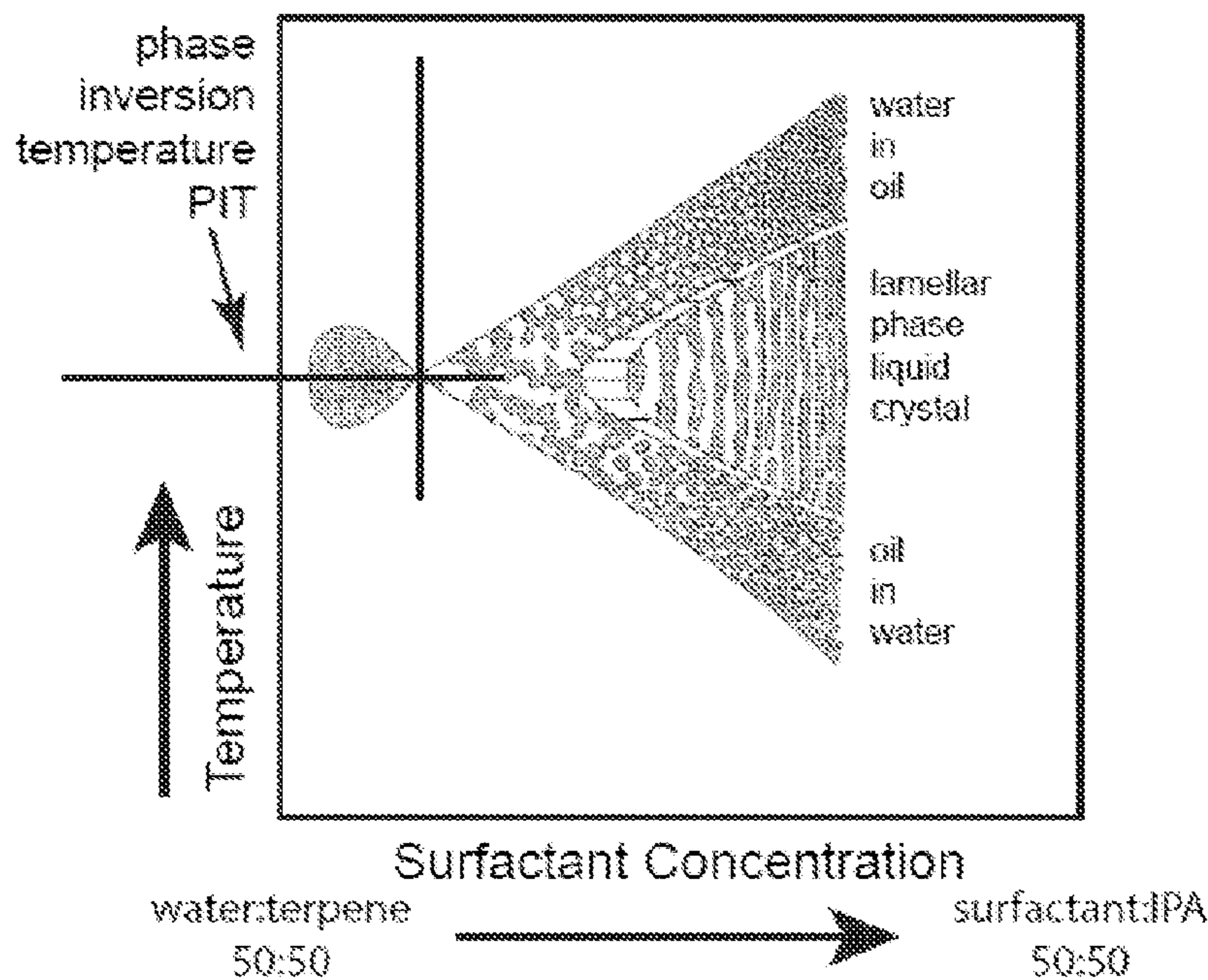




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(57) **Abrégé/Abstract:**

Methods and compositions for stimulating of the production of hydrocarbons (e.g., formation crude oil and/or formation gas) from subterranean formations are provided. In some embodiments, the compositions are emulsions or microemulsions, which may include water, a terpene, and a surfactant. In some embodiments, methods of selecting a composition for treating an oil or gas well are provided.

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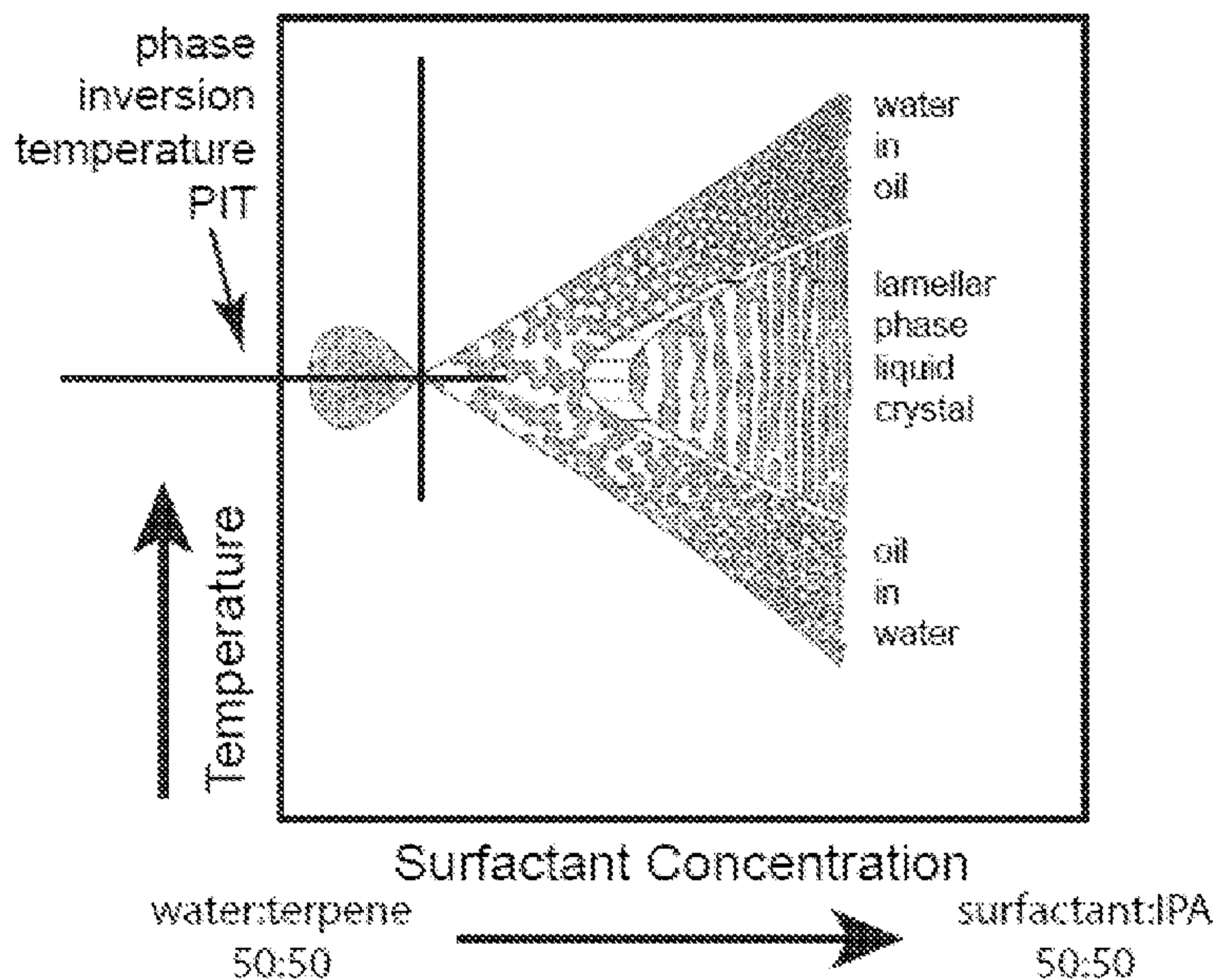
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Figure 1

(57) Abstract: Methods and compositions for
stimulating of the production of hydrocar-
bons (e.g., formation crude oil and/or forma-
tion gas) from subterranean formations are
provided. In some embodiments, the composi-
tions are emulsions or microemulsions,
which may include water, a terpene, and a
surfactant. In some embodiments, methods of
selecting a composition for treating an oil or
gas well are provided.

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detrimental effect on gas permeability and can impair well productivity. In addition, fluids may become trapped in the formation due to capillary end effects in and around the vicinity of the formation fractures.

In efforts to reduce phase trapping, additives have been incorporated into well-treatment fluids. Generally, the composition of additives comprises multi-component chemical substances and compositions that contain mutually distributed nanodomains of normally immiscible solvents, such as water and hydrocarbon-based organic solvents, stabilized by surfactants (e.g., microemulsions). The incorporation of additives into well-treatment fluids can increase crude oil or formation gas, for example by reducing capillary pressure and/or minimizing capillary end effects.

Although a number of additives are known in the art, there is a continued need for more effective additives for increasing crude oil or formation gas for wellbore remediation, drilling operations, and formation stimulation.

Summary of Invention

Methods and compositions for stimulating the production of hydrocarbons (e.g., formation crude oil and/or formation gas) from subterranean formations are provided.

In some embodiments, methods of selecting a composition for treating an oil or gas well having a wellbore are provided comprising determining whether displacement of residual aqueous treatment fluid by formation crude oil or displacement of residual aqueous treatment fluid by formation gas is preferentially stimulated for the oil or gas well having a wellbore; and selecting an emulsion or a microemulsion for injection into the wellbore to increase formation crude oil or formation gas production by the well, wherein the emulsion or the microemulsion comprises water, a terpene, and a surfactant, the ratio of water to terpene by weight is between about 3:1 and about 1:2; wherein the terpene has a phase inversion temperature greater than 43 °C when displacement of residual aqueous treatment fluid by formation crude oil is preferentially stimulated, or wherein the terpene has a phase inversion temperature less than 43 °C when displacement of residual aqueous treatment fluid by formation gas is preferentially stimulated. In some embodiments, the method further comprises injecting the emulsion or the microemulsion into the wellbore to increase production of formation crude oil or formation gas by the well.

In some embodiments, methods of treating an oil or gas well having a wellbore are provided comprising injecting an emulsion or a microemulsion into the wellbore of the oil or gas well to stimulate displacement of residual aqueous treatment fluid by formation crude oil and increase production of formation crude oil by the well, wherein
5 the emulsion or the microemulsion comprises water, a terpene, and a surfactant; wherein the ratio of water to terpene by weight is between about 3:1 and about 1:2; and wherein the terpene has a phase inversion temperature greater than 43 °C.

In some embodiments, methods of treating an oil or gas well having a wellbore are provided comprising injecting an emulsion or a microemulsion into the wellbore of
10 the oil or gas well to stimulate displacement of residual aqueous treatment fluid by formation gas and increase production of formation gas by the well, wherein the emulsion or the microemulsion comprises water, a terpene, and a surfactant; wherein the ratio of water to terpene by weight is between about 3:1 and about 1:2; and wherein the terpene has a phase inversion temperature less than 43 °C.

In some embodiments, methods of treating an oil or gas well having a wellbore are provided comprising using an emulsion or a microemulsion to stimulate displacement
15 of residual aqueous treatment fluid by formation crude oil or displacement of residual aqueous treatment fluid by formation gas by injecting the emulsion or the microemulsion into the wellbore of the oil or gas well, and increase production of formation crude oil or
20 formation gas by the well, wherein the emulsion or the microemulsion comprises water, a terpene, and a surfactant; wherein the ratio of water to terpene by weight is between about 10:1 and about 3:1; and wherein the terpene has a phase inversion temperature of greater than 43 °C.

In some embodiments, methods of treating an oil or gas well having a wellbore
25 are provided comprising using an emulsion or a microemulsion to stimulate displacement of residual aqueous treatment fluid by oil or displacement of residual aqueous treatment fluid by gas by injecting the emulsion or the microemulsion into the wellbore of the oil or gas well, and increase production of formation crude oil or formation gas by the well, wherein the emulsion or the microemulsion comprises water, a terpene, and a surfactant;
30 wherein the ratio of water to terpene by weight is between about 10:1 and about 3:1; and wherein the terpene has a phase inversion temperature of less than 43 °C.

In some embodiments, an emulsion or a microemulsion for stimulating an oil or gas well is provided comprising an aqueous phase; a surfactant; a freezing point depression agent; and a terpene, wherein the terpene is nopol.

In some embodiments, an emulsion or a microemulsion for stimulating an oil or gas well is provided comprising an aqueous phase; a surfactant; a freezing point depression agent; and a terpene, wherein the terpene is eucalyptol.

Other aspects, embodiments, and features of the invention will become apparent from the following detailed description when considered in conjunction with the accompanying drawings. All patent applications and patents incorporated herein by reference are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will control.

Brief Description of the Drawings

The accompanying drawings are not intended to be drawn to scale. In the drawings, each identical or nearly identical component that is illustrated in various figures is represented by a like numeral. For purposes of clarity, not every component may be labeled in every drawing. In the drawings:

Figure 1 shows an exemplary plot for determining the phase inversion temperature of a microemulsion, according to some embodiments.

Detailed Description

The present invention generally relates to methods and well-treatment compositions (e.g., emulsions or microemulsions) for stimulating of the production of liquid hydrocarbons (e.g., formation crude oil and/or formation gas) from subterranean formations. In some embodiments, the compositions comprise an emulsion or a microemulsion, as described in more detail herein. The emulsions or the microemulsions may include water, a terpene, a surfactant, and optionally a freezing point depression agent or other components. In some embodiments, the methods relate to stimulating displacement of residual aqueous treatment fluid by formation crude oil or formation gas to increase production of liquid hydrocarbons, as described in more detail below. In some embodiments, methods of selecting an emulsion or a microemulsion comprising a terpene are provided, wherein the emulsion or the microemulsion is selected so as to increase liquid hydrocarbon production.

As described herein, in some embodiments, the inventors have found that microemulsions or emulsions comprising certain terpenes increase the displacement (e.g., flowback) of residual aqueous treatment fluid by liquid hydrocarbons (e.g., crude oil) as compared to other terpenes. In other embodiments, emulsions or microemulsions comprising certain terpenes increase the displacement of residual aqueous treatment fluid by gaseous hydrocarbons as compared to other terpenes. Laboratory tests may be conducted, as described herein, to determine the displacement of residual aqueous treatment fluid by liquid hydrocarbons and/or gaseous hydrocarbons of an emulsion or a microemulsion

Petroleum is generally recovered from subterranean reservoirs through the use of drilled wells and production equipment. Wells are “stimulated” using various treatments (e.g., fracturing, acidizing) of geological formations to improve the recovery of liquid hydrocarbons. Oil and natural gas are found in, and produced from, porous and permeable subterranean formations. Based on techniques known in the art, as well as the preference for the desired product isolated (e.g., formation crude oil or formation gas), it may be preferential to stimulate either crude oil production or gas production from each well. A well drilled into a subterranean formation may penetrate formations containing liquid or gaseous hydrocarbons or both, as well as connate water or brine. The gas-to-oil ratio is termed the GOR. The operator of the well may choose to complete the well in such a way as to produce (for example) predominantly liquid hydrocarbons (crude oil). Alternatively, the operator may be fracturing a tight gas shale formation containing predominantly gaseous hydrocarbons.

Incorporation of the emulsions or the microemulsions described herein (e.g., comprising water, a terpene, and a surfactant) into well-treatment fluids (e.g., fracturing fluids) can aid in reducing fluid trapping, for example, by reducing capillary pressure and/or minimizing capillary end effects. In addition, incorporation of the emulsions or the microemulsions described herein into well-treatment fluids can promote increased flow back of aqueous phases following well treatment, and thus, increase production of liquid and/or gaseous hydrocarbons. That is, incorporation of an emulsion or a microemulsion described herein can aid in the displacement of residual aqueous treatment fluid by formation crude oil and/or formation gas. Residual aqueous treatment fluids may include those fluids employed for fracturing, as well as residual aqueous fluids originally present in the well.

In some embodiments, methods of treating an oil or gas well are provided. In some embodiments, the methods comprise injecting an emulsion or a microemulsion into the wellbore of the oil or gas well to stimulate displacement of residual aqueous treatment fluid by formation crude oil or formation gas, and increase production of liquid hydrocarbons by the well.

In some embodiments, methods are provided for selecting a composition for treating an oil or gas well. The inventors have discovered that certain terpenes are more effective at stimulating displacement of residual aqueous treatment fluid by formation crude oil or displacement of residual aqueous treatment fluid by formation gas for the oil or gas well and that the selection of the terpene may be influenced by the ratio of water to terpene in the emulsion or the microemulsion.

In some embodiments, if displacement of residual aqueous treatment fluid by formation crude oil is preferentially stimulated and the emulsion or the microemulsion comprises water to terpene at a ratio between about 3:1 and about 1:2, then the terpene may be selected to have a phase inversion temperature greater than 43 °C, as determined by the method described herein. Alternatively, if displacement of residual aqueous treatment fluid by formation gas is preferentially stimulated and the emulsion or the microemulsion comprises water to terpene at a ratio between about 3:1 and about 1:2, then the terpene may be selected to have a phase inversion temperature less than 43 °C, as determined by the method described herein. In some embodiments, the ratio of water to terpene by weight is between about 3:1 and about 1:1.5, or between about 2:1 and about 1:1.5.

In some embodiments, to stimulate displacement of residual aqueous treatment fluid by formation crude oil, the ratio of water to terpene by weight in the emulsion or the microemulsion may be between about 3:1 and about 1:2, or between about 2:1 and about 1:1.5, and the terpene may be selected to have a phase inversion temperature greater than 43 °C, as determined by the method described herein. In some embodiments, to stimulate displacement of residual aqueous treatment fluid by formation crude oil or formation gas and increase production of formation gas the well, the ratio of water to terpene by weight in the emulsion or the microemulsion may be between about 3:1 and about 1:2, or between about 2:1 and about 1:1.5, and the terpene may be selected to have a phase inversion temperature less than 43 °C, as determined by the method described herein.

In some embodiments, to stimulate displacement of residual aqueous treatment fluid by formation crude oil, wherein the ratio of water to terpene by weight in the emulsion or the microemulsion is between about 10:1 and about 3:1, the terpene may be selected to have a phase inversion temperature greater than 43 °C, as determined by the method described herein. In some embodiments, to stimulate displacement of residual aqueous treatment fluid by formation gas and increase production of formation gas by the well, wherein the ratio of water to terpene by weight in the emulsion or the microemulsion is between about 10:1 and about 3:1, the terpene may be selected to have a phase inversion temperature less than 43 °C, as determined by the method described herein. In some embodiments, the ratio of water to terpene by weight is between about 6:1 and about 5:1.

It should be understood, that in embodiments where a microemulsion is said to be injected into a wellbore, that the microemulsion may be diluted and/or combined with other liquid component(s) prior to and/or during injection. For example, in some embodiments, the microemulsion is diluted with an aqueous carrier fluid (e.g., water, brine, sea water, fresh water, or a treatment fluid such as a fracturing fluid comprising polymers, sand, etc.) prior to and/or during injection into the wellbore. In some embodiments, a composition for injecting into a wellbore is provided comprising a microemulsion as described herein and an aqueous carrier fluid, wherein the microemulsion is present in an amount between about 0.1 and about 50 gallons per thousand gallons of dilution fluid (“gpt”), or between about 0.5 and about 10 gpt, or between about 0.5 and about 2 gpt. Generally, dilution of a microemulsion does not result in the breakdown of the microemulsion.

In some embodiments, emulsions or microemulsions are provided. The terms should be understood to include emulsions or microemulsions that have a water continuous phase, or that have an oil continuous phase, or microemulsions that are bicontinuous or multiple continuous phases of water and oil.

As used herein, the term “emulsion” is given its ordinary meaning in the art and refers to dispersions of one immiscible liquid in another, in the form of droplets, with diameters approximately in the range of 100-1,000 nanometers. Emulsions may be thermodynamically unstable and/or require high shear forces to induce their formation.

As used herein, the term “microemulsion” is given its ordinary meaning in the art and refers to dispersions of one immiscible liquid in another, in the form of droplets,

with diameters approximately in the range between about 1 and about 1000 nm, or between 10 and about 1000 nanometers, or between about 10 and about 500 nm, or between about 10 and about 300 nm, or between about 10 and about 100 nm.

Microemulsions are clear or transparent because they contain particles smaller than the wavelength of visible light. In addition, microemulsions are homogeneous thermodynamically stable single phases, and form spontaneously, and thus, differ markedly from thermodynamically unstable emulsions, which generally depend upon intense mixing energy for their formation. Microemulsions may be characterized by a variety of advantageous properties including, by not limited to, (i) clarity, (ii) very small particle size, (iii) ultra-low interfacial tensions, (iv) the ability to combine properties of water and oil in a single homogeneous fluid, (v) shelf life stability, and (vi) ease of preparation.

In some embodiments, the microemulsions described herein are stabilized microemulsions that are formed by the combination of a solvent-surfactant blend with an appropriate oil-based or water-based carrier fluid. Generally, the microemulsion forms upon simple mixing of the components without the need for high shearing generally required in the formation of ordinary emulsions. In some embodiments, the microemulsion is a thermodynamically stable system, and the droplets remain finely dispersed over time. In some cases, the average droplet size ranges from about 10 nm to about 300 nm.

It should be understood, that while much of the description herein focuses on microemulsions, this is by no means limiting, and emulsions may be employed where appropriate.

In some embodiments, the emulsion or microemulsion is a single emulsion or microemulsion. For example, the emulsion or microemulsion comprises a single layer of a surfactant. In other embodiments, the emulsion or microemulsion may be a double or multilamellar emulsion or microemulsion. For example, the emulsion or microemulsion comprises two or more layers of a surfactant. In some embodiments, the emulsion or microemulsion comprises a single layer of surfactant surrounding a core (e.g., one or more of water, oil, solvent, and/or other additives) or a multiple layers of surfactant (e.g., two or more concentric layers surrounding the core). In certain embodiments, the emulsion or microemulsion comprises two or more immiscible cores (e.g., one or more

of water, oil, solvent, and/or other additives which have equal or about equal affinities for the surfactant).

In some embodiments, a microemulsion comprises water, a terpene, and a surfactant. In some embodiments, the microemulsion may further comprise additional components, for example, a freezing point depression agent. Details of each of the components of the microemulsions are described in detail herein. In some embodiments, the components of the microemulsions are selected so as to reduce or eliminate the hazards of the microemulsion to the environment and/or the subterranean reservoirs.

In some embodiments, the microemulsion comprises a terpene or a terpenoid. The microemulsion may comprise a single terpene or terpenoid or a combination of two or more terpenes and/or terpenoids. For example, in some embodiments, the terpene or terpenoid comprises a first type of terpene or terpenoid and a second type of terpene or terpenoid. Terpenes may be generally classified as monoterpenes (e.g., having two isoprene units), sesquiterpenes (e.g., having 3 isoprene units), diterpenes, or the like.

The term terpenoid also includes natural degradation products, such as ionones, and natural and synthetic derivatives, e.g., terpene alcohols, aldehydes, ketones, acids, esters, epoxides, and hydrogenation products (e.g., see Ullmann's Encyclopedia of Industrial Chemistry, 2012, pages 29-45). It should be understood, that while much of the description herein focuses on terpenes, this is by no means limiting, and terpenoids may be employed where appropriate. In some cases, the terpene is a naturally occurring terpene. In some cases, the terpene is a non-naturally occurring terpene and/or a chemically modified terpene (e.g., saturated terpene, terpene amine, fluorinated terpene, or silylated terpene).

In some embodiments, the terpene is a monoterpene. Monoterpenes may be further classified as acyclic, monocyclic, and bicyclic (e.g., with a total number of carbons in the range between 18 and 20), as well as whether the monoterpene comprises one or more oxygen atoms (e.g., alcohol groups, ester groups, carbonyl groups, etc.). In some embodiments, the terpene is an oxygenated terpene, for example, a terpene comprising an alcohol, an aldehyde, and/or a ketone group. In some embodiments, the terpene comprises an alcohol group. Non-limiting examples of terpenes comprising an alcohol group are linalool, geraniol, nopol, α -terpineol, and menthol. In some embodiments, the terpene comprises an ether-oxygen, for example, eucalyptol, or a

carbonyl oxygen, for example, menthone. In some embodiments, the terpene does not comprise an oxygen atom, for example, d-limonene.

Non-limiting examples of terpenes include linalool, geraniol, nopol, α -terpineol, menthol, eucalyptol, menthone, d-limonene, terpinolene, β -occimene, γ -terpinene, α -pinene, and citronellene. In a particular embodiment, the terpene is selected from the group consisting of α -terpineol, α -pinene, nopol, and eucalyptol. In one embodiment, the terpene is nopol. In another embodiment, the terpene is eucalyptol. In some embodiments, the terpene is not limonene (e.g., d-limonene). In some embodiments, the emulsion is free of limonene

In some embodiments, the terpene is a non-naturally occurring terpene and/or a chemically modified terpene (e.g., saturated terpene). In some cases, the terpene is a partially or fully saturated terpene (e.g., p-menthane, pinane). In some cases, the terpene is a non-naturally occurring terpene. Non-limiting examples of non-naturally occurring terpenes include, menthene, p-cymene, r-carvone, terpinenes (e.g., alpha-terpinenes, beta-terpinenes, gamma-terpinenes), dipentenes, terpinolenes, borneol, alpha-terpinamine, and pine oils.

In some embodiments, the terpene is classified in terms of its phase inversion temperature (PIT). The term phase inversion temperature is given its ordinary meaning in the art and refers to the temperature at which an oil in water microemulsion inverts to a water in oil microemulsion (or vice versa). Those of ordinary skill in the art will be aware of methods for determining the PIT for a microemulsion comprising a terpene (e.g., see Strey, *Colloid & Polymer Science*, 1994. 272(8): p. 1005-1019; Kahlweit et al., *Angewandte Chemie International Edition in English*, 1985. 24(8): p. 654-668). The PIT values described herein were determined using a 1:1 ratio of terpene (e.g., one or more terpenes):de-ionized water and varying amounts (e.g., between about 20 wt% and about 60 wt%; generally, between 3 and 9 different amounts are employed) of a 1:1 blend of surfactant comprising linear C₁₂-C₁₅ alcohol ethoxylates with on average 7 moles of ethylene oxide (e.g., Neodol 25-7):isopropyl alcohol wherein the upper and lower temperature boundaries of the microemulsion region can be determined and a phase diagram may be generated. Those of ordinary skill in the art will recognize that such a phase diagram (e.g., a plot of temperature against surfactant concentration at a constant oil-to-water ratio) may be referred to as fish diagram or a Kahlweit plot. The temperature at the vertex is the PIT. An exemplary fish diagram indicating the PIT is shown in Figure

1. PITs for non-limiting examples of terpenes determined using this experimental procedure outlined above are given in Table 1.

Table 1: Phase inversion temperatures for non-limiting examples of terpenes.

Terpene	Phase Inversion Temperature °C (°F)
linalool	-4 (24.8)
geraniol	-0.5 (31.1)
nopol	2.5 (36.5)
α -terpineol	4.6 (40.3)
menthol	16 (60.8)
eucalyptol	31 (87.8)
menthone	32 (89.6)
d-limonene	43 (109.4)
terpinolene	48 (118.4)
β -occimene	49 (120.2)
γ -terpinene	49 (120.2)
α -pinene	57 (134.6)
citronellene	58 (136.4)

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In some embodiments, as described in more detail herein, the terpene has a PIT greater than and/or less than 43 °C, as determined by the method described herein. In some embodiments, the terpene has a PIT greater than 43 °C, as determined by the method described herein. In some embodiments, the terpene has a PIT less than 43 °C, as determined by the method described herein. In some embodiments, the terpene has a PIT greater than 32 °C, as determined by the method described herein. In some embodiments, the terpene has a PIT less than 32 °C, as determined by the method described herein. In some embodiments, the PIT is between about -10 °C and about 70 °C, or between about -4 °C and about 60 °C, as determined by the method described herein. In some

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embodiments, the minimum PIT is -10 °C, or -4 °C, as determined by the method described herein. In some embodiments, the maximum PIT is 70 °C, or 60 °C, as determined by the method described herein.

In certain embodiments, the solvent utilized in the emulsion or microemulsion herein may comprise one or more impurities. For example, in some embodiments, a

solvent (e.g., a terpene) is extracted from a natural source (e.g., citrus), and may comprise one or more impurities present from the extraction process. In some embodiment, the solvent comprises a crude cut (e.g., uncut crude oil, for example, made by settling, separation, heating, etc.). In some embodiments, the solvent is a crude oil
5 (e.g., naturally occurring crude oil, uncut crude oil, crude oil extracted from the wellbore, synthetic crude oil, etc.). In some embodiments, the solvent is a citrus extract (e.g., crude orange oil, orange oil, etc.).

The terpene may be present in the microemulsion in any suitable amount. In some embodiments, terpene is present in an amount between about 2 wt% and about 60 wt%,
10 or between about 5 wt% and about 40 wt%, or between about 5 wt% and about 30 wt%, versus the total microemulsion composition. In some embodiments, the terpene is present in an amount between about 1 wt% and about 99 wt%, or between about 2 wt% and about 90 wt %, or between about 1 wt% and about 60 wt%, or between about 2 wt% and
15 about 60 wt%, or between about 1 wt% and about 50 wt%, or between about 1 wt% and about 30 wt%, or between about 5 wt% and about 40 wt%, or between about 5 wt% and about 30 wt%, or between about 2 wt% and about 25 wt%, or between about 5 wt% and about 25 wt%, or between about 60 wt% and about 95 wt%, or between about 70 wt% or
20 about 95 wt%, or between about 75 wt% and about 90 wt%, or between about 80 wt% and about 95 wt%, versus the total microemulsion composition.

The water to terpene ratio in a microemulsion may be varied, as described herein. In some embodiments, the ratio of water to terpene, along with other parameters of the terpene (e.g., phase inversion temperature of the terpene) may be varied so that displacement of residual aqueous treatment fluid by formation gas and/or formation
25 crude is preferentially stimulated. In some embodiments, the ratio of water to terpene by weight is between about 3:1 and about 1:2, or between about 2:1 and about 1:1.5. In other embodiments, the ratio of water to terpene is between about 10:1 and about 3:1, or between about 6:1 and about 5:1.

Generally, the microemulsion comprises an aqueous phase comprising water. The water may be provided from any suitable source (e.g., sea water, fresh water, deionized
30 water, reverse osmosis water, water from field production). The water may be present in any suitable amount. In some embodiments, the total amount of water present in the microemulsion is between about 1 wt% about 95 wt%, or between about 1 wt% about 90

wt%, or between about 1 wt% and about 60 wt%, or between about 5 wt% and about 60 wt% or between about 10 and about 55 wt%, or between about 15 and about 45 wt%, versus the total microemulsion composition.

In some embodiments, the emulsion or microemulsion may comprise mutual solvent which is miscible together with the water and the terpene. In some embodiments, the mutual solvent is present in an amount between about at 0.5 wt% to about 30% of mutual solvent. Non-limiting examples of suitable mutual solvents include ethyleneglycolmonobutyl ether (EGMBE), dipropylene glycol monomethyl ether, short chain alcohols (e.g., isopropanol), tetrahydrofuran, dioxane, dimethylformamide, and dimethylsulfoxide.

In some embodiments, the microemulsion comprises a surfactant. The microemulsion may comprise a single surfactant or a combination of two or more surfactants. For example, in some embodiments, the surfactant comprises a first type of surfactant and a second type of surfactant. The term "surfactant," as used herein, is given its ordinary meaning in the art and refers to compounds having an amphiphilic structure which gives them a specific affinity for oil/water-type and water/oil-type interfaces which helps the compounds to reduce the free energy of these interfaces and to stabilize the dispersed phase of a microemulsion. The term surfactant encompasses cationic surfactants, anionic surfactants, amphoteric surfactants, nonionic surfactants, zwitterionic surfactants, and mixtures thereof. In some embodiments, the surfactant is a nonionic surfactant. Nonionic surfactants generally do not contain any charges. Amphoteric surfactants generally have both positive and negative charges, however, the net charge of the surfactant can be positive, negative, or neutral, depending on the pH of the solution. Anionic surfactants generally possess a net negative charge. Cationic surfactants generally possess a net positive charge. Awitterionic surfactants are generally not pH dependent. A zwitterion is a neutral molecule with a positive and a negative electrical charge, though multiple positive and negative charges can be present. Zwitterions are distinct from dipole, at different locations within that molecule.

In some embodiments, the surfactant is an amphiphilic block copolymer where one block is hydrophobic and one block is hydrophilic. In some cases, the total molecular weight of the polymer is greater than 5000 daltons. The hydrophilic block of these polymers can be nonionic, anionic, cationic, amphoteric, or zwitterionic.

The term surface energy, as used herein, is given its ordinary meaning in the art and refers to the extent of disruption of intermolecular bonds that occur when the surface is created (e.g., the energy excess associated with the surface as compared to the bulk). Generally, surface energy is also referred to as surface tension (e.g., for liquid-gas
5 interfaces) or interfacial tension (e.g., for liquid-liquid interfaces). As will be understood by those skilled in the art, surfactants generally orient themselves across the interface to minimize the extent of disruption of intermolecular bonds (i.e. lower the surface energy). Typically, a surfactant at an interface between polar and non-polar phases orient themselves at the interface such that the difference in polarity is minimized.

10 Those of ordinary skill in the art will be aware of methods and techniques for selecting surfactants for use in the microemulsions described herein. In some cases, the surfactant(s) are matched to and/or optimized for the particular oil or solvent in use. In some embodiments, the surfactant(s) are selected by mapping the phase behavior of the microemulsion and choosing the surfactant(s) that gives the desired range of stability. In
15 some cases, the stability of the microemulsion over a wide range of temperatures is targeted as the microemulsion may be subject to a wide range of temperatures due to the environmental conditions present at the subterranean formation and/or reservoir.

Suitable surfactants for use with the compositions and methods described herein will be known in the art. In some embodiments, the surfactant is an alkyl polyglycol
20 ether, for example, having 2-250 ethylene oxide (EO) (e.g., or 2-200, or 2-150, or 2-100, or 2-50, or 2-40) units and alkyl groups of 4-20 carbon atoms. In some embodiments, the surfactant is an alkylaryl polyglycol ether having 2-250 EO units (e.g., or 2-200, or 2-150, or 2-100, or 2-50, or 2-40) and 8-20 carbon atoms in the alkyl and aryl groups. In some embodiments, the surfactant is an ethylene oxide/propylene oxide (EO/PO) block
25 copolymer having 2-250 EO or PO units (e.g., or 2-200, or 2-150, or 2-100, or 2-50, or 2-40). In some embodiments, the surfactant is a fatty acid polyglycol ester having 6-24 carbon atoms and 2-250 EO units (e.g., or 2-200, or 2-150, or 2-100, or 2-50, or 2-40). In some embodiments, the surfactant is a polyglycol ether of hydroxyl-containing triglycerides (e.g., castor oil). In some embodiments, the surfactant is an
30 alkylpolyglycoside of the general formula $R''-O-Z_n$, where R'' denotes a linear or branched, saturated or unsaturated alkyl group having on average 8-24 carbon atoms and Z_n denotes an oligoglycoside group having on average $n=1-10$ hexose or pentose units or mixtures thereof. In some embodiments, the surfactant is a fatty ester of glycerol,

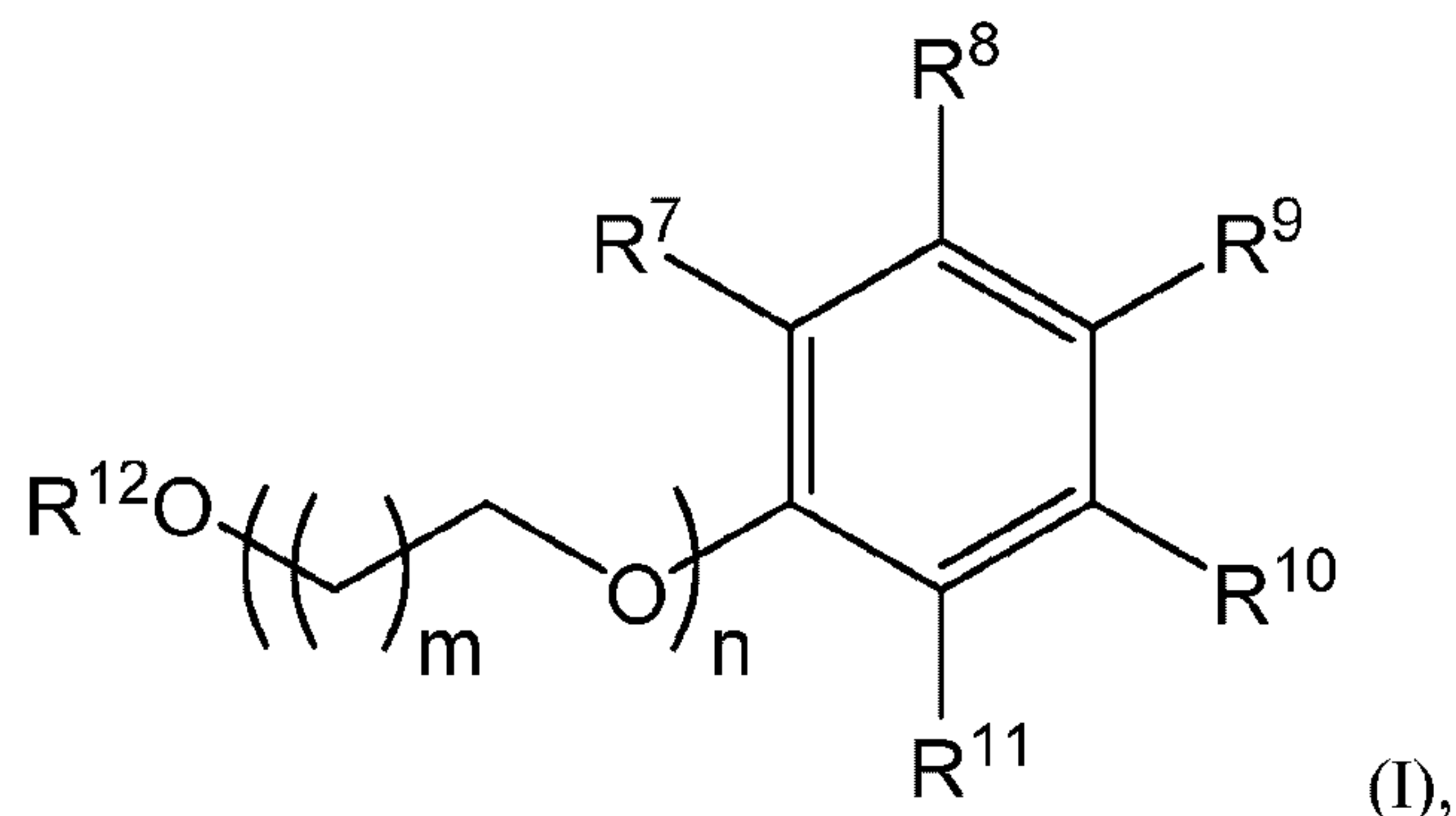
sorbitol, or pentaerythritol. In some embodiments, the surfactant is an amine oxide (e.g., dodecyldimethylamine oxide). In some embodiments, the surfactant is an alkyl sulfate, for example having a chain length of 8-18 carbon atoms, alkyl ether sulfates having 8-18 carbon atoms in the hydrophobic group and 1-40 ethylene oxide (EO) or propylene oxide (PO) units. In some embodiments, the surfactant is a sulfonate, for example, an 5 alkyl sulfonate having 8-18 carbon atoms, an alkylaryl sulfonate having 8-18 carbon atoms, an ester or half ester of sulfosuccinic acid with monohydric alcohols or alkylphenols having 4-15 carbon atoms, or a multisulfonate (e.g., comprising two, three, four, or more, sulfonate groups). In some cases, the alcohol or alkylphenol can also be 10 ethoxylated with 1-250 EO units (e.g., or 2-200, or 2-150, or 2-100, or 2-50, or 2-40). In some embodiments, the surfactant is an alkali metal salt or ammonium salt of a carboxylic acid or poly(alkylene glycol) ether carboxylic acid having 8-20 carbon atoms in the alkyl, aryl, alkaryl or aralkyl group and 1-250 EO or PO units (e.g., or 2-200, or 2-150, or 2-100, or 2-50, or 2-40). In some embodiments, the surfactant is a partial 15 phosphoric ester or the corresponding alkali metal salt or ammonium salt, e.g., an alkyl and alkaryl phosphate having 8-20 carbon atoms in the organic group, an alkylether phosphate or alkarylether phosphate having 8-20 carbon atoms in the alkyl or alkaryl group and 1-250 EO units (e.g., or 2-200, or 2-150, or 2-100, or 2-50, or 2-40). In some embodiments, the surfactant is a salt of primary, secondary, or tertiary fatty amine 20 having 8-24 carbon atoms with acetic acid, sulfuric acid, hydrochloric acid, and phosphoric acid. In some embodiments, the surfactant is a quaternary alkyl- and alkylbenzylammonium salt, whose alkyl groups have 1-24 carbon atoms (e.g., a halide, sulfate, phosphate, acetate, or hydroxide salt). In some embodiments, the surfactant is an alkyipyridinium, an alkylimidazolium, or an alkyloxazolium salt whose alkyl chain 25 has up to 18 carbons atoms (e.g., a halide, sulfate, phosphate, acetate, or hydroxide salt). In some embodiments, the surfactant is amphoteric or zwitterionic, including sultaines (e.g., cocamidopropyl hydroxysultaine), betaines (e.g., cocamidopropyl betaine), or phosphates (e.g., lecithin). Non-limiting examples of specific surfactants include a linear C₁₂-C₁₅ ethoxylated alcohols with 5-12 moles of EO, lauryl alcohol ethoxylate with 4-8 30 moles of EO, nonyl phenol ethoxylate with 5-9 moles of EO, octyl phenol ethoxylate with 5-9 moles of EO, tridecyl alcohol ethoxylate with 5-9 moles of EO, Pluronic® matrix of EO/PO copolymers, ethoxylated cocoamide with 4-8 moles of EO, ethoxylated coco fatty acid with 7-11 moles of EO, and cocoamidopropyl amine oxide.

In some embodiments, the surfactant is a siloxane surfactant as described in U.S. Patent Application Serial No. 13/831,410, filed March 14, 2014.

In some embodiments, the surfactant is a Gemini surfactant. Gemini surfactants generally have the structure of multiple amphiphilic molecules linked
5 together by one or more covalent spacers. In some embodiments, the surfactant is an extended surfactant, wherein the extended surfactant has the structure where a non-ionic hydrophilic spacer (e.g. ethylene oxide or propylene oxide) connects an ionic hydrophilic group (e.g. carboxylate, sulfate, phosphate).

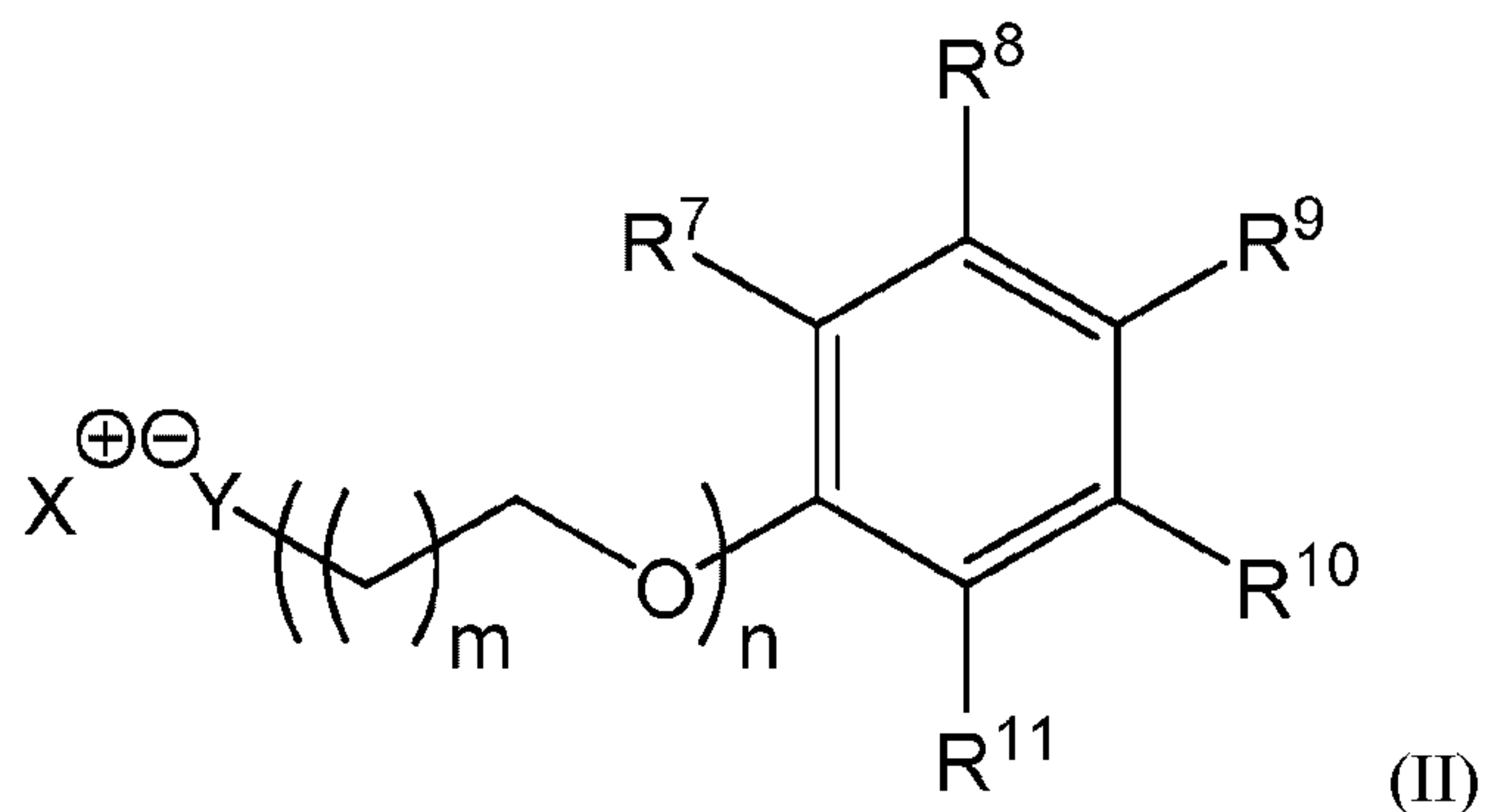
In some embodiments the surfactant is an alkoxyated polyimine with a
10 relative solubility number (RSN) in the range of 5-20. As will be known to those of ordinary skill in the art, RSN values are generally determined by titrating water into a solution of surfactant in 1,4-dioxane. The RSN value is generally defined as the amount of distilled water necessary to be added to produce persistent turbidity. In some embodiments the surfactant is an alkoxyated novolac resin (also known as a
15 phenolic resin) with a relative solubility number in the range of 5-20. In some embodiments the surfactant is a block copolymer surfactant with a total molecular weight greater than 5000 daltons. The block copolymer may have a hydrophobic block that is comprised of a polymer chain that is linear, branched, hyperbranched, dendritic or cyclic. Non-limiting examples of monomeric repeat units in the
20 hydrophobic chains of block copolymer surfactants are isomers of acrylic, methacrylic, styrenic, isoprene, butadiene, acrylamide, ethylene, propylene and norbornene. The block copolymer may have a hydrophilic block that is comprised of a polymer chain that is linear, branched, hyper branched, dendritic or cyclic. Non-limiting examples of monomeric repeat units in the hydrophilic chains of the block
25 copolymer surfactants are isomers of acrylic acid, maleic acid, methacrylic acid, ethylene oxide, and acrylamine.

In some embodiments, the surfactant has a structure as in Formula I:



wherein each of R^7 , R^8 , R^9 , R^{10} , and R^{11} are the same or different and are selected from the group consisting of hydrogen, optionally substituted alkyl, and $-\text{CH}=\text{CHAr}$, wherein Ar is an aryl group, provided at least one of R^7 , R^8 , R^9 , R^{10} , and R^{11} is $-\text{CH}=\text{CHAr}$, R^{12} is hydrogen or alkyl, n is 1-100, and each m is independently 1 or 2. In some
 5 embodiments, for a compound of Formula (I), R^{12} is hydrogen or C_{1-6} alkyl. In some embodiments, for a compound of Formula (I), R^{12} is H, methyl, or ethyl. In some embodiments, for a compound of Formula (I), R^{12} is H.

In some embodiments, the surfactant has a structure as in Formula II:

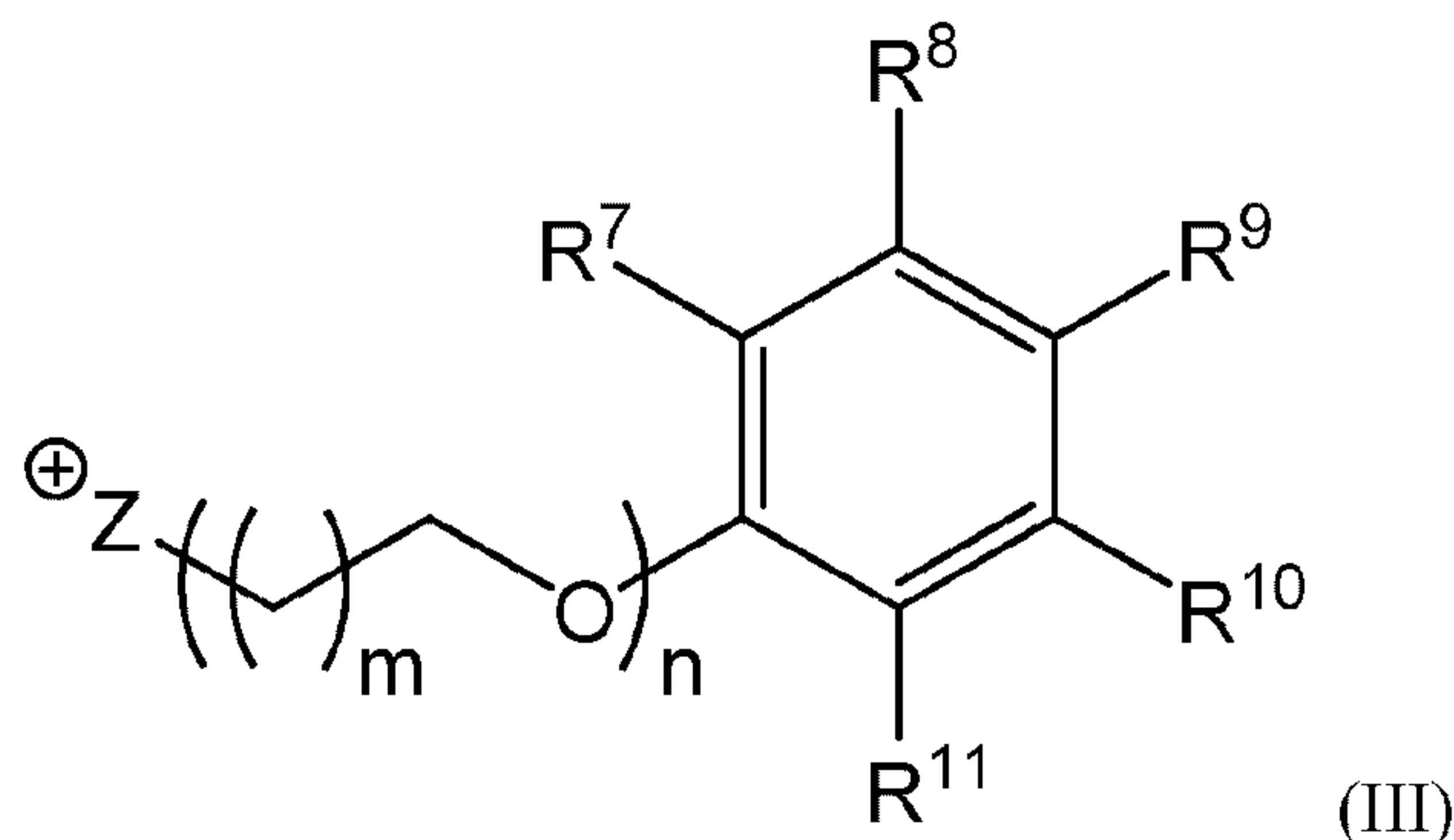


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wherein each of R^7 , R^8 , R^9 , R^{10} , and R^{11} are the same or different and are selected from the group consisting of hydrogen, optionally substituted alkyl, and $-\text{CH}=\text{CHAr}$, wherein Ar is an aryl group, provided at least one of R^7 , R^8 , R^9 , R^{10} , and R^{11} is $-\text{CH}=\text{CHAr}$, Y^- is an anionic group, X^+ is a cationic group, n is 1-100, and each m is independently 1 or 2.
 15 In some embodiments, for a compound of Formula (II), X^+ is a metal cation or $\text{N}(\text{R}^{13})_4$, wherein each R^{13} is independently selected from the group consisting of hydrogen, optionally substituted alkyl, or optionally substituted aryl. In some embodiments, X^+ is NH_4 . Non-limiting examples of metal cations are Na^+ , K^+ , Mg^{+2} , and Ca^{+2} . In some embodiments, for a compound of Formula (II), Y^- is $-\text{O}^-$, $-\text{SO}_2\text{O}^-$, or $-\text{OSO}_2\text{O}^-$.

20

In some embodiments, the surfactant has a structure as in Formula III:



wherein each of R^7 , R^8 , R^9 , R^{10} , and R^{11} are the same or different and are selected from the group consisting of hydrogen, optionally substituted alkyl, and $-\text{CH}=\text{CHAr}$, wherein Ar is an aryl group, provided at least one of R^7 , R^8 , R^9 , R^{10} , and R^{11} is $-\text{CH}=\text{CHAr}$, Z^+ is a cationic group, n is 1-100, and each m is independently 1 or 2. In some embodiments, for a compound of Formula (III), Z^+ is $\text{N}(\text{R}^{13})_3$, wherein each R^{13} is independent selected from the group consisting of hydrogen, optionally substituted alkyl, or optionally substituted aryl.

In some embodiments, for a compound of Formula (I), (II), or (III), two of R^7 , R^8 , R^9 , R^{10} , and R^{11} are $-\text{CH}=\text{CHAr}$. In some embodiments, for a compound of Formula (I), (II), or (III), one of R^7 , R^8 , R^9 , R^{10} , and R^{11} is $-\text{CH}=\text{CHAr}$ and each of the other groups is hydrogen. In some embodiments, for a compound of Formula (I), (II), or (III), two of R^7 , R^8 , R^9 , R^{10} , and R^{11} are $-\text{CH}=\text{CHAr}$ and each of the other groups is hydrogen. In some embodiments, for a compound of Formula (I), (II), or (III), R^7 and R^8 are $-\text{CH}=\text{CHAr}$ and R^9 , R^{10} , and R^{11} are each hydrogen. In some embodiments, for a compound of Formula (I), (II), or (III), three of R^7 , R^8 , R^9 , R^{10} , and R^{11} are $-\text{CH}=\text{CHAr}$ and each of the other groups is hydrogen. In some embodiments, for a compound of Formula (I), (II), or (III), R^7 , R^8 , and R^9 are $-\text{CH}=\text{CHAr}$ and R^{10} and R^{11} are each hydrogen. In some embodiments, for a compound of Formula (I), (II), or (III), Ar is phenyl. In some embodiments, for a compound of Formula (I), (II), or (III), each m is 1. In some embodiments, for a compound of Formula (I), (II), or (III), each m is 2. In some embodiments, for a compound of Formula (I), (II), or (III), n is 6-100, or 1-50, or 6-50, or 6-25, or 1-25, or 5-50, or 5-25, or 5-20.

Those of ordinary skill in the art will be aware of methods and techniques for selecting surfactant for use in the microemulsions described herein. In some cases, the surfactant(s) are matched to and/or optimized for the particular oil or solvent in use. In some embodiments, the surfactant(s) are selected by mapping the phase behavior of the

microemulsion and choosing the surfactant(s) that gives the desired range of stability. In some cases, the stability of the microemulsion over a wide range of temperatures is targeting as the microemulsion may be subject to a wide range of temperatures due to the environmental conditions present at the subterranean formation.

5 In some embodiments, the emulsion or microemulsion may comprise one or more additives in addition to water, solvent (e.g., one or more types of solvents), and surfactant (e.g., one or more types of surfactants). In some embodiments, the additive is an alcohol, a freezing point depression agent, an acid, a salt, a proppant, a scale inhibitor, a friction reducer, a biocide, a corrosion inhibitor, a buffer, a viscosifier, a clay swelling
10 inhibitor, an oxygen scavenger, and/or a clay stabilizer.

 The surfactant may be present in the microemulsion in any suitable amount. In some embodiments, the surfactant is present in an amount between about 10 wt% and about 70 wt%, or between about 15 wt% and about 55 wt% versus the total microemulsion composition, or between about 20 wt% and about 50 wt%, versus the
15 total microemulsion composition. In some embodiments, the surfactant is present in an amount between about 0 wt% and about 99 wt%, or between about 10 wt% and about 70 wt%, or between about 0 wt% and about 60 wt%, or between about 1 wt% and about 60 wt%, or between about 5 wt% and about 60 wt%, or between about 10 wt% and about 60 wt%, or between 5 wt% and about 65 wt%, or between 5 wt% and about 55 wt%, or
20 between about 0 wt% and about 40 wt%, or between about 15 wt% and about 55 wt%, or between about 20 wt% and about 50 wt%, versus the total microemulsion composition.

 In some embodiments, the microemulsion comprises an alcohol. The alcohol may serve as a coupling agent between the solvent and the surfactant and aid in the stabilization of the microemulsion. The alcohol may also lower the freezing point of the
25 microemulsion. The microemulsion may comprise a single alcohol or a combination of two or more alcohols. In some embodiments, the alcohol is selected from primary, secondary and tertiary alcohols having between 1 and 20 carbon atoms. In some embodiments, the alcohol comprises a first type of alcohol and a second type of alcohol. Non-limiting examples of alcohols include methanol, ethanol, isopropanol, n-propanol,
30 n-butanol, i-butanol, sec-butanol, iso-butanol, and t-butanol. In some embodiments, the alcohol is ethanol or isopropanol. In some embodiments, the alcohol is isopropanol.

 The alcohol may be present in the emulsion in any suitable amount. In some embodiments, the alcohol is present in an amount between about 0 wt% and about 50

wt%, or between about 0.1 wt% and about 50 wt%, or between about 1 wt% and about 50 wt%, or between about 5 wt% and about 40 wt%, or between about 5 wt% and 35 wt%, versus the total microemulsion composition.

In some embodiments, the microemulsion comprises a freezing point depression agent. The microemulsion may comprise a single freezing point depression agent or a combination of two or more freezing point depression agents. For example, in some embodiments, the freezing point depression agent comprises a first type of freezing point depression agent and a second type of freezing point depression agent. The term “freezing point depression agent” is given its ordinary meaning in the art and refers to a compound which is added to a solution to reduce the freezing point of the solution. That is, a solution comprising the freezing point depression agent has a lower freezing point as compared to an essentially identical solution not comprising the freezing point depression agent. Those of ordinary skill in the art will be aware of suitable freezing point depression agents for use in the microemulsions described herein. Non-limiting examples of freezing point depression agents include primary, secondary, and tertiary alcohols with between 1 and 20 carbon atoms. In some embodiments, the alcohol comprises at least 2 carbon atoms, alkylene glycols including polyalkylene glycols, and salts. Non-limiting examples of alcohols include methanol, ethanol, i-propanol, n-propanol, t-butanol, n-butanol, n-pentanol, n-hexanol, and 2-ethyl-hexanol. In some embodiments, the freezing point depression agent is not methanol (e.g., due to toxicity). Non-limiting examples of alkylene glycols include ethylene glycol (EG), polyethylene glycol (PEG), propylene glycol (PG), and triethylene glycol (TEG). In some embodiments, the freezing point depression agent is not ethylene oxide (e.g., due to toxicity). In some embodiments, the freezing point depression agent comprises an alcohol and an alkylene glycol. In some embodiments, the freezing point depression agent comprises a carboxycyclic acid salt and/or a di-carboxycyclic acid salt. Another non-limiting example of a freezing point depression agent is a combination of choline chloride and urea. In some embodiments, the microemulsion comprising the freezing point depression agent is stable over a wide range of temperatures, for example, between about -25 °F to 150 °F, or between about -50 °F to 200 °F.

The freezing point depression agent may be present in the microemulsion in any suitable amount. In some embodiments, the freezing point depression agent is present in an amount between about 1 wt% and about 40 wt%, or between about 3 wt% and about

20 wt%, or between about 8 wt% and about 16 wt%, versus the total microemulsion composition. In some embodiments, the freezing point depression agent is present in an amount between about 0 wt% and about 70 wt%, or between about 1 wt% and about 40 wt%, or between about 0 wt% and about 25 wt%, or between about 1 wt% and about 25 wt%, or between about 1 wt% and about 20 wt%, or between about 3 wt% and about 20 wt%, or between about 8 wt% and about 16 wt%, versus the total microemulsion composition.

Further non-limiting examples of other additives include proppants, scale inhibitors, friction reducers, biocides, corrosion inhibitors, buffers, viscosifiers, clay swelling inhibitors, paraffin dispersing additives, asphaltene dispersing additives, and oxygen scavengers.

Non-limiting examples of proppants (e.g., propping agents) include grains of sand, glass beads, crystalline silica (e.g., Quartz), hexamethylenetetramine, ceramic proppants (e.g., calcined clays), resin coated sands, and resin coated ceramic proppants. Other proppants are also possible and will be known to those skilled in the art.

Non-limiting examples of scale inhibitors include one or more of methyl alcohol, organic phosphonic acid salts (e.g., phosphonate salt), polyacrylate, ethane-1,2-diol, calcium chloride, and sodium hydroxide. Other scale inhibitors are also possible and will be known to those skilled in the art.

Non-limiting examples of buffers include acetic acid, acetic anhydride, potassium hydroxide, sodium hydroxide, and sodium acetate. Other buffers are also possible and will be known to those skilled in the art.

Non-limiting examples of corrosion inhibitors include isopropanol, quaternary ammonium compounds, thiourea/formaldehyde copolymers, propargyl alcohol and methanol. Other corrosion inhibitors are also possible and will be known to those skilled in the art.

Non-limiting examples of biocides include didecyl dimethyl ammonium chloride, gluteral, Dazomet, bronopol, tributyl tetradecyl phosphonium chloride, tetrakis (hydroxymethyl) phosphonium sulfate, AQUICAR™, UCARCIDE™, glutaraldehyde, sodium hypochlorite, and sodium hydroxide. Other biocides are also possible and will be known to those skilled in the art.

Non-limiting examples of clay swelling inhibitors include quaternary ammonium chloride and tetramethylammonium chloride. Other clay swelling inhibitors are also possible and will be known to those skilled in the art.

5 Non-limiting examples of friction reducers include petroleum distillates, ammonium salts, polyethoxylated alcohol surfactants, and anionic polyacrylamide copolymers. Other friction reducers are also possible and will be known to those skilled in the art.

Non-limiting examples of oxygen scavengers include sulfites, and bisulfites. Other oxygen scavengers are also possible and will be known to those skilled in the art.

10 Non-limiting examples of paraffin dispersing additives and asphaltene dispersing additives include active acidic copolymers, active alkylated polyester, active alkylated polyester amides, active alkylated polyester imides, aromatic naphthas, and active amine sulfonates. Other paraffin dispersing additives are also possible and will be known to those skilled in the art.

15 In some embodiments, for the formulations above, the other additives are present in an amount between about 0 wt% about 70 wt%, or between about 0 wt % and about 30 wt%, or between about 1 wt% and about 30 wt%, or between about 1 wt% and about 25 wt%, or between about 1 and about 20 wt%, versus the total microemulsion composition. In some embodiments, the microemulsion comprises an acid or an acid precursor. For
20 example, the microemulsion may comprise an acid when used during acidizing operations. The microemulsion may comprise a single acid or a combination of two or more acids. For example, in some embodiments, the acid comprises a first type of acid and a second type of acid. Non-limiting examples of acids or di-acids include hydrochloric acid, acetic acid, formic acid, succinic acid, maleic acid, malic acid, lactic
25 acid, and hydrochloric-hydrofluoric acids. In some embodiments, the microemulsion comprises an organic acid or organic di-acid in the ester (or di-ester) form, whereby the ester (or diester) is hydrolyzed in the wellbore and/or reservoir to form the parent organic acid and an alcohol in the wellbore and/or reservoir. Non-limiting examples of esters or di-esters include isomers of methyl formate, ethyl formate, ethylene glycol diformate,
30 α,α -4-trimethyl-3-cyclohexene-1-methylformate, methyl lactate, ethyl lactate, α,α -4-trimethyl 3-cyclohexene-1-methyl lactate, ethylene glycol dilactate, ethylene glycol diacetate, methyl acetate, ethyl acetate, α,α -4-trimethyl-3-cyclohexene-1-methylacetate, dimethyl succinate, dimethyl maleate, di(α,α -4-trimethyl-3-cyclohexene-1-

methyl)succinate, 1-methyl-4-(1-methylethenyl)-cyclohexylformate, 1-methyl-4-(1-ethylethenyl)cyclohexylactate, 1-methyl-4-(1-methylethenyl)cyclohexylacetate, di(1-methyl-4-(1-methylethenyl)cyclohexyl)succinate.

In some embodiments, the microemulsion comprises a salt. The presence of the salt may reduce the amount of water needed as a carrier fluid, and in addition, may lower the freezing point of the microemulsion. The microemulsion may comprise a single salt or a combination of two or more salts. For example, in some embodiments, the salt comprises a first type of salt and a second type of salt. Non-limiting examples of salts include salts comprising K, Na, Br, Cr, Cs, or Li, for example, halides of these metals, including NaCl, KCl, CaCl₂, and MgCl₂.

In some embodiments, the microemulsion comprises a clay stabilizer. The microemulsion may comprise a single clay stabilizer or a combination of two or more clay stabilizers. For example, in some embodiments, the salt comprises a first type of clay stabilizer and a second type of clay stabilizer. Non-limiting examples of clay stabilizers include salts above, polymers (PAC, PHPA, etc.), glycols, sulfonated asphalt, lignite, sodium silicate, and choline chloride.

In some embodiments, for the formulations above, the other additives are present in an amount between about 0 wt% about 70 wt%, or between about 1 wt% and about 30 wt%, or between about 1 wt% and about 25 wt%, or between about 1 and about 20 wt%, versus the total microemulsion composition.

In some embodiments, the components of the microemulsion and/or the amounts of the components may be selected so that the microemulsion is stable over a wide-range of temperatures. For example, the microemulsion may exhibit stability between about -40 °F and about 400 °F, or between -40 °F and about 300 °F, or between about -40 °F and about 150 °F. Those of ordinary skill in the art will be aware of methods and techniques for determining the range of stability of the microemulsion. For example, the lower boundary may be determined by the freezing point and the upper boundary may be determined by the cloud point and/or using spectroscopy methods. Stability over a wide range of temperatures may be important in embodiments where the microemulsions are being employed in applications comprising environments wherein the temperature may vary significantly, or may have extreme highs (e.g., desert) or lows (e.g., artic).

The microemulsions described herein may be formed using methods known to those of ordinary skill in the art. In some embodiments, the aqueous and non-aqueous

phases may be combined (e.g., the water and the terpene(s)), followed by addition of a surfactant(s) and optionally other components (e.g., freezing point depression agent(s)) and agitation. The strength, type, and length of the agitation may be varied as known in the art depending on various factors including the components of the microemulsion, the quantity of the microemulsion, and the resulting type of microemulsion formed. For example, for small samples, a few seconds of gentle mixing can yield a microemulsion, whereas for larger samples, longer agitation times and/or stronger agitation may be required. Agitation may be provided by any suitable source, for example, a vortex mixer, a stirrer (e.g., magnetic stirrer), etc.

10 Any suitable method for injecting the microemulsion (e.g., a diluted microemulsion) into a wellbore may be employed. For example, in some embodiments, the microemulsion, optionally diluted, may be injected into a subterranean formation by injecting it into a well or wellbore in the zone of interest of the formation and thereafter pressurizing it into the formation for the selected distance. Methods for achieving the placement of a selected
15 quantity of a mixture in a subterranean formation are known in the art. The well may be treated with the microemulsion for a suitable period of time. The microemulsion and/or other fluids may be removed from the well using known techniques, including producing the well.

In some embodiments, experiments may be carried out to determine displacement of residual aqueous treatment fluid by formation crude oil or formation gas by a microemulsion
20 (e.g., a diluted microemulsion). For example, displacement of residual aqueous treatment fluid by formation crude oil may be determined using the method described in Example 3 and/or displacement of residual aqueous treatment fluid by formation gas may be determined using the method described in Example 2.

For convenience, certain terms employed in the specification, examples, and
25 appended claims are listed here.

Definitions of specific functional groups and chemical terms are described in more detail below. For purposes of this invention, the chemical elements are identified in accordance with the Periodic Table of the Elements, CAS version, *Handbook of Chemistry and Physics*, 75th Ed., inside cover, and specific functional groups are generally defined as
30 described therein. Additionally, general principles of organic chemistry, as well as specific functional moieties and reactivity, are described in *Organic Chemistry*, Thomas Sorrell, University Science Books, Sausalito: 1999.

Certain compounds of the present invention may exist in particular geometric or stereoisomeric forms. The present invention contemplates all such compounds, including *cis-*

and *trans*-isomers, *R*- and *S*-enantiomers, diastereomers, (D)-isomers, (L)-isomers, the racemic mixtures thereof, and other mixtures thereof, as falling within the scope of the invention. Additional asymmetric carbon atoms may be present in a substituent such as an alkyl group. All such isomers, as well as mixtures thereof, are intended to be included in this
5 invention.

Isomeric mixtures containing any of a variety of isomer ratios may be utilized in accordance with the present invention. For example, where only two isomers are combined, mixtures containing 50:50, 60:40, 70:30, 80:20, 90:10, 95:5, 96:4, 97:3, 98:2, 99:1, or 100:0 isomer ratios are all contemplated by the present invention. Those of ordinary skill in the art
10 will readily appreciate that analogous ratios are contemplated for more complex isomer mixtures.

The term "aliphatic," as used herein, includes both saturated and unsaturated, nonaromatic, straight chain (i.e. unbranched), branched, acyclic, and cyclic (i.e. carbocyclic) hydrocarbons, which are optionally substituted with one or more functional groups. As will
15 be appreciated by one of ordinary skill in the art, "aliphatic" is intended herein to include, but is not limited to, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, and cycloalkynyl moieties. Thus, as used herein, the term "alkyl" includes straight, branched and cyclic alkyl groups. An analogous convention applies to other generic terms such as "alkenyl", "alkynyl", and the like. Furthermore, as used herein, the terms "alkyl", "alkenyl", "alkynyl", and the like
20 encompass both substituted and unsubstituted groups. In certain embodiments, as used herein, "aliphatic" is used to indicate those aliphatic groups (cyclic, acyclic, substituted, unsubstituted, branched or unbranched) having 1–20 carbon atoms. Aliphatic group substituents include, but are not limited to, any of the substituents described herein, that result in the formation of a stable moiety (*e.g.*, aliphatic, alkyl, alkenyl, alkynyl, heteroaliphatic,
25 heterocyclic, aryl, heteroaryl, acyl, oxo, imino, thiooxo, cyano, isocyano, amino, azido, nitro, hydroxyl, thiol, halo, aliphaticamino, heteroaliphaticamino, alkylamino, heteroalkylamino, arylamino, heteroarylamino, alkylaryl, arylalkyl, aliphaticoxy, heteroaliphaticoxy, alkyloxy, heteroalkyloxy, aryloxy, heteroaryloxy, aliphaticthioxy, heteroaliphaticthioxy, alkylthioxy, heteroalkylthioxy, arylthioxy, heteroarylthioxy, acyloxy, and the like, each

of which may or may not be further substituted).

The term “alkane” is given its ordinary meaning in the art and refers to a saturated hydrocarbon molecule. The term “branched alkane” refers to an alkane that includes one or more branches, while the term “unbranched alkane” refers to an alkane that is straight-chained. The term “cyclic alkane” refers to an alkane that includes one or more ring structures, and may be optionally branched. The term “acyclic alkane” refers to an alkane that does not include any ring structures, and may be optionally branched.

The term “alkene” is given its ordinary meaning in the art and refers to an unsaturated hydrocarbon molecule that includes one or more carbon-carbon double bonds. The term “branched alkene” refers to an alkene that includes one or more branches, while the term “unbranched alkene” refers to an alkene that is straight-chained. The term “cyclic alkene” refers to an alkene that includes one or more ring structures, and may be optionally branched. The term “acyclic alkene” refers to an alkene that does not include any ring structures, and may be optionally branched.

The term “aromatic” is given its ordinary meaning in the art and refers to aromatic carbocyclic groups, having a single ring (e.g., phenyl), multiple rings (e.g., biphenyl), or multiple fused rings in which at least one is aromatic (e.g., 1,2,3,4-tetrahydronaphthyl, naphthyl, anthryl, or phenanthryl). That is, at least one ring may have a conjugated pi electron system, while other, adjoining rings can be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls and/or heterocyclyls.

The term “aryl” is given its ordinary meaning in the art and refers to aromatic carbocyclic groups, optionally substituted, having a single ring (e.g., phenyl), multiple rings (e.g., biphenyl), or multiple fused rings in which at least one is aromatic (e.g., 1,2,3,4-tetrahydronaphthyl, naphthyl, anthryl, or phenanthryl). That is, at least one ring may have a conjugated pi electron system, while other, adjoining rings can be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls and/or heterocyclyls. The aryl group may be optionally substituted, as described herein. Substituents include, but are not limited to, any of the previously mentioned substituents, i.e., the substituents recited for aliphatic moieties, or for other moieties as disclosed herein, resulting in the formation of a stable compound. In some cases, an aryl group is a stable mono- or polycyclic unsaturated moiety having preferably 3-14 carbon atoms, each of which may be substituted or unsubstituted.

These and other aspects of the present invention will be further appreciated upon consideration of the following Examples, which are intended to illustrate certain particular embodiments of the invention but are not intended to limit its scope, as defined by the claims.

5

Examples

10 **Example 1:**

A series of laboratory tests were conducted to characterize the effectiveness of a series of microemulsions incorporating a range of terpenes. For these experiments, samples of a base microemulsion were prepared in which a detergent range alcohol ethoxylate surfactant was first blended in a 1:1 ratio with isopropyl alcohol. Suitable detergent range alcohol ethoxylate surfactants include Neodol 25-7 (obtained from Shell
15 Chemical Co.; e.g., a surfactant comprising linear C₁₂-C₁₅ alcohol ethoxylates with on average 7 moles of ethylene oxide), or comparable linear and branched alcohol ethoxylate surfactants available from SASOL, Huntsman or Stepan. The examples in Table 2 were prepared using Neodol 25-7. 46 parts by weight of this blend was mixed
20 with 27 parts by weight of terpene and 27 parts by weight of water. Although substantial differences in the microemulsion phase behavior of the different terpenes were observed, this composition was chosen because at this composition, the exemplary terpenes that were tested spontaneously formed transparent stable microemulsions with gentle mixing of the ingredients. Subsequently, 1-2 gallons per thousand (gpt) dilutions were prepared
25 and tested.

A transparent low-viscosity mixture that exhibited the characteristic properties of a microemulsion was prepared using 46% by weight of a blend of Neodol 25-7 and isopropyl alcohol, 27% by weight of water, and 27% by weight of technical grade d-limonene. This mixture was identified as a microemulsion based on the spontaneous
30 formation with minimal mechanical energy input to form a clear dispersion from an immiscible mixture of water and d-limonene upon addition of an appropriate amount of surfactant and co-solvent. The order of mixing of this and other compositions described in this example were not necessary, but for convenience, a procedure was generally

followed in which a mixture of the surfactant and the isopropyl alcohol was first prepared then combined that with a mixture of the terpene and water. With small samples, in the laboratory, a few seconds of gentle mixing yielded a transparent dispersion.

5 The non-limiting terpenes used this example were classified by measuring their phase inversion temperature (PIT) using methods described in the literature (e.g., see Strey, *Microemulsion microstructure and interfacial curvature. Colloid & Polymer Science*, 1994. 272(8): p. 1005-1019; Kahlweit et al., *Phase Behavior of Ternary Systems of the Type H₂O-Oil-Nonionic Amphiphile (Microemulsions). Angewandte Chemie International Edition in English*, 1985. 24(8): p. 654-668.). As will be known in the art, the PIT measured for a given oil or solvent depends on the surfactant and aqueous phase in which it is measured. In this example, a 1:1 mixture of terpene solvent and de-ionized water was combined with varying amounts of a 1:1 blend of Neodol 25-7 and IPA and the upper and lower temperature boundaries of the one-phase
10 microemulsion region were determined. A phase diagram such as this, plotting temperature against surfactant concentration at a constant oil-to-water ratio is often called a “fish” diagram or a Kahlweit plot. The phase inversion temperature was determined as the point at the “fish-tail” at which the temperature range of one-phase microemulsion closes to a vertex. In this example, the temperature at the vertex was
15 selected as the PIT. An exemplary fish diagram indicating the PIT is shown in Figure 1. For the terpene solvents used in this example, the PIT values which were measured using this above-described procedure are shown in Table 2. Those terpenes containing alcohol groups (linalool, geraniol, nopol, α -terpineol and menthol), gave PIT values between -4 °C and 16 °C. Eucalyptol, containing an ether-oxygen, and menthone, containing a
20 carbonyl oxygen, gave somewhat higher values near 30 °C. D-limonene gave 43 °C, while other non-oxygen containing terpenes gave values between 48-58 °C. As described in more detail below, displacement of residual treatment fluid (containing 1-2 gpt of the microemulsion well treatment) from a sand pack by crude oil or gas was found to correlate to the PIT values.

30 Table 2 shows results for displacement of residual aqueous treatment fluid by oil and gas for formulations (e.g., using the experimental procedures outlined in Examples 3 and 4) using dilutions of the microemulsions prepared in this example (e.g., the microemulsions comprising 46 parts of 1:1 Neodol 25-7, 27 parts deionized water, and

27 parts terpene solvent). The dilutions were prepared of each microemulsion in 2% KCl, at 2 gpt. The table shows that the terpene solvents with PIT values higher than 43 °C all give approximately 90% recovery, while those below 43 °C give significantly lower recovery. Table 2 also shows displacement by gas results for the dilutions that

5 demonstrates that terpene solvents with PIT values higher than 43 °C give approximately 40% recovery, while those with PIT values below 43 °C give significantly higher recovery.

10 **Table 2.** PIT values for various terpene solvents (e.g., measured at 1:1 water-oil). Displacement results for 2 gpt dilution of microemulsions comprising 46:27:27 surfactant:water:terpene + isopropanol formulations.

Terpene	Phase Inversion Temperature (°C)	% displacement of brine by crude oil	% displacement of brine by gas
Linalool	-4	-	81.9
Geraniol	-0.5	69.3	67.8
Nopol	2.5	80.3	58.8
α -Terpineol	4.6	80	92.9
Menthol	16	49.7	-
Eucalyptol	31	-	54.6
Menthone	32	79.4	-
d-Limonene	43	89.3	45.6
Terpinolene	48	90.5	41.8
β -Occimene	49	90.2	44.2
γ -Terpinene	49	89	32.2
α -Pinene	57	89.9	38.7
Citronellene	58	88.2	40.5

Table 3. Oil and Gas displacement results for α -pinene and α -terpineol as a function of surfactant concentration and solvent-to-water ratio.

Formulation T/S/W*	Terpene	% displacement of brine by crude oil	% displacement of brine by gas
27-46-27	α -terpineol	80	92.9
27-46-27	α -pinene	89.9	38.7
21-46-33	α -terpineol	88	83
21-46-33	α -pinene	87	46
11-46-43	α -terpineol	88.5	80
11-46-43	α -pinene	96	47
15-56-28	α -terpineol	87.8	85
15-56-28	α -pinene	88.6	52

5 *T/S/W stands for terpene weight %/1:1 surfactant-IPA weight %/deionized water wt%

The results shown in Table 3 demonstrate that at a 1:1 ratio of terpene to water, and 46 weight % surfactant-IPA, the high PIT α -pinene performed better on oil displacement and much poorer on gas displacement than the low PIT α -terpineol. As the
 10 terpene-to-water ratio decreases from 27-27 to 21-33 to 11-43, the difference in oil displacement performance decreased, then increased again at the lower level. Higher surfactant levels did not substantially increase or decrease the displacement (which may suggest that the microemulsion is performing differently than a surfactant package lacking the terpene solvent). The displacement by gas was better for the low PIT α -
 15 terpeneol than for the high PIT α -pinene.

20 Example 2:

Microemulsions were prepared having the following formulation, wherein the terpene was varied as indicated in Table 4. The water to terpene ratio was about 5.5:1..

Microemulsion formulation:

	Water	27.35 wt%
	Ethoxylated alcohol surfactant	52.5 wt%
	2-propanol	8.75 wt%
5	Triethylene Glycol	3 wt%
	Propylene Glycol	3.3 wt%
	Ethoxylated castor oil	0.1 wt%
	Terpene	5 wt%

10 1 gallon per thousand dilutions were prepared of each microemulsion in 2% KCl. The dilutions were then employed to determine the displacement of brine by oil and gas (e.g., using the experimental procedures outlined in Examples 3 and 4). The results are given in Table 4.

15

Table 4: Brine displacement by oil and gas

Terpene	Effectiveness of brine displacement by gas (%)	Effectiveness of brine displacement by oil (%)
d-limonene	79	64
α -terpineol	90	88
α -pinene	86	87
geraniol	87	89
linalool	88	87
nopol	89	88
turpentine	83	76
menthol	82	90
eucalyptol	77	90
terpinolene	79	72
β -ocimene	71	68
λ -terpinene	74	60
citronellene	73	88

Example 3:

20 This example described a non-limiting experiment for determining displacement of residual aqueous treatment fluid by formation crude oil. A 25 cm long, 2.5 cm diameter capped glass chromatography column was packed with 77 grams of 100 mesh

sand. The column was left open on one end and a PTFE insert containing a recessed bottom, 3.2 mm diameter outlet, and nipple was placed into the other end. Prior to placing the insert into the column, a 3 cm diameter filter paper disc (Whatman, #40) was pressed firmly into the recessed bottom of the insert to prevent leakage of 100 mesh sand. A 2" piece of vinyl tubing was placed onto the nipple of the insert and a clamp was fixed in place on the tubing prior to packing. The columns were gravity-packed by pouring approximately 25 grams of the diluted microemulsions (e.g., the microemulsions described in Examples 1 or 2, and diluted with 2% KCl, e.g., to about 2 gpt, or about 1 gpt) into the column followed by a slow, continuous addition of sand. After the last portion of sand had been added and was allowed to settle, the excess of brine was removed from the column so that the level of liquid exactly matched the level of sand. Pore volume in the packed column was calculated as the difference in mass of fluid prior to column packing and after the column had been packed. Three additional pore volumes of brine were passed through the column. After the last pore volume was passed, the level of brine was adjusted exactly to the level of sand bed. Light condensate oil was then added on the top of sand bed to form the 5 cm oil column above the bed. Additional oil was placed into a separatory funnel with a side arm open to an atmosphere. Once the setup was assembled, the clamp was released from the tubing, and timer was started. Throughout the experiment the level of oil was monitored and kept constant at a 5 cm mark above the bed. Oil was added from the separatory funnel as necessary, to ensure this constant level of head in the column. Portions of effluent coming from the column were collected into plastic beakers over a measured time intervals. The amount of fluid was monitored. When both brine and oil were produced from the column, they were separated with a syringe and weighed separately. The experiment was conducted for 3 hours at which the steady-state conditions were typically reached. The cumulative % or aqueous fluid displaced from the column over 120 minute time period, and the steady-state mass flow rate of oil at t=120 min through the column were determined.

30 **Example 4:**

This example described a non-limiting experiment for determining displacement of residual aqueous treatment fluid by formation gas. A 51 cm long, 2.5 cm inner-diameter capped glass chromatography column was filled with approximately

410 ± 20 g of 20/40 mesh Ottawa sand and the diluted microemulsions (e.g., the microemulsions described in Examples 1 or 2, and diluted with 2% KCl, e.g., to about 2 gpt, or about 1 gpt) To ensure uniform packing, small amounts of proppant were interchanged with small volumes of liquid. Periodically the mixture in the column was
5 homogenized with the help of an electrical hand massager, in order to remove possible air pockets. Sand and brine were added to completely fill the column to the level of the upper cap. The exact amounts of fluid and sand placed in the column were determined in each experiment. The column was oriented vertically and was connected at the bottom to a nitrogen cylinder via a gas flow controller pre-set at a flow rate of 60 cm³/min. The
10 valve at the bottom was slowly opened and liquid exiting the column at the top was collected into a tarred jar placed on a balance. Mass of collected fluid was recorded as a function of time by a computer running a data logging software. The experiments were conducted until no more brine could be displaced from the column. The total % of fluid recovered was then calculated.

15

Example 5:

This examples describes a general preparation method for the production of diluted microemulsion. The microemulsions were prepared in the laboratory by mixing
20 the ingredients listed in specific examples. All ingredients are commercially available materials. In some embodiments, the components were mixed together in the order water-alcohol-surfactant- citrus terpene solvent, but other order of addition may also be employed. The mixtures were then agitated on a magnetic stirrer for 5-10 minutes. The microemulsions were then diluted to concentrations of 1 or 2 gallons per 1000 gallons
25 with 2% KCl brine and these diluted fluids were used in displacement experiments described in Examples 3 and 4.

It will be evident to one skilled in the art that the present disclosure is not limited
30 to the foregoing illustrative examples, and that it can be embodied in other specific forms without departing from the essential attributes thereof. It is therefore desired that the examples be considered in all respects as illustrative and not restrictive, reference being made to the appended claims, rather than to the foregoing examples, and all changes

which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

While several embodiments of the present invention have been described and illustrated herein, those of ordinary skill in the art will readily envision a variety of other means and/or structures for performing the functions and/or obtaining the results and/or one or more of the advantages described herein, and each of such variations and/or modifications is deemed to be within the scope of the present invention. More generally, those skilled in the art will readily appreciate that all parameters, dimensions, materials, and configurations described herein are meant to be exemplary and that the actual parameters, dimensions, materials, and/or configurations will depend upon the specific application or applications for which the teachings of the present invention is/are used. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described and claimed. The present invention is directed to each individual feature, system, article, material, kit, and/or method described herein. In addition, any combination of two or more such features, systems, articles, materials, kits, and/or methods, if such features, systems, articles, materials, kits, and/or methods are not mutually inconsistent, is included within the scope of the present invention.

The indefinite articles “a” and “an,” as used herein in the specification and in the claims, unless clearly indicated to the contrary, should be understood to mean “at least one.”

The phrase “and/or,” as used herein in the specification and in the claims, should be understood to mean “either or both” of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Other elements may optionally be present other than the elements specifically identified by the “and/or” clause, whether related or unrelated to those elements specifically identified unless clearly indicated to the contrary. Thus, as a non-limiting example, a reference to “A and/or B,” when used in conjunction with open-ended language such as “comprising” can refer, in one embodiment, to A without B (optionally including elements other than

B); in another embodiment, to B without A (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other elements); *etc.*

As used herein in the specification and in the claims, “or” should be understood to have the same meaning as “and/or” as defined above. For example, when separating
5 items in a list, “or” or “and/or” shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as “only one of” or “exactly one of,” or, when used in the claims, “consisting of,” will refer to the inclusion of exactly one element or a list of elements. In general, the term “or” as
10 used herein shall only be interpreted as indicating exclusive alternatives (i.e. “one or the other but not both”) when preceded by terms of exclusivity, such as “either,” “one of,” “only one of,” or “exactly one of.” “Consisting essentially of,” when used in the claims, shall have its ordinary meaning as used in the field of patent law.

As used herein in the specification and in the claims, the phrase “at least one,” in
15 reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the
20 elements specifically identified within the list of elements to which the phrase “at least one” refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, “at least one of A and B” (or, equivalently, “at least one of A or B,” or, equivalently “at least one of A and/or B”) can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally
25 including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one, A, and at least one, optionally including more than one, B (and optionally including other elements); *etc.*

30 In the claims, as well as in the specification above, all transitional phrases such as “comprising,” “including,” “carrying,” “having,” “containing,” “involving,” “holding,” and the like are to be understood to be open-ended, i.e., to mean including but not limited to. Only the transitional phrases “consisting of” and “consisting essentially of” shall be

closed or semi-closed transitional phrases, respectively.

What is claimed is:

1. A method comprising:
 - selecting an emulsion or a microemulsion for injection into a wellbore of a well based on a determination of whether formation crude oil is produced;
 - wherein, when the formation crude oil is produced by the well, the emulsion or the microemulsion is selected to comprise a terpene having a phase inversion temperature greater than 43 °C and
 - injecting the emulsion or the microemulsion into the wellbore.
2. A method of treating an oil well having a wellbore comprising:
 - injecting an emulsion or a microemulsion into the wellbore of the oil well to stimulate displacement of residual aqueous treatment fluid by formation crude oil and increase production of formation crude oil by the well,
 - wherein the emulsion or the microemulsion comprises water, a terpene, and a surfactant;
 - wherein the ratio by weight of the water to the terpene is between about 3:1 and about 1:2; and
 - wherein the terpene has a phase inversion temperature greater than 43 °C.
3. A method of treating an oil well having a wellbore comprising:
 - using an emulsion or a microemulsion to stimulate displacement of residual aqueous treatment fluid by formation crude oil by injecting the emulsion or the microemulsion into the wellbore of the oil well, and increase production of formation crude oil by the well,
 - wherein the emulsion or the microemulsion comprises water, a terpene, and a surfactant;
 - wherein the ratio by weight of the water to the terpene is between about 10:1 and about 3:1; and
 - wherein the terpene has a phase inversion temperature of greater than 43 °C.
4. The method of any one of claims 2 or 3, wherein the ratio of the water to the terpene is about 1:1.
5. The method of any one of claims 1, 2 or 3, wherein the terpene is selected from the group consisting of terpinolene, β -ocimene, γ -terpinene, α -pinene, and citronellene.

6. The method of any one of claims 1, 2 or 3, wherein the terpene comprises a first type of terpene and a second type of terpene.
7. The method of any one of claims 1, 2 or 3, wherein the emulsion or the microemulsion is diluted with an aqueous fluid prior to injection into the wellbore.
8. The method of claim 7, wherein the emulsion or the microemulsion is diluted with the aqueous fluid prior to injection into the wellbore between about 0.1 wt% and about 2 wt% versus the total weight of the emulsion or the microemulsion.
9. The method of claim 7, wherein the emulsion or the microemulsion is diluted with the aqueous fluid prior to injection into the wellbore between about 0.2 wt% and about 0.4 wt% versus the total weight of the emulsion or the microemulsion.
10. The method of claim 7, wherein the aqueous fluid comprises water or brine.
11. The method of any one of claims 1, 2 or 3, wherein the emulsion or the microemulsion further comprises a freezing point depression agent.
12. The method of claim 11, wherein the freezing point depression agent comprises a first type of freezing point depression agent and a second type of freezing point depression agent.
13. The method of claim 11, wherein the freezing point depression agent comprises an alkylene glycol, an alcohol, or a salt.
14. The method of claim 11, wherein the freezing point depression agent is present in an amount between about 5 wt% and about 40 wt% versus the total weight of the emulsion or the microemulsion.
15. The method of any one of claims 2 or 3, wherein the surfactant comprises a first type of surfactant and a second type of surfactant.

16. The method of any one of claims 2 or 3, wherein the surfactant is selected from the group consisting of alkyl polyglycol nonionic surfactants, alkyl polyglycoside nonionic surfactants and mixtures of said nonionic surfactants with an ionic surfactant.
17. The method of any one of claims 2 or 3, wherein the surfactant is present in an amount between about 15 wt% and 55 wt% versus the total weight of the emulsion or the microemulsion.
18. The method of any one of claims 2 or 3, wherein the phase inversion temperature is determined using a 1:1 ratio by weight of terpene:de-ionized water and a 1:1 ratio by weight of the surfactant, further comprising linear C₁₂-C₁₅ alcohol ethoxylates with on average 7 moles of ethylene oxide and isopropyl alcohol.

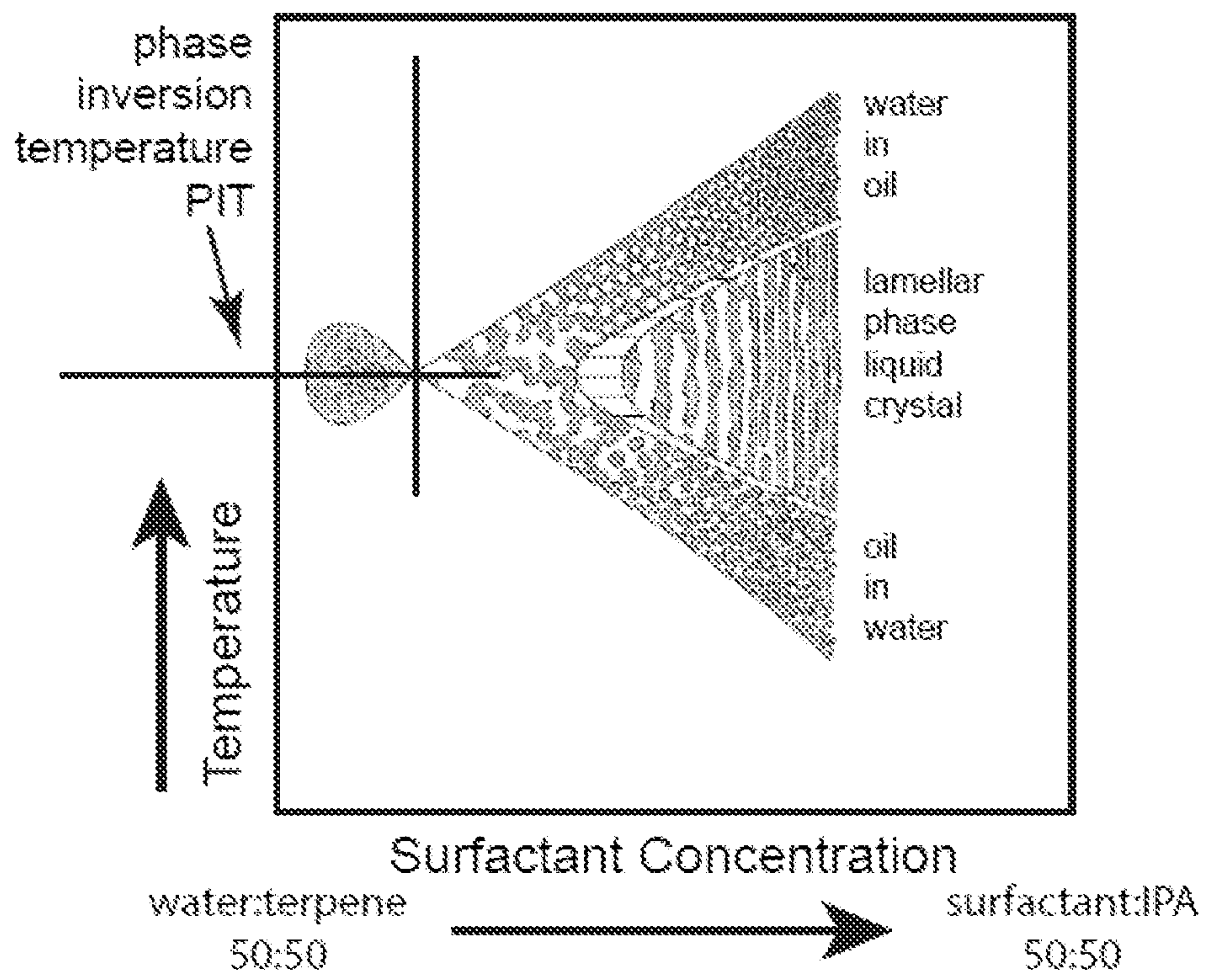


Figure 1

