycol, polyethylene glycol, propylene glycols, and triethylene glycol. In some embodiments, the co-surfactant may be included in the fracturing fluids of the present invention in an amount ranging from about 0.001% to about 20% by weight of the fracturing fluid.

In some optional embodiments, the addition of an amphiphilic polymer to the fracturing fluids of the present invention may improve the stability of microemulsions. Without being limited by theory, it is believed that this stabilization may be achieved by tuning the curvature of a surfactant film with the hydrophilic and hydrophobic blocks that make up the amphiphilic polymers. In some embodiments, the amphiphilic polymers may integrate into the surfactant film to form a “tethered polymer,” resulting in a stabilization of various surfactant structures ranging from micelles to flat bi-layers. This stabilization can create an “efficiency boosting effect,” allowing the surfactant structures to absorb more non-polar and/or oleaginous fluid and remain in a single phase. In some embodiments, these stabilized microemulsions enable fracturing fluids of the present invention to absorb up to 50% more, or alternatively, up to 60% more non-polar and/or oleaginous fluid than other emulsions or microemulsion fluids not comprising an amphiphilic polymer.

The amphiphilic polymer used in the present invention may comprise a variety of polymers known in the art that comprise a hydrophobic component and a hydrophilic component. In some embodiments, the amphiphilic polymer may comprise between 2 and 50 monomer units. In some embodiments, the amphiphilic polymer may comprise between 2 and 10 monomer units. Examples of hydrophobic components that may be suitable for use include, but are not limited to, alkyl groups, polybutadiene, polyisoprene, polystyrene, polyoxystyrene, any derivatives thereof, and any combinations thereof. Examples of hydrophilic components that may be suitable for use include, but are not limited to, polyethylene oxide (PEO), polyacrylic acid (PAA), polyethyleneacetae, dimethylacrylamide (DMA), n-isopropylacrylamide (NIPAM), polyvinylpyrrolidone (PVP), polyethyleneimine (PEI), any derivatives thereof, and any combinations thereof. Examples of amphiphilic polymers that may be suitable for use include, but are not limited to polybutadiene-PEO, polystyrene-PEO, polyacrylic acid, polystyrene-PEO, polystyrene-polyethyleneacetae, any derivatives thereof, and any combinations thereof. Other examples of amphiphilic polymers that may be suitable for use in the present invention include those that comprise units based on one or more of the following: acrylamides, vinyl alcohols, vinylpyrrolidones, vinylpyridines, acrylates, polyacrylamides, polyvinyl alcohols, polyvinylpyrrolidones, polyvinylpyridines, polyacrylates, polybutylene succinate, polybutylene succinate-co-adipate, polyhydroxybutyrate-valerate, polyhydroxybutyrate-covalerate, polycaprolactones, polystrene amides, polyethylene terephthalates, sulfonated polyeth-
ylene terephthalate, polyethylene oxides, polyethylenes, polypropylenes, aliphatic aromatic copolyester, polyacrylic acids, polysaccharides (such as dextran or cellulose), chitins, chitosans, proteins, aliphatic polyesters, polyactic acids, poly(glycolides), poly(ε-caprolactones), poly(hydroxy ester ethers), poly(hydroxybutyrate), poly(anhydrides), polycarbonates, poly(orthoesters), poly(amino acids), poly(ethylene oxides), poly(propylene oxides), poly(phosphazenes), poly-ester amides, polyamides, polyurethanes, any derivative thereof, any copolymer, homopolymer, or terpolymer, or any blend thereof. In certain embodiments, the amphiphilic polymer may comprise a compound selected from the group consisting of hydroxyethyl acrylate, acrylamide and hydroxyethyl methacrylate.

[0030] In certain embodiments, the amphiphilic polymer may comprise one or more alkyl ethoxylates. In certain embodiments, the alkyl ethoxylate may comprise an alkyl group, and an ethoxylate group. In certain embodiments, the hydrophilic component may be larger and, for example, have at least 20 oxyethylene units. In certain embodiments, the hydrophilic component may be larger and, for example, have at least 40 oxyethylene units. Commercially available sources of such amphiphilic polymers that may be suitable for use in the present invention include, but are not limited to, certain detergents available under the tradename BREJÆ, such as BREJÆ-30 (comprises polyethylene glycol dodecylether), BREJÆ-35 (comprises polyoxyethylene glycol dodecylether), BREJÆ-58 (comprises polyethylene glycol hexadecylether), BREJÆ-97 (comprises polyoxyethylene (10) oleylether), BREJÆ-98 (comprises polyoxyethylene (20) oleylether), and BREJÆ-700 (comprises polyethylene glycol 100 stearyl ether). Other commercially available sources of such amphiphilic polymers that may be suitable for use in the present invention include, certain detergents available under the tradename IGEPAL®.

[0031] The amphiphilic polymer should be present in a fluid of the present invention in an amount sufficient to impart the desired viscosity (e.g., sufficient viscosity to divert flow, reduce fluid loss, suspend particulates, etc.) to the fluid. In certain embodiments, the amphiphilic polymer may be present in the fracturing fluid in an amount in the range of from about 0.01 mol % to about 5 mol % based on the amount of the microemulsion surfactant.

[0032] The gelling agents suitable for use in the present invention may comprise any substance (e.g., a polymeric material) capable of increasing the viscosity of the fracturing fluid. In certain embodiments, the gelling agent may comprise one or more polymers that have at least two molecules that are capable of forming a crosslink in a crosslinking reaction in the presence of a crosslinking agent, and/or polymers that have at least two molecules that are so crosslinked (i.e., a crosslinked gelling agent). The gelling agents may be naturally-occurring gelling agents, synthetic gelling agents, or a combination thereof. The gelling agents also may be cationic gelling agents, anionic gelling agents, or a combination thereof. Suitable gelling agents include, but are not limited to, polysaccharides, biopolymers, and/or derivatives thereof that contain one or more of these monosaccharide units: galactose, mannose, glucose, glucosyl, xylose, arabinose, fructose, gluconic acid, or pyranose sulfates. Examples of suitable polysaccharides include, but are not limited to, guar gums (e.g., hydroxyethyl guar, hydroxypropyl guar, carboxymethyl guar, carboxymethylhydroxyethyl guar, and carboxymethylhydroxypropyl guar ("CMHPG")), cellulose derivatives (e.g., hydroxethyl cellulose, carboxyethylcellulose, carboxymethylcellulose, and carboxymethyl-hydroxyethylcellulose), xanthan, scleroglucan, diutan, and combinations thereof. In certain embodiments, the gelling agents comprise an organic carboxylated polymer, such as CMHPG.

[0033] Suitable synthetic polymers include, but are not limited to, 2,2'-azo-bis(2,4-dimethyl valeronitrile), 2,2'-azo-bis(2,4-dimethyl-4-methoxy valeronitrile), polymers and copolymers of acrylamide ethyltrimethyl ammonium chloride, acrylamide, acrylamido- and methacrylamido-alkyl trialkyl ammonium salts, acrylamidomethylpropyl sulfonic acid, acrylamidopropyl trimethyl ammonium chloride, acrylamidopropyl methacrylamide, dimethylaminopropyl methacrylamide, dimethylaminopropylmethacrylamide, dimethylammonium chloride, dimethylethyl acrylate, fumaramide, methacrylamide, methacrylamido-propyl trimethyl ammonium chloride, methacrylamidopropylmethacrylamide, N-dodecylammonium chloride, methacrylamidopropylmethacrylamide, N-octylammonium chloride, methacrylamidopropyltrimethylammonium chloride, methacryloylalkyl trialkyl ammonium salts, methacryloyl ethyl trimethyl ammonium chloride, methacrylamidopropylidimethyl acetyl ammonium betaine, N,N-dimethylacrylamide, N-methylacrylamide, nonylphenoxypoly(ethylenoxy)ethylmethacrylate, partially hydrolyzed polyacrylamide, polypropyl-2-amino-2-methyl propane sulfonic acid, polyvinyl alcohol, sodium 2-acrylamido-2-methyl propane sulfonate, quaternized dimethylaminoethylacrylate, quaternized dimethy laminoethylmethacrylate, and derivatives and combinations thereof. In certain embodiments, the gelling agent comprises an acrylamide-2-(methyleneoxy)ethyltrimethylammonium methyl sulfate copolymer. In certain embodiments, the gelling agent may comprise an acrylamide-2-(methacryloxy)ethyltrimethylammonium chloride copolymer. In certain embodiments, the gelling agent may comprise a derivatized cellulose that comprises cellulose grafted with an alkyl or a vinyl monomer, such as those disclosed in U.S. Pat. Nos. 4,982,793, 5,067,565, and 5,122,549, the entire disclosures of which are incorporated herein by reference.

[0034] Additionally, polymers and copolymers that comprise one or more functional groups (e.g., hydroxyl, cis-hydroxyl, carboxylic acids, derivatives of carboxylic acids, sulfate, sulfonate, phosphate, phosphonate, amino, or amide groups) may be used as gelling agents.

[0035] The gelling agent may be present in the fracturing fluids useful in the methods of the present invention in an amount sufficient to provide the desired viscosity. In some embodiments, the gelling agents (i.e., the polymeric material) may be present in an amount in the range of from about 0.1% to about 10% by weight of the treatment fluid. In certain embodiments, the gelling agents may be present in an amount in the range of from about 0.15% to about 2.5% by weight of the fracturing fluid.

[0036] In some embodiments, the present invention provides methods comprising: providing a fracturing fluid comprising: an aqueous fluid, a microemulsion surfactant, and a co-surfactant, wherein the fracturing fluid is substantially free of an organic solvent; and placing the fracturing fluid into a subterranean formation at a rate sufficient to create or enhance at least one fracture in the subterranean formation.
In some embodiments, the present invention provides methods comprising: providing a composition comprising: a microemulsion surfactant, wherein the composition is substantially free of an organic solvent; placing the composition into at least a portion of a fracture in a subterranean formation having a first permeability; and allowing the composition to remove a water block from the subterranean formation to increase permeability of the subterranean formation to a second permeability.

In some embodiments, the increase in permeability of the subterranean formation correlates to a regain permeability of about 50% or greater. In some preferred embodiments, the increase in permeability of the subterranean formation correlates to a regain permeability of about 80% or greater.

To facilitate a better understanding of the present invention, the following examples of preferred embodiments are given. In no way should the following examples be read to limit, or to define, the scope of the invention.

Example 1

Regain permeability tests were performed for various surfactants using a 150g SD Crab Orchard Sandstone core to simulate a tight gas formation. Table 1 summarizes the composition of the surfactants including decyl amine oxide (C10A0), cocoamidopropyl betaine (CTS-485), dodecyl amine oxide (C12A0), microemulsion surfactant/solvent additive (commercially available as GASPERM 1000™ from Halliburton Energy Services, Inc.), microemulsion additive (commercially available as MA-844 from CIESI Chemical), KCl brine, and amphoteric surfactant. Some of the samples also include a cosurfactant (pyrrolidin commercially available as SURFADONE® from ISP Performance Chemicals or butanol). The tests were performed according to the following description.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Cosurfactant</th>
<th>Ratio</th>
<th>Regain Permeability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>decyl amine oxide (C10A0)</td>
<td>pyrrolidin ring (Surfalone 8)</td>
<td>1:2</td>
<td>76</td>
</tr>
<tr>
<td>cocoamidopropyl betaine (CTS-485)</td>
<td>butanol</td>
<td>1:5</td>
<td>100</td>
</tr>
<tr>
<td>dodecyl amine oxide (C12A0)</td>
<td>butanol</td>
<td>1:4</td>
<td>100</td>
</tr>
<tr>
<td>microemulsion surfactant/solvent additive (GASPERM 1000™)</td>
<td></td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>microemulsion additive (MA-844)</td>
<td></td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td></td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>amphoteric</td>
<td></td>
<td>17.5</td>
<td></td>
</tr>
</tbody>
</table>

First, an initial permeability was measured by running nitrogen through a dry core. The core sample was then saturated with 3 wt-% KCl brine neat or with 0.2 volume-% of the additive in brine. Next, nitrogen gas was run through the core to determine the regain permeability. FIG. 1 shows the results of the regain permeability tests.

As shown in FIG. 1, the core saturated in the KCl brine alone suffered severe damage (~70% permeability) due to water blocks. Gas permeability was greatly affected by capillary pressure and water spanning across the throat of the pores, as is evidenced by the major loss in permeability when soaking the core is just brine. By adding a surfactant or surfactant/solvent combination, gas/water interfacial tension was reduced and the surfactant was able to water wet the pore throat surface. It is believed that the surfactants eliminated water blocks, which lead to higher gas production. Due to the low viscosity of air, achieving high regain permeabilities for gas flow in water-saturated cores was difficult.

Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered, combined, or modified and all such variations are considered within the scope and spirit of the present invention. The invention illustratively disclosed herein suitably may be practiced in the absence of any element that is not specifically disclosed herein and/or any optional element disclosed herein. While compositions and methods are described in terms of “comprising,” “containing,” or “including” various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, “from about a to about b,” or, equivalently, “from approximately a to b,” or, equivalently, “from approximately a-b”) disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles “a” or “an,” as used in the claims, are defined herein to mean one or more than one of the element that it introduces. If there is any conflict in the usages of a word or term in this specification and one or more patent or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

The invention claimed is:

1. A method comprising:
   providing a fracturing fluid comprising:
   an aqueous fluid, and
   a microemulsion surfactant,
   wherein the fracturing fluid is substantially free of an organic solvent; and
   placing the fracturing fluid into a subterranean formation at a rate sufficient to create or enhance at least one fracture in the subterranean formation.

2. The method of claim 1, wherein the fracturing fluid further comprises at least one additive selected from the group consisting of: an acid, a biocide, a breaker, a clay stabilizer, a corrosion inhibitor, a friction reducer, a gelling agent, a crosslinking agent, an iron control agent, a scale inhibitor, a surfactant, a proppant, and any combination thereof.

3. The method of claim 1, wherein the microemulsion surfactant is selected from the group consisting of: polymeric surfactant, block copolymer surfactant, di-block polymer surfactant, hydrophobically modified surfactant, fluorosurfactant, non-ionic surfactant, anionic surfactant, cationic surfactant, zwitterionic surfactant, and any combination thereof.
4. The method of claim 1, wherein the aqueous fluid comprises at least one component selected from the group consisting of: fresh water, salt water, glycol, brine, weighted brine, and any combination thereof.

5. The method of claim 1, wherein the microemulsion surfactant is present in the fracturing fluid in an amount from about 0.01% to about 20% by weight of the fracturing fluid.

6. The method of claim 1 further comprising a co-surfactant.

7. The method of claim 6, wherein the co-surfactant is selected from the group consisting of: an alcohol, a glycol, a phenol, a thiol, a carboxylate, a ketone, an acrylamide, a sulfonate, a pyrrolidone, any derivative thereof, and any combination thereof.

8. The method of claim 1, wherein the microemulsion surfactant is selected from the group consisting of: an arginine methyl ester, an alkanoamine, an alkylendiamine, an alkyl ester sulfonate, an alkyl ether sulfonate, an alkyl ether sulfate, an alkali metal alkyl sulfates, an alkyl or an alkylaryl sulfonate, a sulfosuccinate, an alkyl or an alkylaryl disulfonate, an alkyl sulfonate, an alcohol polyoxyethylated and/or polyethoxylated sulfate, a taurate, an amine oxide, an ethoxylated amide, an ethoxylated fatty acid, an ethoxylated alcohol, an ethoxylated fatty amine, an ethoxylated alkyl amine, a betaine, a modified betaine, an alkylamidobetaine, a quaternary ammonium compound, any derivative thereof, and any combination thereof.

9. A method comprising:
providing a fracturing fluid comprising:
an aqueous fluid, and
a microemulsion surfactant, and
co-surfactant,
wherein the fracturing fluid is substantially free of an organic solvent; and
placing the fracturing fluid into a subterranean formation at a rate sufficient to create or enhance at least one fracture in the subterranean formation.

10. The method of claim 8, wherein the microemulsion surfactant is selected from the group consisting of: an arginine methyl ester, an alkanoamine, an alkylendiamine, an alkyl ester sulfonate, an alkyl ether sulfonate, an alkyl ether sulfate, an alkali metal alkyl sulfates, an alkyl or an alkylaryl sulfonate, a sulfosuccinate, an alkyl or an alkylaryl disulfonate, an alkyl sulfonate, an alcohol polyoxyethylated and/or polyethoxylated sulfate, a taurate, an amine oxide, an ethoxylated amide, an ethoxylated fatty acid, an ethoxylated alcohol, an ethoxylated fatty amine, an ethoxylated alkyl amine, a betaine, a modified betaine, an alkylamidobetaine, a quaternary ammonium compound, any derivative thereof, and any combination thereof.

11. The method of claim 8, wherein the co-surfactant is selected from the group consisting of: an alcohol, a glycol, a phenol, a thiol, a carboxylate, a ketone, an acrylamide, a sulfonate, a pyrrolidone, any derivative thereof, and any combination thereof.

12. The method of claim 8, wherein the fracturing fluid further comprises an additive selected from the group consisting of: an acid, a biocide, a breaker, a clay stabilizer, a corrosion inhibitor, a friction reducer, a gelling agent, a crosslinking agent, an iron control agent, a scale inhibitor, a surfactant, a proppant, and any combination thereof.

13. The method of claim 8, wherein the microemulsion surfactant is present in the fracturing fluid in an amount from about 0.01% to about 20% by weight of the fracturing fluid.

14. The method of claim 8, wherein the co-surfactant is present in the fracturing fluid in an amount from about 0.01% to about 20% by weight of the fracturing fluid.

15. A method comprising:
providing a composition comprising:
a microemulsion surfactant,
wherein the composition is substantially free of an organic solvent;
placing the composition into at least a portion of a fracture in a subterranean formation having a first permeability; and
allowing the composition to remove a water block from the subterranean formation to increase permeability of the subterranean formation to a second permeability.

16. The method of claim 15, wherein the microemulsion surfactant is selected from the group consisting of: an arginine methyl ester, an alkanoamine, an alkylendiamine, an alkyl ester sulfonate, an alkyl ether sulfonate, an alkyl ether sulfate, an alkali metal alkyl sulfates, an alkyl or an alkylaryl sulfonate, a sulfosuccinate, an alkyl or an alkylaryl disulfonate, an alkyl sulfonate, an alcohol polyoxyethylated and/or polyethoxylated sulfate, a taurate, an amine oxide, an ethoxylated amide, an ethoxylated fatty acid, an ethoxylated alcohol, an ethoxylated fatty amine, an ethoxylated alkyl amine, a betaine, a modified betaine, an alkylamidobetaine, a quaternary ammonium compound, any derivative thereof, and any combination thereof.

17. The method of claim 15, wherein the increase in permeability of the subterranean formation correlates to a regain permeability of about 50% or greater.

18. The method of claim 15, wherein the increase in permeability of the subterranean formation correlates to a regain permeability of about 80% or greater.

19. The method of claim 15, wherein the composition further comprises a co-surfactant.

20. The method of claim 15, wherein the microemulsion surfactant forms a microemulsion within the subterranean formation.