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(54) **Title:** AMMONIA COMPOSITIONS FOR USE IN GYPSUM CONTAINING WELLS

(57) **Abstract:** Provided herein are, *inter alia*, compositions and methods for enhanced oil recovery in the presence of multivalent mineral cations. The aqueous and emulsion compositions provided herein include an ammonia compound and may be useful for the recovery of unrefined petroleum materials from mineral-bearing reservoirs.



## AMMONIA COMPOSITIONS FOR USE IN GYPSUM CONTAINING WELLS

### CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims benefit of U.S. Provisional Application No. 61/950,721, filed  
5 March 10, 2014, which is hereby incorporated herein by reference in its entirety.

### BACKGROUND

Enhanced Oil Recovery (abbreviated EOR) refers to techniques for increasing the  
amount of unrefined petroleum, or crude oil, which may be extracted from an oil reservoir (e.g.,  
an oil field). Using EOR, 40-60% of the reservoir's original oil can typically be extracted  
10 compared with only 20-40% using primary and secondary recovery (e.g., by water injection or  
natural gas injection). Enhanced oil recovery may also be referred to as improved oil recovery or  
tertiary recovery (as opposed to primary and secondary recovery).

Enhanced oil recovery may be achieved by a variety of methods including miscible gas  
injection (which includes carbon dioxide flooding), chemical injection (which includes polymer  
15 flooding, alkaline flooding and surfactant flooding or any combination thereof), microbial  
injection, or thermal recovery (which includes cyclic steam, steam flooding, and fire flooding) or  
a combination of different injection methods (e.g., chemical injection and gas injection). The  
injection of various chemicals during chemical EOR, usually as dilute aqueous solutions, has  
been used to improve oil recovery. Injection of alkaline or caustic solutions into reservoirs with  
20 oil that has organic acids naturally occurring in the oil (also referred to herein as "unrefined  
petroleum acids") will result in the production of soap that may lower the interfacial tension  
enough to increase production. Injection of a dilute solution of a water soluble polymer to  
increase the viscosity of the injected water can increase the amount of oil recovered from  
geological formations. Aqueous solutions of surfactants such as petroleum sulfonates may be  
25 injected to lower the interfacial tension or capillary pressure that impedes oil droplets from  
moving through a reservoir. Special formulations of oil, water and surfactant microemulsions,  
have also proven useful. Application of these methods is usually limited by the cost of the  
chemicals and their adsorption and loss onto the rock of the oil containing formation.

Some unrefined petroleum contains carboxylic acids having, for example, C<sub>11</sub> to C<sub>20</sub>  
30 alkyl chains, including naphthenic acid mixtures (also referred to herein as "unrefined petroleum  
acids"). The recovery of such "reactive" oils may be performed using alkali agents (e.g., NaOH,  
Na<sub>2</sub>CO<sub>3</sub>) in a surfactant composition. The alkali reacts with the acid (unrefined petroleum acid)  
in the reactive oil to form soap. These soaps serve as an additional source of surfactants

enabling the use of much lower level of surfactants initially added to effect enhanced oil recovery (EOR). However, when the available water supply is hard, the added alkali causes precipitation of cations, such as multivalent mineral cations (e.g.,  $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$ ). In order to prevent such precipitation a somewhat expensive chelant such as EDTA may be required in the surfactant composition or a water softening processes may be used. Applicants have developed surfactant formulations (e.g., alkoxy carboxylate surfactants), which can be effectively used for enhanced oil recovery in hard brine in the absence of alkali agents. These surfactant formulations are particularly effective at neutral pH. However, at low pH (e.g., pH 7 or lower) the non-alkaline surfactant formulations are associated with higher adsorption of the surfactant to the rock. At a pH above 7 (e.g., 9, 10, or 11), on the other hand, the surfactant adsorption can only be significantly reduced for these surfactant formulations by addition of alkaline agents. However, where the rock surface of the reservoir contains sulfate minerals (e.g., gypsum or anhydrite), the above-mentioned precipitation of multivalent mineral cations (e.g.,  $\text{Ca}^{+2}$ ) due to the presence of alkali agents (e.g., sodium carbonate) reduces the pH and the surfactant solubility and therefore, the efficiency of the oil recovery process. Thus, there is a need in the art, particularly where the oil reservoir includes sulfate minerals, for an alkali agent capable of stably propagating a pH where the adsorption of surfactant to the rock is minimized without causing precipitation of multivalent mineral cations such as  $\text{Ca}^{+2}$  from the rock surface.

The compositions and methods provided herein overcome these and other needs in the art. Therefore, the methods and compositions provided are particularly useful for cost effective enhanced oil recovery using chemical injection.

### SUMMARY

Provided herein, in a first aspect, is an aqueous composition that includes water, a surfactant, an ammonia compound, an ionic strength adjusting agent, and a multivalent mineral cation. The ammonia compound is  $\text{R}^3\text{H}_2\text{N}$ ,  $(\text{R}^3)_2\text{HN}$ ,  $(\text{R}^3)_3\text{N}$ , or  $\text{NH}_3$ , wherein  $\text{R}^3$  is independently unsubstituted  $\text{C}_1\text{-C}_5$  alkyl. In another aspect is an aqueous composition that includes water, a co-solvent, an ammonia compound, an ionic strength adjusting agent and a multivalent mineral cation. The ammonia compound is  $\text{R}^3\text{H}_2\text{N}$ ,  $(\text{R}^3)_2\text{HN}$ ,  $(\text{R}^3)_3\text{N}$ , or  $\text{NH}_3$ , wherein  $\text{R}^3$  is independently unsubstituted  $\text{C}_1\text{-C}_5$  alkyl. In another aspect is an aqueous composition that includes water, a hydrolyzed or partially hydrolyzed viscosity enhancing water soluble polymer and an ammonia compound at a pH of at least about 10. The ammonia compound is  $\text{R}^3\text{H}_2\text{N}$ ,  $(\text{R}^3)_2\text{HN}$ ,  $(\text{R}^3)_3\text{N}$ , or  $\text{NH}_3$ , wherein  $\text{R}^3$  is independently unsubstituted  $\text{C}_1\text{-C}_5$  alkyl.

Also provided herein is an emulsion that includes an unrefined petroleum, water, a surfactant, an ammonia compound, and a multivalent mineral cation. In another aspect is an emulsion that includes an unrefined petroleum, water, a co-solvent, an ammonia compound, and a multivalent mineral cation.

5            Provided herein are methods of displacing an unrefined petroleum material in contact with a solid material. In one aspect, the method includes contacting an unrefined petroleum material with an aqueous composition as described herein, including embodiments thereof. The unrefined petroleum material is in contact with a solid material that includes a mineral. The water dissolves multivalent mineral cations from the mineral. The unrefined petroleum material  
10 is allowed to separate from the solid material thereby displacing the unrefined petroleum material in contact with the solid material.

            Provided herein are methods of converting an unrefined petroleum acid into a surfactant. In one aspect, the method includes contacting a petroleum material with an aqueous composition as described herein, including embodiments thereof, thereby forming an emulsion in contact with  
15 the petroleum material. The unrefined petroleum acid within the unrefined petroleum material is allowed to enter into the emulsion, thereby converting the unrefined petroleum acid into a surfactant.

#### BRIEF DESCRIPTION OF THE FIGURES

**Figure 1:** Clear solutions containing 2,500 ppm to 10,000 ppm calcium in the presence  
20 of 3 wt%  $\text{NH}_4\text{OH}$  (0.9 wt%  $\text{NH}_3$ ) at 59°C.

**Figure 2:** Effect of increasing initial calcium concentration on calcium and boron concentration in the aqueous solutions.

**Figure 3:** Effect of increasing initial  $\text{NaBO}_2$  concentration on calcium and total boron concentration in the aqueous solutions.

25            **Figure 4:** Effluent  $\text{NH}_4\text{OH}$  concentration and pH on injection of 1 wt%  $\text{NH}_4\text{OH}$  in carbonate core with gypsum.

**Figure 5:** Effluent  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  concentration in mol/g on injection of 1 wt%  $\text{NH}_4\text{OH}$  in carbonate core containing gypsum.

**Figure 6:** Effluent pH and sulfate on injection of 1 wt%  $\text{NaBO}_2$  and 3.5 wt%  $\text{Na}_2\text{CO}_3$  in  
30 a carbonate core with gypsum.

**Figure 7:** Effluent pH and pressure drop on 3 wt%  $\text{NaBO}_2$  injection in a sandstone core containing anhydrite at 0.89 ft/d.

**Figure 8:** Effluent pH and concentrations of calcium sulfate and total boron on injecting  $\text{NaBO}_2$  solution at 0.67 ft/d.

**Figure 9:** Effluent pH, calcium and sulfate ions during injection of NaBO<sub>2</sub> solution at varying injection rates.

**Figure 10:** Effluent sulfate concentration as a function of residence time.

**Figure 11:** Oil and water solubilization ratios of the formulation used for coreflood R1.

5 **Figure 12:** Oil and water solubilization ratios of the formulation used for coreflood R2.

**Figure 13:** Oil and water solubilization ratios of the formulation used for experiment P2 in the absence of calcium ions.

**Figure 14:** Oil and water solubilization ratio of the formulation used for experiment P2 with 1000 ppm calcium ions.

10 **Figure 15:** Oil and water solubilization ratio of the formulation used for coreflood R3.

**Figure 16:** Conductance as a function of concentration for NaCl and NH<sub>3</sub>.

**Figure 17:** Core Flood R1 Oil Recovery and Pressure Data.

**Figure 18:** Core Flood R1 Surfactant, Oil cut, Salinity and pH Data.

**Figure 19:** Core Flood R2 Surfactant, Oil recovery, Oil cut, Salinity and pH Data.

15 **Figure 20:** Divalent ion concentrations of the effluent for Core Flood R2.

**Figure 21:** Coreflood R<sup>3</sup> tertiary oil recovery, oil cut, residual saturation, effluent pH and salinity data. The scale for pH is 0 to 10.

**Figure 22:** Coreflood R<sup>3</sup> tertiary oil recovery, oil cut, residual saturation and salinity data.

20 **Figure 23:** Solubilization plot of a low IFT formulation in presence of calcium.

**Figure 24:** Effluent salinity and pH profile in a carbonate core with gypsum.

**Figure 25:** Effluent ion concentrations on 1% ammonium hydroxide injection in core with gypsum.

25 **Figure 26:** Effluent ion concentrations on 1% ammonium hydroxide injection in core with gypsum.

**Figure 27:** Effluent ammonium hydroxide concentration from core with gypsum.

**Figure 28:** Phase behavior tubes for the alkali-cosolvent formulation developed using oil#1.

30 **Figure 29:** Phase behavior tubes for the alkali-cosolvent formulation developed using oil#2.

**Figure 30:** Solubilization ratios for oil#3 with 800 ppm calcium at 25 °C.

**Figure 31:** Solubilization ratios for oil#3 with 1200 ppm calcium at 25 °C

**Figure 32:** Solubilization ratios for oil#4 in the absence of calcium at 59 °C.

**Figure 33:** Solubilization ratios for oil#4 with 1000 ppm calcium at 59 °C.

**Figure 34:** pH and viscosity (at 10 sec<sup>-1</sup> shear rate and 25°C) of AN-125 samples in the presence of 1000 ppm Ca<sup>2+</sup> kept at 59 °C.

**Figure 35:** Tertiary oil recovery, oil cut and residual oil saturation profile during the ASP coreflood D1.

**Figure 36:** Comparison of Phreeqc and experimental results obtained by Sharma et al. (2014) on injection of ammonia in a gypsum containing core at 25°C.

**Figure 37:** Calcium concentration expected from dissolution of gypsum as a function of Na<sub>2</sub>SO<sub>4</sub> concentration at two different salinities and two different temperatures.

**Figure 38:** Tertiary oil recovery, oil cut, residual oil saturation and pressure drop profile during the ASP coreflood D2.

**Figure 39:** Oil bank, surfactant concentration and effluent salinity profile obtained during the ASP coreflood D2.

**Figure 40:** Effluent calcium and sulfate concentrations and pH obtained during the ASP coreflood D2.

**Figure 41:** Comparison of geochemistry calculations performed in Phreeqc to calculate calcium effluent profile and its comparison with the ASP coreflood D2 data.

#### DETAILED DESCRIPTION

The abbreviations used herein have their conventional meaning within the chemical and biological arts. The chemical structures and formulae set forth herein are constructed according to the standard rules of chemical valency known in the chemical arts.

Where substituent groups are specified by their conventional chemical formulae, written from left to right, they equally encompass the chemically identical substituents that would result from writing the structure from right to left, e.g., -CH<sub>2</sub>O- is equivalent to -OCH<sub>2</sub>-.

The term “alkyl,” by itself or as part of another substituent, means, unless otherwise stated, a straight (i.e., unbranched) or branched carbon chain (or carbon), or combination thereof, which may be fully saturated, mono- or polyunsaturated and can include di- and multivalent radicals, having the number of carbon atoms designated (i.e., C<sub>1</sub>-C<sub>10</sub> means one to ten carbons). Alkyl is not cyclized. Examples of saturated hydrocarbon radicals include, but are not limited to, groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, isobutyl, sec-butyl, (cyclohexyl)methyl, homologs and isomers of, for example, n-pentyl, n-hexyl, n-heptyl, n-octyl, and the like. An unsaturated alkyl group is one having one or more double bonds or triple bonds (e.g., alkene, alkyne). Examples of unsaturated alkyl groups include, but are not limited to, vinyl, 2-propenyl, crotyl, 2-isopentenyl, 2-(butadienyl), 2,4-pentadienyl, 3-(1,4-pentadienyl),

ethynyl, 1- and 3-propynyl, 3-butyryl, and the higher homologs and isomers. An alkoxy is an alkyl attached to the remainder of the molecule via an oxygen linker (-O-).

The term "alkylene," by itself or as part of another substituent, means, unless otherwise stated, a divalent radical derived from an alkyl, as exemplified, but not limited by, -

CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-. Typically, an alkyl (or alkylene) group will have from 1 to 24 carbon atoms, with those groups having 10 or fewer carbon atoms being preferred in the present invention. A "lower alkyl" or "lower alkylene" is a shorter chain alkyl or alkylene group, generally having eight or fewer carbon atoms. The term "alkenylene," by itself or as part of another substituent, means, unless otherwise stated, a divalent radical derived from an alkene.

The term "heteroalkyl," by itself or in combination with another term, means, unless otherwise stated, a stable straight or branched chain, or combinations thereof, including at least one carbon atom and at least one heteroatom selected from the group consisting of O, N, P, Si, and S, and wherein the nitrogen and sulfur atoms may optionally be oxidized, and the nitrogen heteroatom may optionally be quaternized. Heteroalkyl is not cyclized. The heteroatom(s) O, N, P, S, and Si may be placed at any interior position of the heteroalkyl group or at the position at which the alkyl group is attached to the remainder of the molecule. Examples include, but are not limited to: -CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>3</sub>, -CH<sub>2</sub>-CH<sub>2</sub>-NH-CH<sub>3</sub>, -CH<sub>2</sub>-CH<sub>2</sub>-N(CH<sub>3</sub>)-CH<sub>3</sub>, -CH<sub>2</sub>-S-CH<sub>2</sub>-CH<sub>3</sub>, -CH<sub>2</sub>-CH<sub>2</sub>-, -S(O)-CH<sub>3</sub>, -CH<sub>2</sub>-CH<sub>2</sub>-S(O)<sub>2</sub>-CH<sub>3</sub>, -CH=CH-O-CH<sub>3</sub>, -Si(CH<sub>3</sub>)<sub>3</sub>-, -CH<sub>2</sub>-CH=N-OCH<sub>3</sub>, -CH=CH-N(CH<sub>3</sub>)-CH<sub>3</sub>, -O-CH<sub>3</sub>, -O-CH<sub>2</sub>-CH<sub>3</sub>, and -CN. Up to two or three heteroatoms may be consecutive, such as, for example, -CH<sub>2</sub>-NH-OCH<sub>3</sub> and -CH<sub>2</sub>-O-Si(CH<sub>3</sub>)<sub>3</sub>.

Similarly, the term "heteroalkylene," by itself or as part of another substituent, means, unless otherwise stated, a divalent radical derived from heteroalkyl, as exemplified, but not limited by, -CH<sub>2</sub>-CH<sub>2</sub>-S-CH<sub>2</sub>-CH<sub>2</sub>- and -CH<sub>2</sub>-S-CH<sub>2</sub>-CH<sub>2</sub>-NH-CH<sub>2</sub>-. For heteroalkylene groups, heteroatoms can also occupy either or both of the chain termini (e.g., alkyleneoxy, alkylenedioxy, alkyleneamino, alkylenediamino, and the like). Still further, for alkylene and heteroalkylene linking groups, no orientation of the linking group is implied by the direction in which the formula of the linking group is written. For example, the formula -C(O)<sub>2</sub>R'- represents both -C(O)<sub>2</sub>R'- and -R'C(O)<sub>2</sub>-. As described above, heteroalkyl groups, as used herein, include those groups that are attached to the remainder of the molecule through a heteroatom, such as -C(O)R', -C(O)NR', -NR'R", -OR', -SR', and/or -SO<sub>2</sub>R'. Where "heteroalkyl" is recited, followed by recitations of specific heteroalkyl groups, such as -NR'R" or the like, it will be understood that the terms heteroalkyl and -NR'R" are not redundant or mutually exclusive. Rather, the specific heteroalkyl groups are recited to add clarity. Thus, the term "heteroalkyl" should not be interpreted herein as excluding specific heteroalkyl groups, such as -NR'R" or the like.

The terms “cycloalkyl” and “heterocycloalkyl,” by themselves or in combination with other terms, mean, unless otherwise stated, cyclic versions of “alkyl” and “heteroalkyl,” respectively. Additionally, for heterocycloalkyl, a heteroatom can occupy the position at which the heterocycle is attached to the remainder of the molecule. Cycloalkyl and heterocycloalkyl are non-aromatic. Examples of cycloalkyl include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, 1-cyclohexenyl, 3-cyclohexenyl, cycloheptyl, and the like. Examples of heterocycloalkyl include, but are not limited to, 1-(1,2,5,6-tetrahydropyridyl), 1-piperidinyl, 2-piperidinyl, 3-piperidinyl, 4-morpholinyl, 3-morpholinyl, tetrahydrofuran-2-yl, tetrahydrofuran-3-yl, tetrahydrothien-2-yl, tetrahydrothien-3-yl, 1-piperazinyl, 2-piperazinyl, and the like. A “cycloalkylene” and a “heterocycloalkylene,” alone or as part of another substituent, means a divalent radical derived from a cycloalkyl and heterocycloalkyl, respectively.

The terms “halo” or “halogen,” by themselves or as part of another substituent, mean, unless otherwise stated, a fluorine, chlorine, bromine, or iodine atom. Additionally, terms such as “haloalkyl” are meant to include monohaloalkyl and polyhaloalkyl. For example, the term “halo(C<sub>1</sub>-C<sub>4</sub>)alkyl” includes, but is not limited to, fluoromethyl, difluoromethyl, trifluoromethyl, 2,2,2-trifluoroethyl, 4-chlorobutyl, 3-bromopropyl, and the like.

The term “acyl” means, unless otherwise stated, -C(O)R where R is a substituted or unsubstituted alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl.

The term “aryl” means, unless otherwise stated, a polyunsaturated, aromatic, hydrocarbon substituent, which can be a single ring or multiple rings (preferably from 1 to 3 rings) that are fused together (i.e., a fused ring aryl) or linked covalently. A fused ring aryl refers to multiple rings fused together wherein at least one of the fused rings is an aryl ring. The term “heteroaryl” refers to aryl groups (or rings) that contain at least one heteroatom such as N, O, or S, wherein the nitrogen and sulfur atoms are optionally oxidized, and the nitrogen atom(s) are optionally quaternized. Thus, the term “heteroaryl” includes fused ring heteroaryl groups (i.e., multiple rings fused together wherein at least one of the fused rings is a heteroaromatic ring). A 5,6-fused ring heteroarylene refers to two rings fused together, wherein one ring has 5 members and the other ring has 6 members, and wherein at least one ring is a heteroaryl ring. Likewise, a 6,6-fused ring heteroarylene refers to two rings fused together, wherein one ring has 6 members and the other ring has 6 members, and wherein at least one ring is a heteroaryl ring. And a 6,5-fused ring heteroarylene refers to two rings fused together, wherein one ring has 6 members and the other ring has 5 members, and wherein at least one ring is a heteroaryl ring. A



heteroaryl group can be attached to the remainder of the molecule through a carbon or heteroatom. Non-limiting examples of aryl and heteroaryl groups include phenyl, 1-naphthyl, 2-naphthyl, 4-biphenyl, 1-pyrrolyl, 2-pyrrolyl, 3-pyrrolyl, 3-pyrazolyl, 2-imidazolyl, 4-imidazolyl, pyrazinyl, 2-oxazolyl, 4-oxazolyl, 2-phenyl-4-oxazolyl, 5-oxazolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyridyl, 3-pyridyl, 4-pyridyl, 2-pyrimidyl, 4-pyrimidyl, 5-benzothiazolyl, purinyl, 2-benzimidazolyl, 5-indolyl, 1-isoquinolyl, 5-isoquinolyl, 2-quinoxalyl, 5-quinoxalyl, 3-quinolyl, and 6-quinolyl. Substituents for each of the above noted aryl and heteroaryl ring systems are selected from the group of acceptable substituents described below. An “arylene” and a “heteroarylene,” alone or as part of another substituent, mean a divalent radical derived from an aryl and heteroaryl, respectively. Non-limiting examples of heteroaryl groups include pyridinyl, pyrimidinyl, thiophenyl, thienyl, furanyl, indolyl, benzoxadiazolyl, benzodioxolyl, benzodioxanyl, thianaphthanyl, pyrrolopyridinyl, indazolyl, quinolinyl, quinoxalyl, pyridopyrazinyl, quinazolinonyl, benzoisoxazolyl, imidazopyridinyl, benzofuranyl, benzothienyl, benzothiophenyl, phenyl, naphthyl, biphenyl, pyrrolyl, pyrazolyl, imidazolyl, pyrazinyl, oxazolyl, isoxazolyl, thiazolyl, furylthienyl, pyridyl, pyrimidyl, benzothiazolyl, purinyl, benzimidazolyl, isoquinolyl, thiadiazolyl, oxadiazolyl, pyrrolyl, diazolyl, triazolyl, tetrazolyl, benzothiadiazolyl, isothiazolyl, pyrazolopyrimidinyl, pyrrolopyrimidinyl, benzotriazolyl, benzoxazolyl, or quinolyl. The examples above may be substituted or unsubstituted and divalent radicals of each heteroaryl example above are non-limiting examples of heteroarylene.

A fused ring heterocycloalkyl-aryl is an aryl fused to a heterocycloalkyl. A fused ring heterocycloalkyl-heteroaryl is a heteroaryl fused to a heterocycloalkyl. A fused ring heterocycloalkyl-cycloalkyl is a heterocycloalkyl fused to a cycloalkyl. A fused ring heterocycloalkyl-heterocycloalkyl is a heterocycloalkyl fused to another heterocycloalkyl. Fused ring heterocycloalkyl-aryl, fused ring heterocycloalkyl-heteroaryl, fused ring heterocycloalkyl-cycloalkyl, or fused ring heterocycloalkyl-heterocycloalkyl may each independently be unsubstituted or substituted with one or more of the substituents described herein.

As used herein, the terms “heteroatom” or “ring heteroatom” are meant to include, oxygen (O), nitrogen (N), sulfur (S), phosphorus (P), and silicon (Si).

The term “oxo,” as used herein, means an oxygen that is double bonded to a carbon atom.

Each R-group as provided in the formulae provided herein can appear more than once. Where a R-group appears more than once each R group can be optionally different.

The symbol “~” denotes the point of attachment of a chemical moiety to the remainder of a molecule or chemical formula.

The term "contacting" as used herein, refers to materials or compounds being sufficiently close in proximity to react or interact. For example, in methods of contacting a hydrocarbon material (i.e., unrefined petroleum material)-bearing formation and/or a well bore, the term "contacting" includes placing an aqueous composition (e. g. chemical, surfactant or polymer) within a hydrocarbon material-bearing formation using any suitable manner known in the art (e.g., pumping, injecting, pouring, releasing, displacing, spotting or circulating the chemical into a well, well bore or hydrocarbon-bearing formation).

The terms "unrefined petroleum" and "crude oil" are used interchangeably and in keeping with the plain ordinary usage of those terms. "Unrefined petroleum" and "crude oil" may be found in a variety of petroleum reservoirs (also referred to herein as a "reservoir," "oil field deposit" "deposit" and the like) and in a variety of forms including oleaginous materials, oil shales (i.e., organic-rich fine-grained sedimentary rock), tar sands, light oil deposits, heavy oil deposits, and the like. "Crude oils" or "unrefined petroleum" generally refer to a mixture of naturally occurring hydrocarbons (i.e., unrefined petroleum material) that may be refined into diesel, gasoline, heating oil, jet fuel, kerosene, and other products called fuels or petrochemicals. Crude oils or unrefined petroleum are named according to their contents and origins, and are classified according to their per unit weight (specific gravity). Heavier crudes generally yield more heat upon burning, but have lower gravity as defined by the American Petroleum Institute (API) and market price in comparison to light (or sweet) crude oils. Crude oil may also be characterized by its Equivalent Alkane Carbon Number (EACN).

Crude oils vary widely in appearance and viscosity from field to field. They range in color, odor, and in the properties they contain. While all crude oils are mostly hydrocarbons, the differences in properties, especially the variation in molecular structure, determine whether a crude oil is more or less easy to produce, pipeline, and refine. The variations may even influence its suitability for certain products and the quality of those products. Crude oils are roughly classified into three groups, according to the nature of the hydrocarbons they contain. (i) Paraffin based crude oils contain higher molecular weight paraffins, which are solid at room temperature, but little or no asphaltic (bituminous) matter. They can produce high-grade lubricating oils. (ii) Asphaltene based crude oils contain large proportions of asphaltic matter, and little or no paraffin. Some are predominantly naphthenes and so yield lubricating oils that are more sensitive to temperature changes than the paraffin-based crudes. (iii) Mixed based crude oils contain both paraffin and naphthenes, as well as aromatic hydrocarbons. Most crude oils fit this latter category.

"Heavy crude oils" as provided herein are crude oils, with an API gravity of less than 20. The heavy crude oils may have a viscosity greater than 100 cP. In embodiments, the heavy crude oil has a viscosity of at least 100 cP. In embodiments, the heavy crude oil has a viscosity of at least 1,000 cP. In embodiments, the heavy crude oil has a viscosity of at least 10,000 cP. In  
5       embodiments, the heavy crude oil has a viscosity of at least 100,000 cP. In embodiments, the heavy crude oil has a viscosity of at least 1,000,000 cP.

"Reactive" or "active" heavy crude oil as referred to herein is heavy crude oil containing natural organic acidic components (also referred to herein as unrefined petroleum acid) or their precursors such as esters or lactones. These reactive heavy crude oils can generate soaps  
10       (carboxylates, surfactants) when reacted with alkali or an organic base. More terms used interchangeably for heavy crude oil throughout this disclosure are hydrocarbon material or reactive petroleum material or unrefined petroleum material. An "oil bank" or "oil cut" as referred to herein, is the heavy crude oil that does not contain the injected chemicals and is pushed by the injected fluid during an enhanced oil recovery process.

"Unrefined petroleum acids" as referred to herein are carboxylic acids contained in active petroleum material (reactive heavy crude oil). The unrefined petroleum acids contain C<sub>11</sub> to C<sub>20</sub> alkyl chains, including naphthenic acid mixtures. The recovery of such "reactive" oils may be performed using alkali, as described herein, including embodiments thereof, in a surfactant composition. The alkali reacts with the acid in the reactive oil to form soap in situ. These in situ  
20       generated soaps serve as a source of surfactants enabling efficient oil recovery from the reservoir as well as heavy crude oil transport.

Terms used interchangeably for crude oil throughout this disclosure are "hydrocarbon material" or "unrefined petroleum material". An "oil bank" or "oil cut" as referred to herein, is the crude oil that does not contain the injected chemicals and is pushed by the injected fluid  
25       during an enhanced oil recovery process.

The term "polymer" refers to a molecule having a structure that essentially includes the multiple repetitions of units derived, actually or conceptually, from molecules of low relative molecular mass. In embodiments, the polymer is an oligomer.

The term "bonded" refers to having at least one of covalent bonding, hydrogen bonding,  
30       ionic bonding, Van Der Waals interactions, pi interactions, London forces or electrostatic interactions.

The term "productivity" as applied to a petroleum or oil well refers to the capacity of a well to produce hydrocarbons (e.g., unrefined petroleum material); that is, the ratio of the hydrocarbon flow rate to the pressure drop, where the pressure drop is the difference between the

average reservoir pressure and the flowing bottom hole well pressure (i.e., flow per unit of driving force).

The term "oil solubilization ratio" is defined as the volume of oil solubilized divided by the volume of surfactant in microemulsion. All the surfactant is presumed to be in the microemulsion phase. The oil solubilization ratio is applied for Winsor type I and type III behavior. The volume of oil solubilized is found by reading the change between initial aqueous level and excess oil (top) interface level. The oil solubilization ratio is calculated as follows:

$$\sigma_o = \frac{V_o}{V_s}, \text{ wherein}$$

$\sigma_o$  = oil solubilization ratio;

$V_o$  = volume of oil solubilized;

$V_s$  = volume of surfactant.

The term "water solubilization ratio" is defined as the volume of water solubilized divided by the volume of surfactant in microemulsion. All the surfactant is presumed to be in the microemulsion phase. The water solubilization ratio is applied for Winsor type III and type II behavior. The volume of water solubilized is found by reading the change between initial aqueous level and excess water (bottom) interface level. The water solubilization parameter is calculated as follows:

$$\sigma_w = \frac{V_w}{V_s}, \text{ wherein}$$

$\sigma_w$  = water solubilization ratio;

$V_w$  = volume of water solubilized.

The optimum solubilization ratio occurs where the oil and water solubilization ratios are equal. The coarse nature of phase behavior screening often does not include a data point at optimum, so the solubilization ratio curves are drawn for the oil and water solubilization ratio data and the intersection of these two curves is defined as the optimum. The following is true for the optimum solubilization ratio:

$$\sigma_o = \sigma_w = \sigma^*;$$

$\sigma^*$  = optimum solubilization ratio.

The term "solubility" or "solubilization" in general refers to the property of a solute, which can be a solid, liquid or gas, to dissolve in a solid, liquid or gaseous solvent thereby forming a homogenous solution of the solute in the solvent. Solubility occurs under dynamic equilibrium, which means that solubility results from the simultaneous and opposing processes of dissolution and phase joining (e.g., precipitation of solids). The solubility equilibrium occurs when the two processes proceed at a constant rate. The solubility of a given solute in a given solvent typically depends on temperature. For many solids dissolved in liquid water, the solubility increases with temperature. In liquid water at high temperatures, the solubility of ionic solutes tends to decrease due to the change of properties and structure of liquid water. In more particular, solubility and solubilization as referred to herein is the property of oil to dissolve in water and vice versa.

"Viscosity" refers to a fluid's internal resistance to flow or being deformed by shear or tensile stress. In other words, viscosity may be defined as thickness or internal friction of a liquid. Thus, water is "thin", having a lower viscosity, while oil is "thick", having a higher viscosity. More generally, the less viscous a fluid is, the greater its ease of fluidity.

The term "salinity" as used herein, refers to concentration of salt dissolved in a aqueous phases. Examples for such salts are without limitation, sodium chloride, magnesium and calcium sulfates, and bicarbonates. In more particular, the term salinity as it pertains to the present invention refers to the concentration of salts in brine and surfactant solutions.

The term "aqueous solution or aqueous formulation" refers to a solution in which the solvent is water. The term "emulsion, emulsion solution or emulsion formulation" refers to a mixture of two or more liquids, which are normally immiscible. A non-limiting example for an emulsion is a mixture of oil and water.

An "alkali agent" is used according to its conventional meaning and includes basic, ionic salts of alkali metals or alkaline earth metals. Alkali agents as provided herein are typically capable of reacting with an unrefined petroleum acid (e.g., the acid in crude oil (reactive oil)) to form soap (a surfactant salt of a fatty acid) *in situ*. These *in situ* generated soaps serve as a source of surfactants causing a reduction of the interfacial tension of the oil in water emulsion, thereby reducing the viscosity of the emulsion. Examples of alkali agents useful for the provided invention include, but are not limited to, amines (e.g., mono-, di- and tri-alkyl amines such as methyl amine, dimethyl amine, trimethyl amine), carbonates (e.g., bicarbonates), borates, silicates, acetates, and EDTA tetrasodium salt. In embodiments, the alkali is not sodium hydroxide.

A "co-solvent" refers to a compound having the ability to increase the solubility of a solute in the presence of an unrefined petroleum acid. In embodiments, the co-solvents provided herein have a hydrophobic portion (alkyl or aryl chain), a hydrophilic portion (e.g., an alcohol) and optionally an alkoxy portion. Co-solvents as provided herein include alcohols (e.g., 25 C<sub>1</sub>-C<sub>6</sub> alcohols, C<sub>1</sub>-C<sub>6</sub> diols), alkoxy alcohols (e.g., C<sub>1</sub>-C<sub>6</sub> alkoxy alcohols, C<sub>1</sub>-C<sub>6</sub> alkoxy diols, phenyl alkoxy alcohols), glycol ether, glycol and glycerol.

A "microemulsion" as referred to herein is a thermodynamically stable mixture of oil, water, and a stabilizing agents such as a surfactant or a co-solvent that may also include additional components such as alkali agents, polymers (e.g., water-soluble polymers) and a salt. In contrast, a "macroemulsion" as referred to herein is a thermodynamically unstable mixture of oil and water that may also include additional components. An "emulsion" as referred to herein may be a microemulsion or a macroemulsion.

## I. Compositions

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

Provided herein, *inter alia*, are aqueous compositions and methods of using the same for a variety of applications including enhanced oil recovery. In one aspect, the aqueous composition provided herein includes water, a surfactant (or a combination of multiple surfactants), an ammonia compound, an ionic strength adjusting agent, and a multivalent mineral cation (i.e., a divalent or trivalent cation derived from a mineral). The ammonia compound can be R<sup>3</sup>H<sub>2</sub>N, (R<sup>3</sup>)<sub>2</sub>HN, (R<sup>3</sup>)<sub>3</sub>N, or NH<sub>3</sub>, wherein R<sup>3</sup> is independently unsubstituted C<sub>1</sub>-C<sub>5</sub> alkyl. The aqueous composition may further include a co-solvent.

In another aspect, the aqueous composition provided herein includes water, a co-solvent, an ammonia compound as described herein, a multivalent mineral cation, and an ionic strength adjusting agent. The aqueous composition may further include a surfactant.

In embodiments, R<sup>3</sup> is independently unsubstituted C<sub>1</sub>-C<sub>3</sub> alkyl. R<sup>3</sup> may independently be methyl, ethyl, or propyl. R<sup>3</sup> may independently be methyl or ethyl. R<sup>3</sup> may be methyl. R<sup>3</sup> may be ethyl. R<sup>3</sup> may be propyl. In embodiments, the ammonia compound is NH<sub>2</sub>(CH<sub>3</sub>), NH<sub>2</sub>(CH<sub>2</sub>CH<sub>3</sub>), NH(CH<sub>3</sub>)<sub>2</sub>, NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, NH(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>3</sub>), N(CH<sub>3</sub>)<sub>3</sub>, or NH(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>. In embodiments, the ammonia compound is NH<sub>3</sub>. In embodiments, the ammonia compound is not NH<sub>3</sub>.

The aqueous compositions can be used with broad oil concentrations, at a wide range of salinities and are surprisingly effective for oil recovery from mineral-containing reservoirs (e.g., reservoirs containing minerals wherein, upon contact with water, a multivalent mineral cation is dissolved as described herein). The aqueous compositions provided herein may be functional at high reservoir temperatures (e.g., about 10 °C to about 160 °C, about 60 °C to about 120 °C, about 90 °C to about 120 °C, or about 100 °C to about 120 °C, or about 110 °C to about 120 °C) and/or particularly at alkaline pH (e.g., about pH 10 or higher). The ammonia compound included in the aqueous composition may prevent surfactant precipitation and minimize surfactant adsorption to solid reservoir material (e.g., rock). Thus, using the aqueous composition provided herein, the organic acids in the oil (heavy oil/unrefined petroleum) may be readily available (i.e., mobilized), even at high pH (e.g., at least about 10) to form soap that may lower the interfacial tension enough to increase oil production from the well. The compositions provided herein are useful for the recovery of active and non-active crude oils. Thus, in embodiments, the aqueous compositions and emulsions provided herein provide an elevated pH (e.g., above about 9.0 or 9.5, or about 10) conducive for soap formation in active oils where minerals and/or multivalent mineral cations are present.

In embodiments, the aqueous composition is within a petroleum reservoir. The petroleum reservoir may be below an ocean or a sea. In embodiments, the petroleum reservoir is at a temperature of between about 10 °C and about 160 °C. The petroleum reservoir may be at a temperature of about between 10 °C and about 150 °C. The petroleum reservoir may be at a temperature of about between 10 °C and about 140 °C. The petroleum reservoir may be at a temperature of about between 10 °C and about 130 °C. The petroleum reservoir may be at a temperature of about between 10 °C and about 120 °C. The petroleum reservoir may be at a temperature of about between 10 °C and about 110 °C. The petroleum reservoir may be at a temperature of about between 10 °C and about 100 °C. The petroleum reservoir may be at a temperature of about between 10 °C and about 90 °C. The petroleum reservoir may be at a temperature of about between 10 °C and about 80 °C. The petroleum reservoir may be at a temperature of about between 10 °C and about 70 °C. The petroleum reservoir may be at a temperature of about between 10 °C and about 60 °C. The petroleum reservoir may be at a temperature of about between 10 °C and about 50 °C. The petroleum reservoir may be at a temperature of about between 10 °C and about 40 °C.

The petroleum reservoir may be at a temperature of at least 10 °C. The petroleum reservoir may be at a temperature of at least 20 °C. The petroleum reservoir may be at a temperature of at least 30 °C. The petroleum reservoir may be at a temperature of at least 40 °C.

The petroleum reservoir may be at a temperature of at least 50 °C. The petroleum reservoir may be at a temperature of at least 60 °C. The petroleum reservoir may be at a temperature of at least 70 °C. The petroleum reservoir may be at a temperature of at least 80 °C. The petroleum reservoir may be at a temperature of at least 90 °C. The petroleum reservoir may be at a temperature of at least 100 °C. The petroleum reservoir may be at a temperature of at least 110 °C. The petroleum reservoir may be at a temperature of at least 120 °C. The petroleum reservoir may be at a temperature of at least 130 °C. The petroleum reservoir may be at a temperature of at least 140 °C. The petroleum reservoir may be at a temperature of at least 150 °C. The petroleum reservoir may be at a temperature of at least 160 °C.

In embodiments, the aqueous composition is in contact with a mineral. The multivalent mineral cation may be derived from the mineral. Thus, in embodiments, water dissolves the multivalent mineral cation from the mineral. The mineral may be a sulfate mineral, such as gypsum, anhydrite, barite or magnesium sulfate. A “sulfate mineral” as provided herein refers to a mineral, which includes the sulfate ion  $\text{SO}_4^{2-}$  within its structure. Non-limiting examples of sulfate minerals include anhydrous sulfates such as barite ( $\text{BaSO}_4$ ), celestite ( $\text{SrSO}_4$ ), anglesite ( $\text{PbSO}_4$ ), anhydrite ( $\text{CaSO}_4$ ), and hanksite ( $\text{Na}_2\text{K}(\text{SO}_4)_9(\text{CO}_3)_2\text{Cl}$ ); and hydroxide or hydrous sulfates such as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), chalcantinite ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), kieserite  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ , starkeyite  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ , hexahydrate  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , epsomite  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , meridianiite  $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ , melanterite  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , antlerite  $\text{Cu}_3\text{SO}_4(\text{OH})_4$ , brochantite  $\text{Cu}_4\text{SO}_4(\text{OH})_6$ , alunite  $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ , and jarosite  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ . In embodiments, the sulfate mineral is gypsum. In embodiments, the sulfate mineral (e.g., gypsum) forms part of the solid reservoir material (e.g., rock). In embodiments, the mineral (e.g., sulfate mineral) forms part of the solid reservoir material and the aqueous composition provided herein including embodiments thereof.

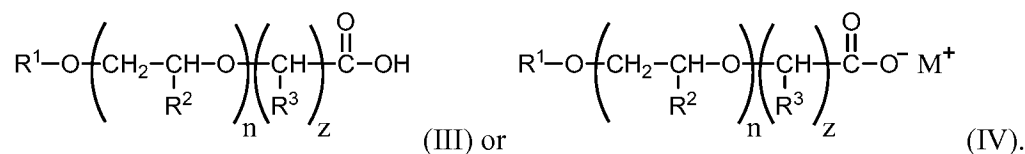
The multivalent mineral cation may be an alkaline earth metal cation (i.e., a cation of beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), or radium (Ra)). The multivalent mineral cation may be  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  or  $\text{Be}^{2+}$ . The multivalent mineral cation may be  $\text{Ca}^{2+}$ . Where the multivalent mineral cation is  $\text{Ca}^{2+}$ , the multivalent cation may be derived from  $\text{CaCl}_2$ . The  $\text{CaCl}_2$  may be dissolved from the mineral or added as an exogenous component (e.g., a component not found in the aqueous composition) to the compositions described herein, including embodiments thereof.

The aqueous composition provided herein including embodiments thereof may include a surfactant or a combination of multiple surfactants (e.g., a plurality of surfactant types or a surfactant blend). The surfactant provided herein may be any appropriate surfactant useful in the field of enhanced oil recovery. In embodiments, the surfactant is a single surfactant type in the



aqueous composition. In embodiments, the surfactant is a surfactant blend. A "surfactant blend" as provided herein is a mixture of a plurality of surfactant types. In embodiments, the surfactant blend includes a first surfactant type, a second surfactant type, or a third surfactant type. The first, second and third surfactant type may be independently different (e.g., anionic or cationic surfactants; or two cationic surfactant having a different hydrocarbon chain length but are otherwise the same). Thus, the aqueous composition may include a first surfactant, a second surfactant and a third surfactant, wherein the first surfactant is chemically different from the second and the third surfactant, and the second surfactant is chemically different from the third surfactant. Therefore, a person having ordinary skill in the art will immediately recognize that the terms "surfactant" and "surfactant type(s)" have the same meaning and can be used interchangeably. In embodiments, the surfactant is an anionic surfactant, a non-ionic surfactant, a zwitterionic surfactant or a cationic surfactant. In embodiments, the surfactant is an anionic surfactant, a non-ionic surfactant, or a cationic surfactant. In embodiments, the co-surfactant is a zwitterionic surfactant. "Zwitterionic" or "zwitterion" as used herein refers to a neutral molecule with a positive (or cationic) and a negative (or anionic) electrical charge at different locations within the same molecule. Examples for zwitterionics are without limitation betains and sultains.

The surfactant provided herein may be any appropriate anionic surfactant. In embodiments, the surfactant is an anionic surfactant. In embodiments, the anionic surfactant is an anionic surfactant blend. Where the anionic surfactant is an anionic surfactant blend the aqueous composition includes a plurality (i.e., more than one) of anionic surfactant types. In embodiments, the anionic surfactant is an alkoxy carboxylate surfactant, an alkoxy sulfate surfactant, an alkoxy sulfonate surfactant, an alkyl sulfonate surfactant, an aryl sulfonate surfactant or an olefin sulfonate surfactant. An "alkoxy carboxylate surfactant" as provided herein is a compound having an alkyl or aryl attached to one or more alkoxy groups (typically  $-\text{CH}_2-\text{CH}(\text{ethyl})-\text{O}-$ ,  $-\text{CH}_2-\text{CH}(\text{methyl})-\text{O}-$ , or  $-\text{CH}_2-\text{CH}_2-\text{O}-$ ) which, in turn is attached to  $-\text{COO}^-$  or acid or salt thereof including metal cations such as sodium. In embodiments, the alkoxy carboxylate surfactant has the formula:

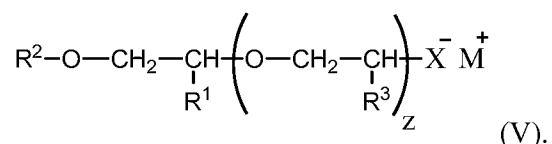


In formula (III) or (IV)  $\text{R}^1$  is substituted or unsubstituted  $\text{C}_8-\text{C}_{150}$  alkyl or substituted or unsubstituted aryl,  $\text{R}^2$  is independently hydrogen or unsubstituted  $\text{C}_1-\text{C}_6$  alkyl,  $\text{R}^3$  is independently hydrogen or unsubstituted  $\text{C}_1-\text{C}_6$  alkyl,  $n$  is an integer from 2 to 210,  $z$  is an

integer from 1 to 6 and  $M^+$  is a monovalent, divalent or trivalent cation. In embodiments of formula (III) or (IV),  $R^1$  is unsubstituted linear or branched  $C_8$ - $C_{36}$  alkyl. In embodiments of formula (III) or (IV),  $R^1$  is  $(C_6H_5-CH_2CH_2)_3C_6H_2$ -(TSP),  $(C_6H_5-CH_2CH_2)_2C_6H_3$ -(DSP),  $(C_6H_5-CH_2CH_2)_1C_6H_4$ -(MSP), or substituted or unsubstituted naphthyl. In embodiments of formula (III) or (IV), the alkoxy carboxylate is  $C_{28}$ -25PO-25EO-carboxylate (i.e., unsubstituted  $C_{28}$  alkyl attached to 25  $-CH_2-CH$ (methyl)-O-linkers, attached in turn to 25  $-CH_2-CH_2-O$ - linkers, attached in turn to  $-COO^-$  or acid or salt thereof including metal cations such as sodium).

In embodiments, the surfactant is an alkoxy sulfate surfactant. An alkoxy sulfate surfactant as provided herein is a surfactant having an alkyl or aryl attached to one or more alkoxy groups (typically  $-CH_2-CH$ (ethyl)-O-,  $-CH_2-CH$ (methyl)-O-, or  $-CH_2-CH_2-O$ -) which, in turn is attached to  $-SO_3^-$  or acid or salt thereof including metal cations such as sodium. In embodiments, the alkoxy sulfate surfactant has the formula  $R^A-(BO)_e-(PO)_f-(EO)_g-SO_3^-$  or acid or salt (including metal cations such as sodium) thereof, wherein  $R^A$  is  $C_8$ - $C_{30}$  alkyl, BO is  $-CH_2-CH$ (ethyl)-O-, PO is  $-CH_2-CH$ (methyl)-O-, and EO is  $-CH_2-CH_2-O$ -. The symbols e, f and g are integers from 0 to 25 wherein at least one is not zero. In embodiments, the alkoxy sulfate surfactant is  $C_{15}$ -13PO-sulfate (i.e., an unsubstituted  $C_{15}$  alkyl attached to 13  $-CH_2-CH$ (methyl)-O- linkers, in turn attached to  $-SO_3^-$  or acid or salt thereof including metal cations such as sodium). In embodiments, the alkoxy sulfate surfactant is  $C_{13}$ -13PO-sulfate (i.e., an unsubstituted  $C_{13}$  alkyl attached to 13  $-CH_2-CH$ (methyl)-O- linkers, in turn attached to  $-SO_3^-$  or acid or salt thereof including metal cations such as sodium).

In embodiments, the alkoxy sulfate surfactant has the formula:



In formula (V)  $R^1$  and  $R^2$  are independently substituted or unsubstituted  $C_8$ - $C_{150}$  alkyl or substituted or unsubstituted aryl.  $R^3$  is independently hydrogen or unsubstituted  $C_1$ - $C_6$  alkyl.  $z$

is an integer from 2 to 210.  $X^-$  is  $\begin{array}{c} | \\ \text{---O---SO}_3^- \end{array}$ ,  $\begin{array}{c} \text{O} \\ || \\ \text{---O---C---O}^- \end{array}$ ,  $\begin{array}{c} \text{O} \\ || \\ \text{---O---CH}_2\text{---C---O}^- \end{array}$ ,  $\begin{array}{c} | \\ \text{---O---PO}_3^- \end{array}$ ,

$\begin{array}{c} | \\ \text{---O---BO}_2^- \end{array}$ ,  $\begin{array}{c} | \\ \text{---O---CH}_2\text{---CH}_2\text{---CH}_2\text{---SO}_3^- \end{array}$ , or  $\begin{array}{c} \text{OH} \\ | \\ \text{---O---CH}_2\text{---CH---CH}_2\text{---SO}_3^- \end{array}$  and  $M^+$  is a

monovalent, divalent or trivalent cation. In embodiments of formula (V),  $R^1$  is branched unsubstituted  $C_8$ - $C_{150}$ . In embodiments of formula (V),  $R^1$  is branched or linear unsubstituted  $C_{12}$ - $C_{100}$  alkyl,  $(C_6H_5-CH_2CH_2)_3C_6H_2$ -(TSP),  $(C_6H_5-CH_2CH_2)_2C_6H_3$ -(DSP),  $(C_6H_5-CH_2CH_2)_1C_6H_4$ -(MSP), or substituted or unsubstituted naphthyl. In embodiments of formula

(V), the alkoxy sulfate is C<sub>16</sub>-C<sub>16</sub>-epoxide-15PO-10EO-sulfate (i.e., a linear unsubstituted C<sub>16</sub> alkyl attached to an oxygen, which in turn is attached to a branched unsubstituted C<sub>16</sub> alkyl, which in turn is attached to 15 -CH<sub>2</sub>-CH(methyl)-O- linkers, in turn attached to 10 -CH<sub>2</sub>-CH<sub>2</sub>-O- linkers, in turn attached to -SO<sub>3</sub><sup>-</sup> or acid or salt thereof including metal cations such as sodium.

The alkoxy sulfate surfactant provided herein may be an aryl alkoxy sulfate surfactant. An aryl alkoxy surfactant as provided herein is an alkoxy surfactant having an aryl attached to one or more alkoxy groups (typically -CH<sub>2</sub>-CH(ethyl)-O-, -CH<sub>2</sub>-CH(methyl)-O-, or -CH<sub>2</sub>-CH<sub>2</sub>-O-) which, in turn is attached to -SO<sub>3</sub><sup>-</sup> or acid or salt thereof including metal cations such as sodium. In embodiments of formula (V), the aryl alkoxy sulfate surfactant is (C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>-7PO-10EO-sulfate (i.e., tri-styrylphenol attached to 7 -CH<sub>2</sub>-CH(methyl)-O- linkers, in turn attached to 10 -CH<sub>2</sub>-CH<sub>2</sub>-O- linkers, in turn attached to -SO<sub>3</sub><sup>-</sup> or acid or salt thereof including metal cations such as sodium).

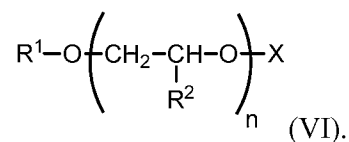
In embodiments, the surfactant is an unsubstituted alkyl sulfate or an unsubstituted alkyl sulfonate surfactant. An alkyl sulfate surfactant as provided herein is a surfactant having an alkyl group attached to -O-SO<sub>3</sub><sup>-</sup> or acid or salt thereof including metal cations such as sodium. An alkyl sulfonate surfactant as provided herein is a surfactant having an alkyl group attached to -SO<sub>3</sub><sup>-</sup> or acid or salt thereof including metal cations such as sodium. In embodiments, the surfactant is an unsubstituted aryl sulfate surfactant or an unsubstituted aryl sulfonate surfactant. An aryl sulfate surfactant as provided herein is a surfactant having an aryl group attached to -O-SO<sub>3</sub><sup>-</sup> or acid or salt thereof including metal cations such as sodium. An aryl sulfonate surfactant as provided herein is a surfactant having an aryl group attached to -SO<sub>3</sub><sup>-</sup> or acid or salt thereof including metal cations such as sodium. In embodiments, the surfactant is an alkyl aryl sulfonate. Non-limiting examples of alkyl sulfate surfactants, aryl sulfate surfactants, alkyl sulfonate surfactants, aryl sulfonate surfactants and alkyl aryl sulfonate surfactants useful in the embodiments provided herein are alkyl aryl sulfonates (ARS) (e.g., alkyl benzene sulfonate (ABS)), alkane sulfonates, petroleum sulfonates, and alkyl diphenyl oxide (di)sulfonates. Additional surfactants useful in the embodiments provided herein are alcohol sulfates, alcohol phosphates, alkoxy phosphate, sulfosuccinate esters, alcohol ethoxylates, alkyl phenol ethoxylates, quaternary ammonium salts, betains and sultains.

The surfactant as provided herein may be an olefin sulfonate surfactant. In embodiments, the olefin sulfonate surfactant is an internal olefin sulfonate (IOS) or an alpha olefin sulfonate (AOS). In embodiments, the olefin sulfonate surfactant is a C<sub>10</sub>-C<sub>30</sub> (IOS). In embodiments, the olefin sulfonate surfactant is C<sub>15</sub>-C<sub>18</sub> IOS. In embodiments, the olefin sulfonate surfactant is

C<sub>19</sub>-C<sub>28</sub> IOS. Where the olefin sulfonate surfactant is C<sub>15</sub>-C<sub>18</sub> IOS, the olefin sulfonate surfactant is a mixture (combination) of C<sub>15</sub>, C<sub>16</sub>, C<sub>17</sub> and C<sub>18</sub> alkene, wherein each alkene is attached to a -SO<sub>3</sub><sup>-</sup> or acid or salt thereof including metal cations such as sodium. Likewise, where the olefin sulfonate surfactant is C<sub>19</sub>-C<sub>28</sub> IOS, the olefin sulfonate surfactant is a mixture (combination) of C<sub>19</sub>, C<sub>20</sub>, C<sub>21</sub>, C<sub>22</sub>, C<sub>23</sub>, C<sub>24</sub>, C<sub>25</sub>, C<sub>26</sub>, C<sub>27</sub> and C<sub>28</sub> alkene, wherein each alkene is attached to a -SO<sub>3</sub><sup>-</sup> or acid or salt thereof including metal cations such as sodium. In embodiments, the olefin sulfonate surfactant is C<sub>19</sub>-C<sub>23</sub> IOS. As mentioned above, the aqueous composition provided herein may include a plurality of surfactants (i.e., a surfactant blend). In embodiments, the surfactant blend includes a first olefin sulfonate surfactant and a second olefin sulfonate surfactant. In embodiments, the first olefin sulfonate surfactant is C<sub>15</sub>-C<sub>18</sub> IOS and the second olefin sulfonate surfactant is C<sub>19</sub>-C<sub>28</sub> IOS.

In embodiments, the aqueous composition includes a plurality of surfactants. In embodiments, the aqueous composition includes a first surfactant and a second surfactant. In embodiments, the first surfactant is an alkoxy sulfate surfactant and the second surfactant is an olefin sulfonate surfactant. In embodiments, the alkoxy sulfate surfactant is C<sub>13</sub>-13PO-sulfate (i.e., an unsubstituted C<sub>13</sub> alkyl attached to 13 -CH<sub>2</sub>-CH(methyl)-O- linkers, in turn attached to -SO<sub>3</sub><sup>-</sup> or acid or salt thereof including metal cations such as sodium) and the olefin sulfonate surfactant is C<sub>19</sub>-C<sub>23</sub> IOS.

In embodiments, the surfactant has the formula:



In formula (VI) R<sup>1</sup> is R<sup>4</sup>-substituted or unsubstituted C<sub>8</sub>-C<sub>20</sub> alkyl, R<sup>3</sup>-substituted or unsubstituted aryl or R<sup>3</sup>-substituted or unsubstituted cycloalkyl. R<sup>2</sup> is independently hydrogen or methyl. R<sup>3</sup> is independently R<sup>4</sup>-substituted or unsubstituted C<sub>1</sub>-C<sub>15</sub> alkyl, R<sup>4</sup>-substituted or unsubstituted aryl or R<sup>4</sup>-substituted or unsubstituted cycloalkyl. R<sup>4</sup> is independently unsubstituted aryl or unsubstituted cycloalkyl. n is an integer from 25 to 115. X is -SO<sub>3</sub><sup>-</sup>M<sup>+</sup>, -CH<sub>2</sub>C(O)O-M<sup>+</sup>, -SO<sub>3</sub>H or -CH<sub>2</sub>C(O)OH, and M<sup>+</sup> is a monovalent, divalent or trivalent cation.

In embodiments of formula (VI), the symbol n is an integer from 25 to 115. In embodiments of formula (VI), the symbol n is an integer from 30 to 115. In embodiments of formula (VI), the symbol n is an integer from 35 to 115. In embodiments of formula (VI), the symbol n is an integer from 40 to 115. In embodiments of formula (VI), the symbol n is an integer from 45 to 115. In embodiments of formula (VI), the symbol n is an integer from 50 to

115. In embodiments of formula (VI), the symbol n is an integer from 55 to 115. In  
embodiments of formula (VI), the symbol n is an integer from 60 to 115. In embodiments of  
formula (VI), the symbol n is an integer from 65 to 115. In embodiments of formula (VI), the  
symbol n is an integer from 70 to 115. In embodiments of formula (VI), the symbol n is an  
5 integer from 75 to 115. In embodiments of formula (VI), the symbol n is an integer from 80 to  
115. In embodiments of formula (VI), the symbol n is an integer from 30 to 80. In embodiments  
of formula (VI), the symbol n is an integer from 35 to 80. In embodiments of formula (VI), the  
symbol n is an integer from 40 to 80. In embodiments of formula (VI), the symbol n is an  
integer from 45 to 80. In embodiments of formula (VI), the symbol n is an integer from 50 to  
10 80. In embodiments of formula (VI), the symbol n is an integer from 55 to 80. In embodiments  
of formula (VI), the symbol n is an integer from 60 to 80. In embodiments of formula (VI), the  
symbol n is an integer from 65 to 80. In embodiments of formula (VI), the symbol n is an  
integer from 70 to 80. In embodiments of formula (VI), the symbol n is an integer from 75 to  
80. In embodiments of formula (VI), the symbol n is an integer from 30 to 60. In embodiments  
15 of formula (VI), the symbol n is an integer from 35 to 60. In embodiments of formula (VI), the  
symbol n is an integer from 40 to 60. In embodiments of formula (VI), the symbol n is an  
integer from 45 to 60. In embodiments of formula (VI), the symbol n is an integer from 50 to  
60. In embodiments of formula (VI), the symbol n is an integer from 55 to 60. In embodiments  
of formula (VI), n is 25. In embodiments of formula (VI), n is 50. In embodiments of formula  
20 (VI), n is 55. In embodiments of formula (VI), n is 75. In some related embodiments, R<sup>1</sup> is R<sup>4</sup>-  
substituted or unsubstituted C<sub>8</sub>-C<sub>20</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>4</sup>-substituted  
or unsubstituted C<sub>12</sub>-C<sub>20</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>4</sup>-substituted or  
unsubstituted C<sub>13</sub>-C<sub>20</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>4</sup>-substituted or  
unsubstituted C<sub>13</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is unsubstituted C<sub>13</sub> alkyl. In other  
25 related embodiments, R<sup>1</sup> is a unsubstituted tridecyl (i.e., a C<sub>13</sub>H<sub>27</sub>- alkyl radical derived from  
tridecylalcohol). In yet embodiments, R<sup>1</sup> is R<sup>4</sup>-substituted or unsubstituted C<sub>15</sub>-C<sub>20</sub> alkyl. In  
embodiments of formula (VI), R<sup>1</sup> is R<sup>4</sup>-substituted or unsubstituted C<sub>18</sub> alkyl. In embodiments  
of formula (VI), R<sup>1</sup> is unsubstituted C<sub>18</sub> alkyl. In other related embodiments, R<sup>1</sup> is an  
unsubstituted oleyl (i.e., a C<sub>17</sub>H<sub>33</sub>CH<sub>2</sub>- radical derived from oleyl alcohol).

30 R<sup>1</sup> may be R<sup>4</sup>-substituted or unsubstituted alkyl. In embodiments of formula (VI), R<sup>1</sup> is  
R<sup>4</sup>-substituted or unsubstituted C<sub>8</sub>-C<sub>20</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>4</sup>-  
substituted or unsubstituted C<sub>10</sub>-C<sub>20</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>4</sup>-substituted  
or unsubstituted C<sub>12</sub>-C<sub>20</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>4</sup>-substituted or  
unsubstituted C<sub>13</sub>-C<sub>20</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>4</sup>-substituted or

unsubstituted C<sub>14</sub>-C<sub>20</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>4</sup>-substituted or unsubstituted C<sub>16</sub>-C<sub>20</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>4</sup>-substituted or unsubstituted C<sub>8</sub>-C<sub>15</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>4</sup>-substituted or unsubstituted C<sub>10</sub>-C<sub>15</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>4</sup>-substituted or unsubstituted C<sub>12</sub>-C<sub>15</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>4</sup>-substituted or unsubstituted C<sub>13</sub>-C<sub>15</sub> alkyl. In related embodiments, the alkyl is a saturated alkyl. In other related embodiments, R<sup>1</sup> is R<sup>4</sup>-substituted or unsubstituted C<sub>13</sub> alkyl. In other related embodiments, R<sup>1</sup> is unsubstituted C<sub>13</sub> alkyl. In other related embodiments, R<sup>1</sup> is a tridecyl (i.e., a C<sub>13</sub>H<sub>27</sub>- alkyl radical derived from tridecylalcohol). In other related embodiments, R<sup>1</sup> is R<sup>4</sup>-substituted or unsubstituted C<sub>18</sub> alkyl. In other related embodiments, R<sup>1</sup> is unsubstituted C<sub>18</sub> alkyl. In other related embodiments, R<sup>1</sup> is an oleyl (i.e., a C<sub>17</sub>H<sub>33</sub>CH<sub>2</sub>- radical derived from oleyl alcohol). In other related embodiments, n is as defined in an embodiment above (e.g., n is at least 40, or at least 50, e.g., 55 to 85).

R<sup>1</sup> may be linear or branched unsubstituted C<sub>8</sub>-C<sub>20</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>8</sub>-C<sub>20</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>8</sub>-C<sub>20</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>8</sub>-C<sub>18</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>8</sub>-C<sub>18</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>8</sub>-C<sub>18</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>18</sub> alkyl. In other related embodiments, R<sup>1</sup> is an oleyl (i.e., a C<sub>17</sub>H<sub>33</sub>CH<sub>2</sub>- radical derived from oleyl alcohol). In embodiments of formula (VI), R<sup>1</sup> is linear or branched unsubstituted C<sub>8</sub>-C<sub>16</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>8</sub>-C<sub>16</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>8</sub>-C<sub>16</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is linear or branched unsubstituted C<sub>8</sub>-C<sub>14</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>8</sub>-C<sub>14</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>8</sub>-C<sub>14</sub> alkyl. In other related embodiments, R<sup>1</sup> is branched unsubstituted C<sub>13</sub> alkyl. In other related embodiments, R<sup>1</sup> is a tridecyl (i.e., a C<sub>13</sub>H<sub>27</sub>- alkyl radical derived from tridecylalcohol). In embodiments of formula (VI), R<sup>1</sup> is linear or branched unsubstituted C<sub>8</sub>-C<sub>12</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>8</sub>-C<sub>12</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>8</sub>-C<sub>12</sub> alkyl. In other related embodiments, n is as defined in an embodiment above (e.g., n is at least 40, or at least 50, e.g., 55 to 85).

In embodiments of formula (VI), where R<sup>1</sup> is a linear or branched unsubstituted alkyl (e.g., branched unsubstituted C<sub>10</sub>-C<sub>20</sub> alkyl), the alkyl is a saturated alkyl (e.g., a linear or branched unsubstituted saturated alkyl or branched unsubstituted C<sub>10</sub>-C<sub>20</sub> saturated alkyl). A

“saturated alkyl,” as used herein, refers to an alkyl consisting only of hydrogen and carbon atoms that are bonded exclusively by single bonds. Thus, In embodiments of formula (VI), R<sup>1</sup> may be linear or branched unsubstituted saturated alkyl. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>10</sub>-C<sub>20</sub> saturated alkyl. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>10</sub>-C<sub>20</sub> saturated alkyl. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>12</sub>-C<sub>20</sub> saturated alkyl. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>12</sub>-C<sub>20</sub> saturated alkyl. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>12</sub>-C<sub>16</sub> saturated alkyl. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>12</sub>-C<sub>16</sub> saturated alkyl. In some further embodiment, R<sup>1</sup> is linear unsubstituted C<sub>13</sub> saturated alkyl.

In embodiments of formula (VI), where R<sup>1</sup> is a linear or branched unsubstituted alkyl (e.g., branched unsubstituted C<sub>10</sub>-C<sub>20</sub> alkyl), the alkyl is an unsaturated alkyl (e.g., a linear or branched unsubstituted unsaturated alkyl or branched unsubstituted C<sub>10</sub>-C<sub>20</sub> unsaturated alkyl). An “unsaturated alkyl,” as used herein, refers to an alkyl having one or more double bonds or triple bonds. An unsaturated alkyl as provided herein can be mono- or polyunsaturated and can include di- and multivalent radicals. Thus, In embodiments of formula (VI), R<sup>1</sup> may be linear or branched unsubstituted unsaturated alkyl. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>10</sub>-C<sub>20</sub> unsaturated alkyl. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>10</sub>-C<sub>20</sub> unsaturated alkyl. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>12</sub>-C<sub>20</sub> unsaturated alkyl. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>12</sub>-C<sub>20</sub> unsaturated alkyl. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>12</sub>-C<sub>18</sub> unsaturated alkyl. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>12</sub>-C<sub>18</sub> unsaturated alkyl. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>18</sub> unsaturated alkyl. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>18</sub> unsaturated alkyl. In one embodiment, R<sup>1</sup> is linear unsubstituted C<sub>18</sub> mono-unsaturated alkyl. In another embodiment, R<sup>1</sup> is linear unsubstituted C<sub>18</sub> poly-unsaturated alkyl. In one embodiment, R<sup>1</sup> is branched unsubstituted C<sub>18</sub> mono-unsaturated alkyl. In another embodiment, R<sup>1</sup> is branched unsubstituted C<sub>18</sub> poly-unsaturated alkyl.

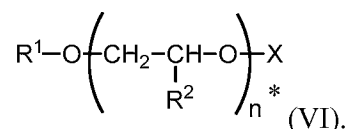
In embodiments of formula (VI), R<sup>2</sup> is independently hydrogen or methyl.

As provided herein R<sup>1</sup> may be R<sup>4</sup>-substituted or unsubstituted C<sub>8</sub>-C<sub>20</sub> (e.g., C<sub>12</sub>-C<sub>18</sub>) alkyl, R<sup>3</sup>-substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> (e.g., C<sub>5</sub>-C<sub>6</sub>) aryl or R<sup>3</sup>-substituted or unsubstituted C<sub>3</sub>-C<sub>8</sub> (e.g., C<sub>5</sub>-C<sub>7</sub>) cycloalkyl. R<sup>3</sup> may be independently R<sup>4</sup>-substituted or unsubstituted C<sub>1</sub>-C<sub>15</sub> (e.g., C<sub>8</sub>-C<sub>12</sub>) alkyl, R<sup>4</sup>-substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> (e.g., C<sub>5</sub>-C<sub>6</sub>) aryl or R<sup>4</sup>-substituted or unsubstituted C<sub>3</sub>-C<sub>8</sub> (e.g., C<sub>5</sub>-C<sub>7</sub>) cycloalkyl. Thus, in embodiments of formula (VI), R<sup>3</sup> is R<sup>4</sup>-substituted or unsubstituted C<sub>1</sub>-C<sub>15</sub> alkyl, R<sup>4</sup>-substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> aryl or R<sup>4</sup>-

substituted or unsubstituted C<sub>3</sub>-C<sub>8</sub> cycloalkyl. R<sup>4</sup> may be independently unsubstituted C<sub>5</sub>-C<sub>10</sub> (e.g., C<sub>5</sub>-C<sub>6</sub>) aryl or unsubstituted C<sub>3</sub>-C<sub>8</sub> (e.g., C<sub>5</sub>-C<sub>7</sub>) cycloalkyl. Thus, in embodiments of formula (VI), R<sup>4</sup> is independently unsubstituted C<sub>5</sub>-C<sub>10</sub> aryl or unsubstituted C<sub>3</sub>-C<sub>8</sub> cycloalkyl.

M<sup>+</sup> may be a monovalent, divalent or trivalent cation. In embodiments of formula (VI), M<sup>+</sup> is a monovalent, divalent or trivalent metal cation. In embodiments of formula (VI), M<sup>+</sup> is a monovalent or divalent cation (e.g., metal cation). In embodiments of formula (VI), M<sup>+</sup> is a monovalent cation (e.g., metal cation). In embodiments of formula (VI), M<sup>+</sup> is a divalent cation (e.g., metal cation). In embodiments of formula (VI), M<sup>+</sup> is Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> or Ba<sup>2+</sup>. A person having ordinary skill in the art will immediately recognize that M<sup>+</sup> may be a divalent cation where X is a monovalent anion (e.g., where M<sup>+</sup> is coordinated with more than one compound provided herein or with an additional anion in the surrounding liquid environment).

In embodiments of formula (VI), where multiple R<sup>2</sup> substituents are present and at least two R<sup>2</sup> substituents are different, R<sup>2</sup> substituents with the fewest number of carbons are present to the side of the compound bound to the X substituent. In this embodiment, the compound will be increasingly hydrophilic in progressing from the R<sup>2</sup> substituent to the side of the compound bound to the X substituent. The term "side of the compound bound to the X substituent" refers to the side of the compound indicated by asterisks in the below structure:



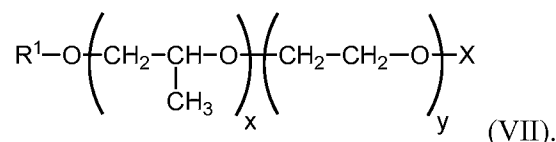
In embodiments of formula (VI) of the compound, or embodiments thereof provided herein, where R<sup>1</sup> is unsubstituted C<sub>10</sub>-C<sub>15</sub> alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 25 to 115. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>10</sub>-C<sub>15</sub> alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 20 to 75. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>10</sub>-C<sub>15</sub> alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 20 to 65. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>10</sub>-C<sub>15</sub> alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 20 to 55. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>10</sub>-C<sub>15</sub> alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 35 to 75. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>10</sub>-C<sub>15</sub> alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 35 to 65. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>10</sub>-C<sub>15</sub> alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 35 to 55. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>10</sub>-C<sub>15</sub> alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 40 to 75. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>10</sub>-



C<sub>15</sub> alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 40 to 65. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>10</sub>-C<sub>15</sub> alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 40 to 55. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>10</sub>-C<sub>15</sub> alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is 55.

In embodiments of formula (VI) of the compound, or embodiments thereof provided herein, where R<sup>1</sup> is unsubstituted C<sub>12</sub>-C<sub>20</sub> unsaturated alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 25 to 115. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>12</sub>-C<sub>20</sub> unsaturated alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 40 to 115. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>12</sub>-C<sub>20</sub> unsaturated alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 50 to 115. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>12</sub>-C<sub>20</sub> unsaturated alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 60 to 115. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>12</sub>-C<sub>20</sub> unsaturated alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 70 to 115. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>12</sub>-C<sub>20</sub> unsaturated alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 75 to 115. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>12</sub>-C<sub>20</sub> unsaturated alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is 75. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>12</sub>-C<sub>20</sub> unsaturated alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 80 to 115. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>12</sub>-C<sub>20</sub> unsaturated alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 85 to 115. In embodiments of formula (VI), where R<sup>1</sup> is unsubstituted C<sub>12</sub>-C<sub>20</sub> unsaturated alkyl and R<sup>2</sup> is independently hydrogen or methyl, the symbol n is an integer from 90 to 115.

In embodiments, the surfactant has the formula:



In formula (VII) R<sup>1</sup> and X are defined as above (e.g., in formula (VI)). y is an integer from 5 to 40, and x is an integer from 35 to 50. In embodiments of formula (VII), y is 10 and x is 45. In embodiments of formula (VII), R<sup>1</sup> is C<sub>13</sub> alkyl. In embodiments of formula (VII), y is 30 and x is 45. In some other embodiments, R<sup>1</sup> is unsubstituted unsaturated C<sub>18</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is linear unsubstituted C<sub>18</sub> unsaturated alkyl. In embodiments of formula (VII), R<sup>1</sup> is branched unsubstituted C<sub>18</sub> unsaturated alkyl. In one embodiment, R<sup>1</sup> is

linear unsubstituted C<sub>18</sub> mono-unsaturated alkyl. In another embodiment, R<sup>1</sup> is linear unsubstituted C<sub>18</sub> poly-unsaturated alkyl. In one embodiment, R<sup>1</sup> is branched unsubstituted C<sub>18</sub> mono-unsaturated alkyl. In another embodiment, R<sup>1</sup> is branched unsubstituted C<sub>18</sub> poly-unsaturated alkyl.

5 In embodiments of formula (VII), or embodiments thereof disclosed herein, where R<sup>1</sup> is unsubstituted C<sub>13</sub> alkyl, n is 55, X is -SO<sub>3</sub><sup>-</sup>M<sup>+</sup>, and M<sup>+</sup> is a divalent cation (e.g., Na<sup>2+</sup>). In embodiments, x is 45 and y is 10. In another embodiment of the compound of formula (VII), or embodiments thereof disclosed herein, where R<sup>1</sup> is unsubstituted C<sub>18</sub> unsaturated alkyl, n is 75, X is -CH<sub>2</sub>C(O)O<sup>-</sup>M<sup>+</sup>, and M<sup>+</sup> is a monovalent cation (e.g., Na<sup>+</sup>). In embodiments of formula  
10 (VII), x is 45 and y is 30.

Useful surfactants are disclosed, for example, in U.S. Patent Nos. 3,811,504, 3,811,505, 3,811,507, 3,890,239, 4,463,806, 6,022,843, 6,225,267, 7,629,299; WIPO Patent Application WO/2008/079855, WO/2012/027757 and WO /2011/094442; as well as U.S. Patent Application Nos. 2005/0199395, 2006/0185845, 2006/018486, 2009/0270281, 2011/0046024,  
15 2011/0100402, 2011/0190175, 2007/0191633, 2010/004843. 2011/0201531, 2011/0190174, 2011/0071057, 2011/0059873, 2011/0059872, 2011/0048721, 2010/0319920, and 2010/0292110. Additional useful surfactants are surfactants known to be used in enhanced oil recovery methods, including those discussed in D. B. Levitt, A. C. Jackson, L. Britton and G. A. Pope, "Identification and Evaluation of High-Performance EOR Surfactants," SPE IX89,  
20 conference contribution for the SPE Symposium on Improved Oil Recovery Annual Meeting, Tulsa, Okla., Apr. 24-26, 2006.

A person having ordinary skill in the art will immediately recognize that many surfactants are commercially available as blends of related molecules (e.g., IOS and ABS surfactants). Thus, where a surfactant is present within a composition provided herein, a person  
25 of ordinary skill would understand that the surfactant might be a blend of a plurality of related surfactant molecules (as described herein and as generally known in the art). In embodiments, the surfactant is a surfactant blend. In embodiments, the surfactant is a single surfactant. Where the surfactant is a single surfactant, the aqueous composition includes one surfactant type.

In embodiments, the total surfactant concentration (i.e., the total amount of all surfactant  
30 types within the aqueous compositions and emulsion compositions provided herein) is from about 0.05% w/w to about 10% w/w. In embodiments, the total surfactant concentration in the aqueous composition is from about 0.25% w/w to about 10% w/w. In embodiments, the total surfactant concentration in the aqueous composition is about 0.05% w/w. In embodiments, the total surfactant concentration in the aqueous composition is about 0.1% w/w. In embodiments,

the total surfactant concentration in the aqueous composition is about 0.2% w/w. In  
embodiments, the total surfactant concentration in the aqueous composition is about 0.25% w/w.  
In embodiments, the total surfactant concentration in the aqueous composition is about 0.4  
% w/w. In embodiments, the total surfactant concentration in the aqueous composition is about  
5 0.5% w/w. In embodiments, the total surfactant concentration in the aqueous composition is  
about 0.6 % w/w. In embodiments, the total surfactant concentration in the aqueous composition  
is about 1.0% w/w. In embodiments, the total surfactant concentration in the aqueous  
composition is about 1.25% w/w. In embodiments, the total surfactant concentration in the  
aqueous composition is about 1.5% w/w. In embodiments, the total surfactant concentration in  
10 the aqueous composition is about 1.75% w/w. In embodiments, the total surfactant  
concentration in the aqueous composition is about 2.0% w/w. In embodiments, the total  
surfactant concentration in the aqueous composition is about 2.5% w/w. In embodiments, the  
total surfactant concentration in the aqueous composition is about 3.0% w/w. In embodiments,  
the total surfactant concentration in the aqueous composition is about 3.5% w/w. In  
15 embodiments, the total surfactant concentration in the aqueous composition is about 4.0% w/w.  
In embodiments, the total surfactant concentration in the aqueous composition is about  
4.5% w/w. In embodiments, the total surfactant concentration in the aqueous composition is  
about 5.0% w/w. In embodiments, the total surfactant concentration in the aqueous composition  
is about 5.5% w/w. In embodiments, the total surfactant concentration in the aqueous  
20 composition is about 6.0% w/w. In embodiments, the total surfactant concentration in the  
aqueous composition is about 6.5% w/w. In embodiments, the total surfactant concentration in  
the aqueous composition is about 7.0% w/w. In embodiments, the total surfactant concentration  
in the aqueous composition is about 7.5% w/w. In embodiments, the total surfactant  
concentration in the aqueous composition is about 8.0% w/w. In embodiments, the total  
25 surfactant concentration in the aqueous composition is about 9.0% w/w. In embodiments, the  
total surfactant concentration in the aqueous composition is about 10% w/w.

In embodiments, the total surfactant concentration (i.e., the total amount of all surfactant  
types within the aqueous compositions and emulsion compositions provided herein) is from at  
least 0.05% w/w to at least 10% w/w. In embodiments, the total surfactant concentration in the  
30 aqueous composition is from at least 0.25% w/w to at least 10% w/w. In embodiments, the total  
surfactant concentration in the aqueous composition is at least 0.05% w/w. In embodiments, the  
total surfactant concentration in the aqueous composition is at least 0.1% w/w. In embodiments,  
the total surfactant concentration in the aqueous composition is at least 0.2% w/w. In  
embodiments, the total surfactant concentration in the aqueous composition is at least

0.25% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 0.5% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 1.0% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 1.25% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 1.5% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 1.75% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 2.0% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 2.5% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 3.0% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 3.5% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 4.0% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 4.5% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 5.0% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 5.5% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 6.0% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 6.5% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 7.0% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 7.5% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 8.0% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 9.0% w/w. In embodiments, the total surfactant concentration in the aqueous composition is at least 10% w/w.

In embodiments, the total surfactant concentration in the aqueous composition is about 0.05% w/w, 0.25% w/w, 0.5% w/w, 1.25% w/w, 1.5% w/w, 1.75% w/w, 2.0% w/w, 2.5% w/w, 3.0% w/w, 3.5% w/w, 4.5% w/w, 4.5% w/w, 5.0% w/w, 5.5% w/w, 6.0% w/w, 6.5% w/w, 7.0% w/w, 7.5% w/w, 8.0% w/w, 8.5% w/w or 10% w/w. In embodiments, the total surfactant concentration in the aqueous composition is about 1% w/w. A person of ordinary skill in the art will immediately recognize that the above referenced values refer to weight percent of surfactant per weight of aqueous composition.

In embodiments, the ammonia compound is present in an amount sufficient to increase the solubility of the surfactant in the aqueous composition relative to the absence of the ammonia compound. In other words, in the presence of a sufficient amount of the ammonia compound, the solubility of the surfactant in the aqueous composition is higher than in the absence of the ammonia compound. In embodiments, the ammonia compound is present in an amount

sufficient to increase the solubility of the surfactant in the aqueous composition relative to the absence of the ammonia compound. Thus, in the presence of a sufficient amount of the ammonia compound the solubility of the surfactant in the aqueous composition is higher than in the absence of the ammonia compound.

5 In embodiments, the ammonia compound is present in an amount sufficient to decrease the adsorption of the surfactant to the solid material in a petroleum reservoir relative to the absence of the ammonia compound. In other words, in the presence of a sufficient amount of the ammonia compound, the adsorption of the surfactant to the solid material in a petroleum reservoir is lower than in the absence of the ammonia compound.

10 In embodiments, the ammonia compound is present in a pH stabilizing amount. A “pH stabilizing amount” means that the ammonia compound is present in an amount in which the pH changes at a slower rate in the presence of ammonia compound than in the absence of the ammonia compound. The rate of change may be 0%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% or 100% slower. In embodiments, the rate of degradation is 2, 3, 4, 5, 6, 7, 8, 9  
15 or 10 times slower. In embodiments, the ammonia compound is present in an amount in which the pH remains constant (i.e., remains the same over time).

In embodiments, the ammonia compound (e.g., ammonia or ammonium hydroxide) is present from about 0.1% w/w to about 10% w/w. The ammonia compound may be present from about 0.2% w/w to about 10% w/w. The ammonia compound may be present from about 0.3%  
20 w/w to about 10% w/w. The ammonia compound may be present from about 0.4% w/w to about 10% w/w. The ammonia compound may be present from about 0.5% w/w to about 10% w/w. The ammonia compound may be present from about 0.6% w/w to about 10% w/w. The ammonia compound may be present from about 0.7% w/w to about 10% w/w. The ammonia compound may be present from about 0.8% w/w to about 10% w/w. The ammonia compound may be present from about 0.9% w/w to about 10% w/w. The ammonia compound may be  
25 present from about 1% w/w to about 10% w/w. The ammonia compound may be present from about 1.5% w/w to about 10% w/w. The ammonia compound may be present from about 2% w/w to about 10% w/w. The ammonia compound may be present from about 2.5% w/w to about 10% w/w. The ammonia compound may be present from about 3% w/w to about 10% w/w. The ammonia compound may be present from about 3.5% w/w to about 10% w/w. The ammonia  
30 compound may be present from about 4% w/w to about 10% w/w. The ammonia compound may be present from about 4.5% w/w to about 10% w/w. The ammonia compound may be present from about 5% w/w to about 10% w/w. The ammonia compound may be present from about 5.5% w/w to about 10% w/w. The ammonia compound may be present from about 6%

w/w to about 10% w/w. The ammonia compound may be present from about 6.5% w/w to about 10% w/w. The ammonia compound may be present from about 7% w/w to about 10% w/w. The ammonia compound may be present from about 7.5% w/w to about 10% w/w. The ammonia compound may be present from about 8% w/w to about 10% w/w. The ammonia compound may be present from about 8.5% w/w to about 10% w/w. The ammonia compound may be present from about 9% w/w to about 10% w/w. The ammonia compound may be present from about 9.5% w/w to about 10% w/w.

The ammonia compound may be present from about 0.1% w/w to about 5% w/w. The ammonia compound may be present from about 0.2% w/w to about 5% w/w. The ammonia compound may be present from about 0.3% w/w to about 5% w/w. The ammonia compound may be present from about 0.4% w/w to about 5% w/w. The ammonia compound may be present from about 0.5% w/w to about 5% w/w. The ammonia compound may be present from about 0.6% w/w to about 5% w/w. The ammonia compound may be present from about 0.7% w/w to about 5% w/w. The ammonia compound may be present from about 0.8% w/w to about 5% w/w. The ammonia compound may be present from about 0.9% w/w to about 5% w/w. The ammonia compound may be present from about 1% w/w to about 5% w/w. The ammonia compound may be present from about 1.5% w/w to about 5% w/w. The ammonia compound may be present from about 2% w/w to about 5% w/w. The ammonia compound may be present from about 2.5% w/w to about 5% w/w. The ammonia compound may be present from about 3% w/w to about 5% w/w. The ammonia compound may be present from about 3.5% w/w to about 5% w/w. The ammonia compound may be present from about 4% w/w to about 5% w/w. The ammonia compound may be present from about 4.5% w/w to about 5% w/w.

The ammonia compound may be present from about 0.1% w/w. The ammonia compound may be present from about 0.2% w/w. The ammonia compound may be present from about 0.3% w/w. The ammonia compound may be present from at least about 0.3% w/w. The ammonia compound may be present from about 0.4% w/w. The ammonia compound may be present from about 0.5% w/w. The ammonia compound may be present from about 0.6% w/w. The ammonia compound may be present from about 0.7% w/w. The ammonia compound may be present from about 0.8% w/w. The ammonia compound may be present from about 0.9% w/w. The ammonia compound may be present from about 1% w/w. The ammonia compound may be present from about 1.5% w/w. The ammonia compound may be present from about 2% w/w. The ammonia compound may be present from about 2.5% w/w. The ammonia compound may be present from about 3% w/w. The ammonia compound may be present from about 3.5% w/w. The ammonia compound may be present from about 4% w/w. The ammonia compound

may be present from about 4.5% w/w. The ammonia compound may be present from about 5% w/w. The ammonia compound may be present from about 5.5% w/w. The ammonia compound may be present from about 6% w/w. The ammonia compound may be present from about 6.5% w/w. The ammonia compound may be present from about 7% w/w. The ammonia compound may be present from about 7.5% w/w. The ammonia compound may be present from about 8% w/w. The ammonia compound may be present from about 8.5% w/w. The ammonia compound may be present from about 9% w/w. The ammonia compound may be present from about 9.5% w/w. The ammonia compound may be present from about 10% w/w.

In embodiments, the aqueous composition further includes a viscosity enhancing water-soluble polymer. In embodiments, the viscosity enhancing water-soluble polymer is a hydrolyzed polymer (e.g., hydrolyzed or partially hydrolyzed polyacrylamide, HPAM). In embodiments, the viscosity enhancing water-soluble polymer may be a biopolymer (e.g., polyhydroxy polymer or polysaccharide) such as xanthan gum or scleroglucan, a synthetic polymer such as polyacrylamide, hydrolyzed polyacrylamide or co-polymers of acrylamide and acrylic acid, 2-acrylamido 2-methyl propane sulfonate or N-vinyl pyrrolidone, a synthetic polymer such as polyethylene oxide, or any other high molecular weight polymer soluble in water or brine. In embodiments, the viscosity enhancing water-soluble polymer is polyacrylamide or a co-polymer of polyacrylamide. In embodiments, the viscosity enhancing water-soluble polymer is a partially (e.g., 20%, 25%, 30%, 35%, 40%, 45%) hydrolyzed anionic polyacrylamide. In embodiments, the viscosity enhancing water-soluble polymer has a molecular weight of approximately about  $8 \times 10^6$ . In embodiments, the viscosity enhancing water-soluble polymer has a molecular weight of approximately about  $18 \times 10^6$ . Non-limiting examples of commercially available polymers useful for the invention including embodiments provided herein are Flopaam 3330S and Flopaam 3630S.

In embodiments, the polymer is present from about 100 ppm to about 5000 ppm. In embodiments, the polymer is present from about 200 ppm to about 5,000 ppm. In embodiments, the polymer is present from about 400 ppm to about 5,000 ppm. In embodiments, the polymer is present from about 600 ppm to about 5,000 ppm. In embodiments, the polymer is present from about 800 ppm to about 5,000 ppm. In embodiments, the polymer is present from about 1,000 ppm to about 5,000 ppm. In embodiments, the polymer is present from about 1,500 ppm to about 5,000 ppm. In embodiments, the polymer is present from about 2,000 ppm to about 5,000 ppm. In embodiments, the polymer is present from about 2,500 ppm to about 5,000 ppm. In embodiments, the polymer is present from about 3,000 ppm to about 5,000 ppm. In embodiments, the polymer is present from about 3,500 ppm to about 5,000 ppm. In

embodiments, the polymer is present from about 4,000 ppm to about 5,000 ppm. In embodiments, the polymer is present from about 4,500 ppm to about 5,000 ppm. In embodiments, the polymer is present at about 800 ppm. In embodiments, the polymer is present at about 2,000 ppm. In embodiments, the polymer is present at about 2,500 ppm.

5 In embodiments, the ammonia compound is present in an amount sufficient to increase the solubility of the viscosity enhancing water-soluble polymer in the aqueous composition relative to the absence of the ammonia compound. In other words, in the presence of a sufficient amount of the ammonia compound, the solubility of the viscosity enhancing water-soluble polymer in the aqueous composition is higher than in the absence of the ammonia compound. In  
10 embodiments, the ammonia compound is present in an amount sufficient to increase the solubility of the viscosity enhancing water-soluble polymer in the aqueous composition relative to the absence of the ammonia compound. Thus, in the presence of a sufficient amount of the ammonia compound the solubility of the viscosity enhancing water-soluble polymer in the aqueous composition is higher than in the absence of the ammonia compound.

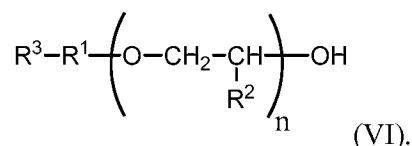
15 The aqueous compositions provided herein may further include a gas. For instance, the gas may be combined with the aqueous composition to reduce its mobility by decreasing the liquid flow in the pores of the solid material (e.g., rock). In embodiments, the gas may be supercritical carbon dioxide, nitrogen, natural gas or mixtures of these and other gases. In embodiments, the gas may increase the viscosity of the aqueous composition or emulsions  
20 provided herein.

In embodiments, the aqueous composition further includes a co-solvent. In embodiments, the co-solvent is an alcohol, alcohol ethoxylate, glycol ether, glycols, or glycerol. In embodiments, the aqueous composition includes water, an ammonia compound, a multivalent mineral cation (e.g., from gypsum), a co-solvent and optionally a surfactant. The ammonia  
25 compound is as described herein, including embodiments thereof. The aqueous compositions provided herein may include more than one co-solvent. Thus, in embodiments, the aqueous composition includes a plurality of different co-solvents. Where the aqueous composition includes a plurality of different co-solvents, the different co-solvents can be distinguished by their chemical (structural) properties. For example, the aqueous composition may include a first  
30 co-solvent, a second co-solvent and a third co-solvent, wherein the first co-solvent is chemically different from the second and the third co-solvent, and the second co-solvent is chemically different from the third co-solvent. In embodiments, the plurality of different co-solvents includes at least two different alcohols (e.g., a C<sub>1</sub>-C<sub>6</sub> alcohol and a C<sub>1</sub>-C<sub>4</sub> alcohol). In embodiments, the aqueous composition includes a C<sub>1</sub>-C<sub>6</sub> alcohol and a C<sub>1</sub>-C<sub>4</sub> alcohol. In

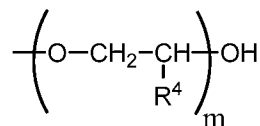


embodiments, the plurality of different co-solvents includes at least two different alkoxy alcohols (e.g., a C<sub>1</sub>-C<sub>6</sub> alkoxy alcohol and a C<sub>1</sub>-C<sub>4</sub> alkoxy alcohol). In embodiments, the aqueous composition includes a C<sub>1</sub>-C<sub>6</sub> alkoxy alcohol and a C<sub>1</sub>-C<sub>4</sub> alkoxy alcohol. In embodiments, the plurality of different co-solvents includes at least two co-solvents selected from the group consisting of alcohols, alkyl alkoxy alcohols and phenyl alkoxy alcohols. For example, the plurality of different co-solvents may include an alcohol and an alkyl alkoxy alcohol, an alcohol and a phenyl alkoxy alcohol, or an alcohol, an alkyl alkoxy alcohol and a phenyl alkoxy alcohol. The alkyl alkoxy alcohols or phenyl alkoxy alcohols provided herein have a hydrophobic portion (alkyl or aryl chain), a hydrophilic portion (e.g., an alcohol) and optionally an alkoxy (ethoxylate or propoxylate) portion. Thus, in embodiments, the co-solvent is an alcohol, alkoxy alcohol, glycol ether, glycol or glycerol.

In embodiments, the co-solvent has the formula



In formula (VI), R<sup>1</sup> is unsubstituted C<sub>1</sub>-C<sub>6</sub> alkylene, unsubstituted phenylene, unsubstituted cyclohexylene, unsubstituted cyclopentylene or methyl-substituted cyclopentylene. R<sup>2</sup> is independently hydrogen, methyl or ethyl. R<sup>3</sup> is independently hydrogen or



R<sup>4</sup> is independently hydrogen, methyl or ethyl, n is an integer from 0 to 30, and m is an integer from 0 to 30. In embodiments of formula (VI), n is an integer from 0 to 25. In embodiments of formula (VI), n is an integer from 0 to 20. In embodiments of formula (VI), n is an integer from 0 to 15. In embodiments of formula (VI), n is an integer from 0 to 10. In embodiments of formula (VI), n is an integer from 0 to 5. In embodiments of formula (VI), n is 1. In embodiments of formula (VI), n is 3. In embodiments of formula (VI), n is 5. In embodiments of formula (VI), m is an integer from 0 to 25. In embodiments of formula (VI), m is an integer from 0 to 20. In embodiments of formula (VI), m is an integer from 0 to 15. In embodiments of formula (VI), m is an integer from 0 to 10. In embodiments of formula (VI), m is an integer from 0 to 5. In embodiments of formula (VI), m is 1. In embodiments of formula (VI), m is 3. In embodiments of formula (VI), m is 5. In formula (VI) each of R<sup>2</sup> and R<sup>4</sup> can appear more than once and can be optionally different. For example, in embodiments where n is

2, R<sup>2</sup> appears twice and can be optionally different. In embodiments of formula (VI), where m is 3, R<sup>4</sup> appears three times and can be optionally different.

R<sup>1</sup> may be linear or branched unsubstituted alkylene. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>1</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>2</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>2</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>3</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>3</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>4</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>4</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted C<sub>4</sub>-alkylene. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted C<sub>4</sub>-alkylene.

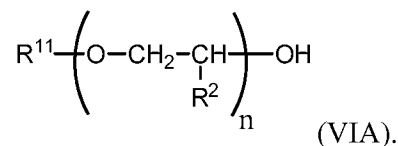
In embodiments of formula (VI), where R<sup>1</sup> is linear or branched unsubstituted alkylene (e.g., branched unsubstituted C<sub>1</sub>-C<sub>6</sub> alkylene), the alkylene is a saturated alkylene (e.g., a linear or branched unsubstituted saturated alkylene or branched unsubstituted C<sub>1</sub>-C<sub>6</sub> saturated alkylene). A "saturated alkylene," as used herein, refers to an alkylene consisting only of hydrogen and carbon atoms that are bonded exclusively by single bonds. Thus, in embodiments of formula (VI), R<sup>1</sup> is linear or branched unsubstituted saturated alkylene. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted saturated C<sub>1</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted saturated C<sub>1</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted saturated C<sub>2</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted saturated C<sub>2</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted saturated C<sub>3</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted saturated C<sub>3</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted saturated C<sub>4</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted saturated C<sub>4</sub>-C<sub>6</sub> alkylene. In embodiments of formula (VI), R<sup>1</sup> is linear unsubstituted saturated C<sub>4</sub>-alkylene. In embodiments of formula (VI), R<sup>1</sup> is branched unsubstituted saturated C<sub>4</sub>-alkylene.

In embodiments of formula (VI), R<sup>1</sup> is substituted or unsubstituted cycloalkylene or unsubstituted arylene. In embodiments of formula (VI), R<sup>1</sup> is R<sup>7</sup>-substituted or unsubstituted cyclopropylene, wherein R<sup>7</sup> is C<sub>1</sub>-C<sub>3</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>8</sup>-substituted or unsubstituted cyclobutylene, wherein R<sup>8</sup> is C<sub>1</sub>-C<sub>2</sub> alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>9</sup>-substituted or unsubstituted cyclopentylene, wherein R<sup>9</sup> is C<sub>1</sub>-alkyl. In embodiments of formula (VI), R<sup>1</sup> is R<sup>10</sup>-substituted or unsubstituted cyclopentylene, wherein R<sup>10</sup> is unsubstituted

cyclohexyl. In embodiments of formula (VI), R<sup>1</sup> is unsubstituted phenylene, unsubstituted cyclohexylene, unsubstituted cyclopentylene or methyl-substituted cyclopentylene.

In embodiments of formula (VI), -R<sup>1</sup>-R<sup>3</sup> is C<sub>1</sub>-C<sub>6</sub> alkyl, unsubstituted phenyl, unsubstituted cyclohexyl, unsubstituted cyclopentyl or a methyl-substituted cycloalkyl.

5 In embodiments, the co-solvent has the structure of formula

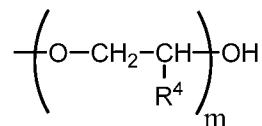


In formula (VIA), R<sup>11</sup> is C<sub>1</sub>-C<sub>6</sub> alkyl, unsubstituted phenyl, unsubstituted cyclohexyl, unsubstituted cyclopentyl or a methyl-substituted cycloalkyl.

In embodiments of formula (VIA), n and m are independently 1 to 20. In embodiments of formula (VIA), n and m are independently 1 to 15. In embodiments of formula (VIA), n and m are independently 1 to 10. In embodiments of formula (VIA), n and m are independently 1 to 6. In embodiments of formula (VIA), n and m are independently 1.

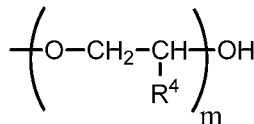
The co-solvent included in the aqueous compositions provided herein may be a monohydric or a dihydric alkoxy alcohol (e.g., C<sub>1</sub>-C<sub>6</sub> alkoxy alcohol or C<sub>1</sub>-C<sub>6</sub> alkoxy diol).

15 Where the co-solvent is a monohydric alcohol, the co-solvent has the formula (VI) and R<sup>3</sup> is hydrogen. Where the co-solvent is a diol, the co-solvent has the formula (VI) and R<sup>3</sup> is

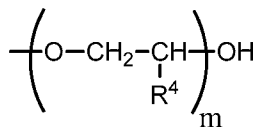


In embodiments of formula (VIA), R<sup>1</sup> is linear unsubstituted C<sub>4</sub> alkylene and n is 3. In embodiments of formula (VIA), the co-solvent is triethyleneglycol butyl ether. In embodiments of formula (VIA), the co-solvent is tetraethylene glycol. In further embodiments, m is 3. In embodiments of formula (VIA), R<sup>1</sup> is linear unsubstituted C<sub>4</sub> alkylene and n is 5. In embodiments of formula (VIA), the co-solvent is pentaethyleneglycol n-butyl ether. In further embodiments, m is 5. In embodiments of formula (VIA), R<sup>1</sup> is branched unsubstituted C<sub>4</sub> alkylene and n is 1. In embodiments of formula (VIA), the co-solvent is ethyleneglycol iso-butyl ether. In further embodiments, m is 1. In embodiments of formula (VIA), R<sup>1</sup> is branched unsubstituted C<sub>4</sub> alkylene and n is 3. In embodiments of formula (VIA), the co-solvent is triethyleneglycol iso-butyl ether. In further embodiments, m is 3. In embodiments of formula (VIA), the co-solvent is ethylene glycol or propylene glycol. In embodiments of formula (VIA), the co-solvent is ethylene glycol alkoxylate or propylene glycol alkoxylate. In embodiments of

formula (VIA), the co-solvent is propylene glycol diethoxylate or propylene glycoltriethoxylate. In embodiments of formula (VIA), the co-solvent is propylene glycol tetraethoxylate.

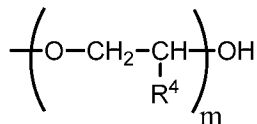


In the structure,  $\text{R}^3$  may be hydrogen or . Thus In embodiments of



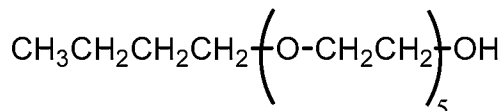
formula (VIA),  $\text{R}^3$  is .

5 In embodiments, the co-solvent provided herein may be an alcohol or diol ( $\text{C}_1$ - $\text{C}_6$  alcohol or  $\text{C}_1$ - $\text{C}_6$  diol). Where the co-solvent is an alcohol, the co-solvent has a structure, where  $\text{R}^3$  is hydrogen and  $n$  is 0. Where the co-solvent is a diol, the co-solvent has a structure, where  $\text{R}^3$  is

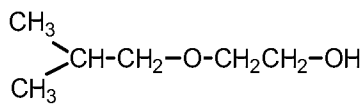


and  $n$  and  $m$  are 0. Thus, in embodiments,  $n$  and  $m$  are independently 0. In

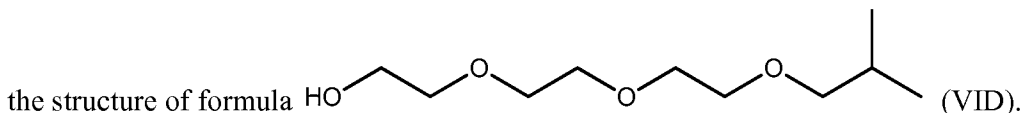
embodiments,  $\text{R}^1$  is linear or branched unsubstituted  $\text{C}_1$ - $\text{C}_6$  alkylene. In embodiments,  $\text{R}^1$  is linear or branched unsubstituted  $\text{C}_2$ - $\text{C}_6$  alkylene. In embodiments,  $\text{R}^1$  is linear or branched unsubstituted  $\text{C}_2$ - $\text{C}_6$  alkylene. In embodiments  $\text{R}^1$  is linear or branched unsubstituted  $\text{C}_3$ - $\text{C}_6$  alkylene. In embodiments,  $\text{R}^1$  is linear or branched unsubstituted  $\text{C}_4$ - $\text{C}_6$  alkylene. In embodiments,  $\text{R}^1$  is linear or branched unsubstituted  $\text{C}_4$ -alkylene. In embodiments,  $\text{R}^1$  is branched unsubstituted butylene. In embodiments, the co-solvent has the structure of formula



15 (VIB). In embodiments, the co-solvent has the



structure of formula (VIC). In embodiments, the co-solvent has

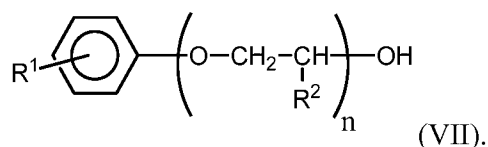


The structure of formula (VID) is also referred to herein as triethylene glycol mono butyl ether (TEGBE). In embodiments, the co-solvent is TEGBE (triethylene glycol mono butyl ether). In embodiments, TEGBE is present at a concentration from about 0.01% to about 2%. In 20 embodiments, TEGBE is present at a concentration from about 0.05% to about 1.5%. In embodiments, TEGBE is present at a concentration from about 0.2% to about 1.25%. In embodiments, TEGBE is present at a concentration from about 0.25% to about 1%. In

embodiments, TEGBE is present at a concentration from about 0.5% to about 0.75%. In  
embodiments, TEGBE is present at a concentration of about 0.25%. In embodiments, TEGBE is  
present at a concentration of about 1%.

In embodiments, the co-solvent is IBA (isobutyl alcohol). In embodiments, IBA is  
present at a concentration from about 0.01% to about 2%. In embodiments, IBA is present at a  
concentration from about 0.05% to about 1.5%. In embodiments, IBA is present at a  
concentration from about 0.2% to about 1.25%. In embodiments, IBA is present at a  
concentration from about 0.25% to about 1%. In embodiments, IBA is present at a concentration  
from about 0.5% to about 0.75%. In embodiments, IBA is present at a concentration of about  
0.25%. In embodiments, IBA is present at a concentration of about 1%.

The co-solvent may have the formula:



In formula (VII) R<sup>1</sup> is independently hydrogen or unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl, R<sup>2</sup> is  
independently hydrogen or unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl and n is an integer from 1 to 30. In  
embodiments of formula (VII), R<sup>1</sup> is unsubstituted C<sub>2</sub>-C<sub>6</sub> alkyl. In embodiments of formula  
(VII), R<sup>1</sup> is unsubstituted C<sub>4</sub>-C<sub>6</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is unsubstituted C<sub>1</sub>-  
C<sub>5</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is unsubstituted C<sub>1</sub>-C<sub>4</sub> alkyl. In embodiments of  
formula (VII), R<sup>1</sup> is unsubstituted C<sub>1</sub>-C<sub>3</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is  
unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is unsubstituted C<sub>2</sub> alkyl. In  
embodiments of formula (VII), R<sup>1</sup> is ethyl. In embodiments of formula (VII), R<sup>1</sup> is methyl. In  
embodiments of formula (VII), R<sup>1</sup> is hydrogen.

R<sup>1</sup> may be linear or branched unsubstituted alkyl. In embodiments of formula (VII), R<sup>1</sup>  
is linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is branched  
unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is linear unsubstituted C<sub>1</sub>-C<sub>5</sub>  
alkyl. In embodiments of formula (VII), R<sup>1</sup> is branched unsubstituted C<sub>1</sub>-C<sub>5</sub> alkyl. In  
embodiments of formula (VII), R<sup>1</sup> is linear unsubstituted C<sub>1</sub>-C<sub>4</sub> alkyl. In embodiments of  
formula (VII), R<sup>1</sup> is branched unsubstituted C<sub>1</sub>-C<sub>4</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is  
linear unsubstituted C<sub>1</sub>-C<sub>3</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is branched unsubstituted  
C<sub>1</sub>-C<sub>3</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is linear unsubstituted ethyl. In embodiments  
of formula (VII), R<sup>1</sup> is branched unsubstituted ethyl.

In embodiments of formula (VII), where R<sup>1</sup> is linear or branched unsubstituted alkyl  
(e.g., branched unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl), the alkyl is a saturated alkyl (e.g., a linear or branched

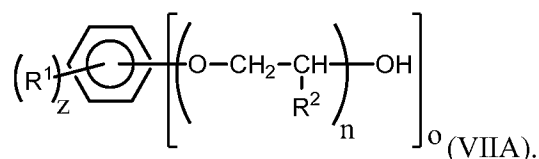
unsubstituted saturated alkyl or branched unsubstituted C<sub>1</sub>-C<sub>6</sub> saturated alkyl). A "saturated alkyl," as used herein, refers to an alkyl consisting only of hydrogen and carbon atoms that are bonded exclusively by single bonds. Thus, in embodiments of formula (VII), R<sup>1</sup> is linear or branched unsubstituted saturated alkyl. In embodiments of formula (VII), R<sup>1</sup> is linear unsubstituted saturated C<sub>1</sub>-C<sub>6</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is branched unsubstituted saturated C<sub>1</sub>-C<sub>6</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is linear unsubstituted saturated C<sub>1</sub>-C<sub>5</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is branched unsubstituted saturated C<sub>1</sub>-C<sub>5</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is linear unsubstituted saturated C<sub>1</sub>-C<sub>4</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is branched unsubstituted saturated C<sub>1</sub>-C<sub>4</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is linear unsubstituted saturated C<sub>1</sub>-C<sub>3</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is branched unsubstituted saturated C<sub>1</sub>-C<sub>3</sub> alkyl. In embodiments of formula (VII), R<sup>1</sup> is linear unsubstituted saturated ethyl. In embodiments of formula (VII), R<sup>1</sup> is branched unsubstituted saturated ethyl.

The symbol n is an integer from 1 to 30. In embodiments of formula (VII), n is an integer from 1 to 25. In embodiments of formula (VII), n is an integer from 1 to 20. In embodiments of formula (VII), n is an integer from 1 to 15. In embodiments of formula (VII), n is an integer from 1 to 10. In embodiments of formula (VII), n is an integer from 1 to 5. In embodiments of formula (VII), n is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, or 30. In embodiments of formula (VII), n is 3. In embodiments of formula (VII), n is 5. In embodiments of formula (VII), n is 6.

In embodiments of formula (VII), R<sup>1</sup> is hydrogen. In embodiments of formula (VII), n is as defined in an embodiment above (e.g., n is at least 1, or at least 20, e.g., 5 to 15). Thus, in embodiments of formula (VII), R<sup>1</sup> is hydrogen and n is 6.

In embodiments of formula (VII), R<sup>1</sup> is methyl. In embodiments of formula (VII), n is as defined in an embodiment above (e.g., n is at least 1, or at least 20, e.g., 5 to 10). Thus, in embodiments of formula (VII), R<sup>1</sup> is methyl and n is 6.

The co-solvent may have the formula:



In formula (VIIA) R<sup>1</sup> is independently hydrogen, unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl or R<sup>5</sup>-OH, R<sup>2</sup> is independently hydrogen or unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl, R<sup>5</sup> is independently a bond or unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl, n is an integer from 1 to 30, o is an integer from 1 to 5 and z is an integer from 1 to 5. In embodiments of formula (VIIA), R<sup>1</sup> is unsubstituted C<sub>2</sub>-C<sub>6</sub> alkyl. In

embodiments of formula (VIIA),  $R^1$  is unsubstituted C<sub>4</sub>-C<sub>6</sub> alkyl. In embodiments of formula (VIIA),  $R^1$  is unsubstituted C<sub>1</sub>-C<sub>5</sub> alkyl. In embodiments of formula (VIIA),  $R^1$  is unsubstituted C<sub>1</sub>-C<sub>4</sub> alkyl. In embodiments of formula (VIIA),  $R^1$  is unsubstituted C<sub>1</sub>-C<sub>3</sub> alkyl. In embodiments of formula (VIIA),  $R^1$  is unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl. In embodiments of formula (VIIA),  $R^1$  is unsubstituted C<sub>2</sub> alkyl. In embodiments of formula (VIIA),  $R^1$  is ethyl. In embodiments of formula (VIIA),  $R^1$  is methyl. In embodiments of formula (VIIA),  $R^1$  is hydrogen.

In embodiments of formula (VIIA),  $R^1$  is independently a bond or  $R^5$ -OH. In embodiments of formula (VIIA),  $R^1$  is  $R^5$ -OH. In embodiments of formula (VIIA),  $R^5$  is unsubstituted C<sub>2</sub>-C<sub>6</sub> alkyl. In embodiments of formula (VIIA),  $R^5$  is unsubstituted C<sub>4</sub>-C<sub>6</sub> alkyl. In embodiments of formula (VIIA),  $R^5$  is unsubstituted C<sub>1</sub>-C<sub>5</sub> alkyl. In embodiments of formula (VIIA),  $R^5$  is unsubstituted C<sub>1</sub>-C<sub>4</sub> alkyl. In embodiments of formula (VIIA),  $R^5$  is unsubstituted C<sub>1</sub>-C<sub>3</sub> alkyl. In embodiments of formula (VIIA),  $R^5$  is unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl. In embodiments of formula (VIIA),  $R^5$  is unsubstituted C<sub>2</sub> alkyl. In embodiments of formula (VIIA),  $R^5$  is ethyl. In embodiments of formula (VIIA),  $R^5$  is methyl. In embodiments of formula (VIIA),  $R^5$  is a bond.

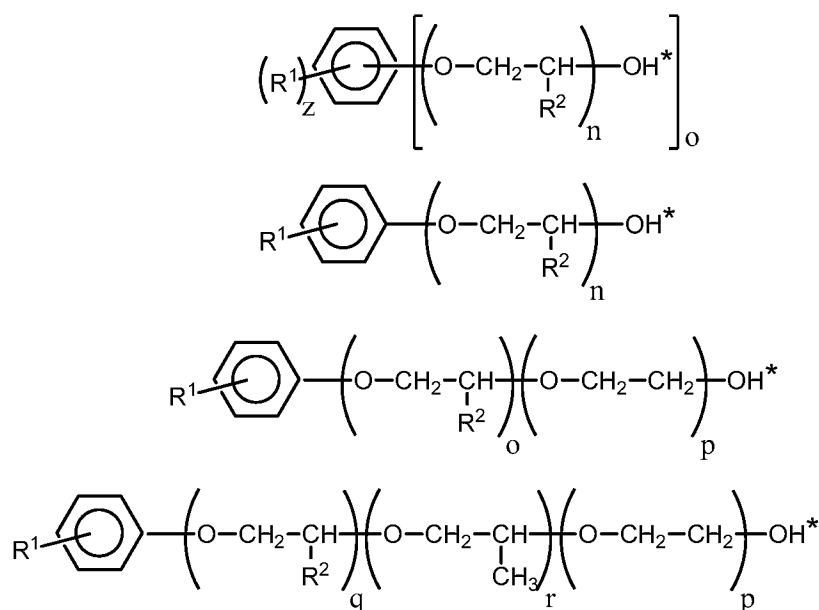
In formula (VIIA) the symbol  $n$  is an integer from 1 to 30. In embodiments of formula (VIIA),  $n$  is an integer from 1 to 25. In embodiments of formula (VIIA),  $n$  is an integer from 1 to 20. In embodiments of formula (VIIA),  $n$  is an integer from 1 to 15. In embodiments of formula (VIIA),  $n$  is an integer from 1 to 10. In embodiments of formula (VIIA),  $n$  is an integer from 1 to 5. In embodiments of formula (VIIA),  $n$  is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, or 30. In embodiments of formula (VIIA),  $n$  is 3. In embodiments of formula (VIIA),  $n$  is 5. In embodiments of formula (VIIA),  $n$  is 6. In embodiments of formula (VIIA),  $n$  is 16.

In formula (VIIA) the symbol  $o$  is an integer from 1 to 5 and the symbol  $z$  is an integer from 1 to 5. In embodiments of formula (VIIA),  $o$  is 1, 2, 3, 4, or 5. In embodiments of formula (VIIA),  $z$  is 1, 2, 3, 4, or 5. In embodiments of formula (VIIA),  $o$  is 1 and  $z$  is 5. In further embodiments,  $R^1$  is independently hydrogen or  $R^5$ -OH and  $R^5$  is a bond. In other further embodiments,  $R^1$  is hydrogen. In other further embodiments,  $R^1$  is  $R^5$ -OH and  $R^5$  is a bond.

In formula (VII), (VIIA), (VIII) or (XIX)  $R^2$  may be independently hydrogen or unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl. In embodiments of formula (VII), (VIIA), (VIII) or (XIX),  $R^2$  is hydrogen or unsubstituted C<sub>1</sub> or C<sub>2</sub> alkyl. In embodiments of formula (VII), (VIIA), (VIII) or (XIX),  $R^2$  is hydrogen or branched unsubstituted C<sub>1</sub> or C<sub>2</sub> saturated alkyl. In embodiments of formula (VII), (VIIA), (VIII) or (XIX),  $R^2$  is hydrogen or a branched unsubstituted C<sub>1</sub> saturated

alkyl. In embodiments of formula (VII), (VIIA), (VIII) or (XIX), R<sup>2</sup> is independently hydrogen or methyl. In embodiments of formula (VII), (VIIA), (VIII) or (XIX), R<sup>2</sup> is independently hydrogen or ethyl. In embodiments of formula (VII), (VIIA), (VIII) or (XIX), R<sup>2</sup> is independently hydrogen, methyl or ethyl. In embodiments of formula (VII), (VIIA), (VIII) or (XIX), R<sup>2</sup> is hydrogen. In embodiments of formula (VII), (VIIA), (VIII) or (XIX), R<sup>2</sup> is methyl. In embodiments of formula (VII), (VIIA), (VIII) or (XIX), R<sup>2</sup> is ethyl. In formula (VII) R<sup>2</sup> can appear more than once and can be optionally different. For example, in embodiments where n is 3, R<sup>2</sup> appears three times and can be optionally different. In embodiments of formula (VII), (VIIA), (VIII) or (XIX), where n is 6, R<sup>2</sup> appears six times and can be optionally different.

In embodiments of formula (VII), (VIIA), (VIII) or (XIX), where multiple R<sup>2</sup> substituents are present and at least two R<sup>2</sup> substituents are different, R<sup>2</sup> substituents with the fewest number of carbons are present at the side of the compound, (VIIA), (VIII) or (XIX) bound to the -OH group. In embodiments of formula (VII), (VIIA), (VIII) or (XIX), the compound will be increasingly hydrophilic in progressing from the R<sup>1</sup> substituent to the side of the compound, of formula (VII), (VIIA), (VIII) or (XIX) bound to the -OH group. The term “side of the compound, of formula (VII), (VIIA), (VIII) or (XIX) bound to the -OH group” refers to the side of the compound indicated by asterisks in the below structures:

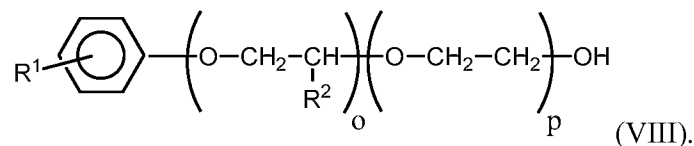


In embodiments of formula (VII), (VIIA), (VIII) or (XIX), R<sup>2</sup> is hydrogen. In embodiments of formula (VII), (VIIA), (VIII) or (XIX), n is as defined in an embodiment above (e.g., n is at least 1, or at least 20, e.g., 5 to 15). Thus, in embodiments of formula (VII), (VIIA), (VIII) or (XIX), R<sup>2</sup> is hydrogen and n is 6.



In embodiments of formula (VII), (VIIA), (VIII) or (XIX),  $R^2$  is methyl. In embodiments of formula (VII), (VIIA), (VIII) or (XIX),  $n$  is as defined in an embodiment above (e.g.,  $n$  is at least 1, or at least 20, e.g., 5 to 10). Thus, in embodiments of formula (VII), (VIIA), (VIII) or (XIX),  $R^2$  is methyl and  $n$  is 6.

In embodiments, the co-solvent has the formula:



In formula (VIII)  $R^1$  is defined as above (e.g., unsubstituted  $C_1$ - $C_6$  alkyl),  $R^2$  is methyl or ethyl,  $o$  is an integer from 0 to 15 and  $p$  is an integer from 1 to 10. In embodiments of formula (VIII)  $R^2$  is methyl. In embodiments of formula (VIII)  $R^2$  is ethyl. In formula (VIII)  $R^2$  can appear more than once and can be optionally different. For example, in embodiments where  $o$  is 3,  $R^2$  appears three times and can be optionally different. In embodiments of formula (VIII) where  $o$  is 6,  $R^2$  appears six times and can be optionally different.

In embodiments of formula (VIII)  $o$  is 0 to 15. In embodiments of formula (VIII)  $o$  is 0 to 12. In embodiments of formula (VIII)  $o$  is 0 to 10. In embodiments of formula (VIII)  $o$  is 0 to 8. In embodiments of formula (VIII)  $o$  is 0 to 6. In embodiments of formula (VIII)  $o$  is 0 to 4. In embodiments of formula (VIII)  $o$  is 0 to 2. Embodiments,  $o$  is 0. In embodiments of formula (VIII)  $p$  is 1 to 10. In embodiments of formula (VIII)  $p$  is 1 to 8. In embodiments of formula (VIII)  $p$  is 1 to 6. In embodiments of formula (VIII)  $p$  is 1 to 4. In embodiments of formula (VIII)  $p$  is 1 to 2. In still embodiments,  $p$  is more than 1. In embodiments of formula (VIII)  $p$  is 6.  $R^1$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^1$  maybe linear unsubstituted  $C_1$ - $C_6$  alkyl,  $R^2$  maybe linear unsubstituted  $C_1$ - $C_2$  alkyl). Thus, in embodiments of formula (VIII)  $R^1$  is hydrogen,  $o$  is 0 and  $p$  is 6.

In embodiments of formula (VIII)  $o$  is 1 to 15. In embodiments of formula (VIII)  $o$  is 1 to 12. In embodiments of formula (VIII)  $o$  is 1 to 10. In embodiments of formula (VIII)  $o$  is 1 to 8. In embodiments of formula (VIII)  $o$  is 1 to 6. In embodiments of formula (VIII)  $o$  is 1 to 4. In embodiments of formula (VIII)  $o$  is 1 to 2. In embodiments of formula (VIII)  $p$  is 1 to 10. In embodiments of formula (VIII)  $p$  is 1 to 8. In embodiments of formula (VIII)  $p$  is 1 to 6. In embodiments of formula (VIII)  $p$  is 1 to 4. In embodiments of formula (VIII)  $p$  is 1 to 2. In still embodiments,  $p$  is more than 1.  $R^1$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^1$  maybe linear unsubstituted  $C_1$ - $C_6$  alkyl,  $R^2$  maybe linear unsubstituted  $C_1$ - $C_2$  alkyl).

In embodiments of formula (VIII)  $o$  is 2 to 15. In embodiments of formula (VIII)  $o$  is 2 to 12. In embodiments of formula (VIII)  $o$  is 2 to 10. In embodiments of formula (VIII)  $o$  is 2 to

8. In embodiments of formula (VIII) o is 2 to 6. In embodiments of formula (VIII) o is 2 to 4. In embodiments of formula (VIII) p is 1 to 10. In embodiments of formula (VIII) p is 1 to 8. In embodiments of formula (VIII) p is 1 to 6. In embodiments of formula (VIII) p is 1 to 4. In embodiments of formula (VIII) p is 1 to 2. In still embodiments, p is more than 1. R<sup>1</sup> and R<sup>2</sup> may be any of the embodiments described above (e.g., R<sup>1</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl, R<sup>2</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

In embodiments of formula (VIII) o is 4 to 15. In embodiments of formula (VIII) o is 4 to 12. In embodiments of formula (VIII) o is 4 to 10. In embodiments of formula (VIII) o is 4 to 8. In embodiments of formula (VIII) o is 4 to 6. In embodiments of formula (VIII) p is 1 to 10. In embodiments of formula (VIII) p is 1 to 8. In embodiments of formula (VIII) p is 1 to 6. In embodiments of formula (VIII) p is 1 to 4. In embodiments of formula (VIII) p is 1 to 2. In still embodiments, p is more than 1. R<sup>1</sup> and R<sup>2</sup> may be any of the embodiments described above (e.g., R<sup>1</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl, R<sup>2</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

In embodiments of formula (VIII) o is 6 to 15. In embodiments of formula (VIII) o is 6 to 12. In embodiments of formula (VIII) o is 6 to 10. In embodiments of formula (VIII) o is 6 to 8. In embodiments of formula (VIII) p is 1 to 10. In embodiments of formula (VIII) p is 1 to 8. In embodiments of formula (VIII) p is 1 to 6. In embodiments of formula (VIII) p is 1 to 4. In embodiments of formula (VIII) p is 1 to 2. In still embodiments, p is more than 1. R<sup>1</sup> and R<sup>2</sup> may be any of the embodiments described above (e.g., R<sup>1</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl, R<sup>2</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

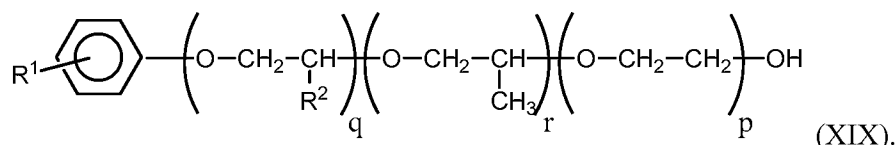
In embodiments of formula (VIII) o is 8 to 15. In embodiments of formula (VIII) o is 8 to 12. In embodiments of formula (VIII) o is 8 to 10. In embodiments of formula (VIII) p is 1 to 10. In embodiments of formula (VIII) p is 1 to 8. In embodiments of formula (VIII) p is 1 to 6. In embodiments of formula (VIII) p is 1 to 4. In embodiments of formula (VIII) p is 1 to 2. In still embodiments, p is more than 1. R<sup>1</sup> and R<sup>2</sup> may be any of the embodiments described above (e.g., R<sup>1</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl, R<sup>2</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

In embodiments of formula (VIII) o is 10 to 15. In embodiments of formula (VIII) o is 10 to 12. In embodiments of formula (VIII) p is 1 to 10. In embodiments of formula (VIII) p is 1 to 8. In embodiments of formula (VIII) p is 1 to 6. In embodiments of formula (VIII) p is 1 to 4. In embodiments of formula (VIII) p is 1 to 2. In still embodiments, p is more than 1. R<sup>1</sup> and R<sup>2</sup> may be any of the embodiments described above (e.g., R<sup>1</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl, R<sup>2</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

In embodiments of formula (VIII) o is 12 to 15. In embodiments of formula (VIII) p is 1 to 10. In embodiments of formula (VIII) p is 1 to 8. In embodiments of formula (VIII) p is 1 to 4.

6. In embodiments of formula (VIII) p is 1 to 4. In embodiments of formula (VIII) p is 1 to 2. In still embodiments, p is more than 1. R<sup>1</sup> and R<sup>2</sup> may be any of the embodiments described above (e.g., R<sup>1</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl, R<sup>2</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

5 In embodiments, the co-solvent has the formula:



In formula (XIX) R<sup>1</sup> is defined as above (e.g., unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl), R<sup>2</sup> is ethyl, q is an integer from 0 to 10, r is an integer from 0 to 10 and p is an integer from 1 to 10.

In embodiments of formula (XIX) q is 0 to 10. In embodiments of formula (XIX) q is 1 to 10. In embodiments of formula (XIX) q is 2 to 10. In embodiments of formula (XIX) q is 3 to 10. In embodiments of formula (XIX) q is 4 to 10. In embodiments of formula (XIX) q is 5 to 10. In embodiments of formula (XIX) q is 6 to 10. In embodiments of formula (XIX) q is 7 to 10. In embodiments of formula (XIX) q is 8 to 10. In embodiments of formula (XIX) q is 9 to 10. Moreover, in embodiments, q is 0. In embodiments of formula (XIX) r is 0 to 10. In  
 15 embodiments of formula (XIX) r is 1 to 10. In embodiments of formula (XIX) r is 2 to 10. In embodiments of formula (XIX) r is 3 to 10. In embodiments of formula (XIX) r is 4 to 10. In embodiments of formula (XIX) r is 5 to 10. In embodiments of formula (XIX) r is 6 to 10. In embodiments of formula (XIX) r is 7 to 10. In embodiments of formula (XIX) r is 8 to 10. In embodiments of formula (XIX) r is 9 to 10. Moreover, in embodiments, r is 0. In embodiments  
 20 of formula (XIX) p is 1 to 10. In embodiments of formula (XIX) p is 2 to 10. In embodiments of formula (XIX) p is 3 to 10. In embodiments of formula (XIX) p is 4 to 10. In embodiments of formula (XIX) p is 5 to 10. In embodiments of formula (XIX) p is 6 to 10. In embodiments of formula (XIX) p is 7 to 10. In embodiments of formula (XIX) p is 8 to 10. In embodiments of formula (XIX) p is 9 to 10. R<sup>1</sup> and R<sup>2</sup> may be any of the embodiments described above (e.g.,  
 25 R<sup>1</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl or hydrogen, R<sup>2</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

In embodiments of formula (XIX) q is 0 to 9. In embodiments of formula (XIX) q is 1 to 9. In embodiments of formula (XIX) q is 2 to 9. In embodiments of formula (XIX) q is 3 to 9. In embodiments of formula (XIX) q is 4 to 9. In embodiments of formula (XIX) q is 5 to 9. In  
 30 embodiments of formula (XIX) q is 6 to 9. In embodiments of formula (XIX) q is 7 to 9. In embodiments of formula (XIX) q is 8 to 9. Moreover, in embodiments, q is 0. In embodiments of formula (XIX) r is 0 to 10. In embodiments of formula (XIX) r is 1 to 10. In embodiments of

formula (XIX) r is 2 to 10. In embodiments of formula (XIX) r is 3 to 10. In embodiments of formula (XIX) r is 4 to 10. In embodiments of formula (XIX) r is 5 to 10. In embodiments of formula (XIX) r is 6 to 10. In embodiments of formula (XIX) r is 7 to 10. In embodiments of formula (XIX) r is 8 to 10. In embodiments of formula (XIX) r is 9 to 10. Moreover, in  
5       embodiments, r is 0. In embodiments of formula (XIX) p is 1 to 10. In embodiments of formula (XIX) p is 2 to 10. In embodiments of formula (XIX) p is 3 to 10. In embodiments of formula (XIX) p is 4 to 10. In embodiments of formula (XIX) p is 5 to 10. In embodiments of formula (XIX) p is 6 to 10. In embodiments of formula (XIX) p is 7 to 10. In embodiments of formula (XIX) p is 8 to 10. In embodiments of formula (XIX) p is 9 to 10. R<sup>1</sup> and R<sup>2</sup> may be any of the  
10       embodiments described above (e.g., R<sup>1</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl or hydrogen, R<sup>2</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

      In embodiments of formula (XIX) q is 0 to 8. In embodiments of formula (XIX) q is 1 to 8. In embodiments of formula (XIX) q is 2 to 8. In embodiments of formula (XIX) q is 3 to 8. In embodiments of formula (XIX) q is 4 to 8. In embodiments of formula (XIX) q is 5 to 8. In  
15       embodiments of formula (XIX) q is 6 to 8. In embodiments of formula (XIX) q is 7 to 8. Moreover, in embodiments, q is 0. In embodiments of formula (XIX) r is 0 to 10. In embodiments of formula (XIX) r is 1 to 10. In embodiments of formula (XIX) r is 2 to 10. In embodiments of formula (XIX) r is 3 to 10. In embodiments of formula (XIX) r is 4 to 10. In embodiments of formula (XIX) r is 5 to 10. In embodiments of formula (XIX) r is 6 to 10. In  
20       embodiments of formula (XIX) r is 7 to 10. In embodiments of formula (XIX) r is 8 to 10. In embodiments of formula (XIX) r is 9 to 10. Moreover, in embodiments, r is 0. In embodiments of formula (XIX) p is 1 to 10. In embodiments of formula (XIX) p is 2 to 10. In embodiments of formula (XIX) p is 3 to 10. In embodiments of formula (XIX) p is 4 to 10. In embodiments of formula (XIX) p is 5 to 10. In embodiments of formula (XIX) p is 6 to 10. In embodiments  
25       of formula (XIX) p is 7 to 10. In embodiments of formula (XIX) p is 8 to 10. In embodiments of formula (XIX) p is 9 to 10. R<sup>1</sup> and R<sup>2</sup> may be any of the embodiments described above (e.g., R<sup>1</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl or hydrogen, R<sup>2</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

      In embodiments of formula (XIX) q is 0 to 7. In embodiments of formula (XIX) q is 1 to 7. In embodiments of formula (XIX) q is 2 to 7. In embodiments of formula (XIX) q is 3 to 7. In embodiments of formula (XIX) q is 4 to 7. In embodiments of formula (XIX) q is 5 to 7. In  
30       embodiments of formula (XIX) q is 6 to 7. Moreover, in embodiments, q is 0. In embodiments of formula (XIX) r is 0 to 10. In embodiments of formula (XIX) r is 1 to 10. In embodiments of formula (XIX) r is 2 to 10. In embodiments of formula (XIX) r is 3 to 10. In embodiments of

formula (XIX) r is 4 to 10. In embodiments of formula (XIX) r is 5 to 10. In embodiments of formula (XIX) r is 6 to 10. In embodiments of formula (XIX) r is 7 to 10. In embodiments of formula (XIX) r is 8 to 10. In embodiments of formula (XIX) r is 9 to 10. Moreover, in  
embodiments, r is 0. In embodiments of formula (XIX) p is 1 to 10. In embodiments of formula  
5 (XIX) p is 2 to 10. In embodiments of formula (XIX) p is 3 to 10. In embodiments of formula (XIX) p is 4 to 10. In embodiments of formula (XIX) p is 5 to 10. In embodiments of formula (XIX) p is 6 to 10. In embodiments of formula (XIX) p is 7 to 10. In embodiments of formula (XIX) p is 8 to 10. In embodiments of formula (XIX) p is 9 to 10. R<sup>1</sup> and R<sup>2</sup> may be any of the  
embodiments described above (e.g., R<sup>1</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl or hydrogen, R<sup>2</sup>  
10 maybe linear unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

In embodiments of formula (XIX) q is 0 to 6. In embodiments of formula (XIX) q is 1 to 6. In embodiments of formula (XIX) q is 2 to 6. In embodiments of formula (XIX) q is 3 to 6. In embodiments of formula (XIX) q is 4 to 6. In embodiments of formula (XIX) q is 5 to 6. Moreover, in embodiments, q is 0. In embodiments of formula (XIX) r is 0 to 10. In  
15 embodiments of formula (XIX) r is 1 to 10. In embodiments of formula (XIX) r is 2 to 10. In embodiments of formula (XIX) r is 3 to 10. In embodiments of formula (XIX) r is 4 to 10. In embodiments of formula (XIX) r is 5 to 10. In embodiments of formula (XIX) r is 6 to 10. In embodiments of formula (XIX) r is 7 to 10. In embodiments of formula (XIX) r is 8 to 10. In  
embodiments of formula (XIX) r is 9 to 10. Moreover, in embodiments, r is 0. In embodiments  
20 of formula (XIX) p is 1 to 10. In embodiments of formula (XIX) p is 2 to 10. In embodiments of formula (XIX) p is 3 to 10. In embodiments of formula (XIX) p is 4 to 10. In embodiments of formula (XIX) p is 5 to 10. In embodiments of formula (XIX) p is 6 to 10. In embodiments of formula (XIX) p is 7 to 10. In embodiments of formula (XIX) p is 8 to 10. In embodiments of formula (XIX) p is 9 to 10. R<sup>1</sup> and R<sup>2</sup> may be any of the embodiments described above (e.g.,  
25 R<sup>1</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl or hydrogen, R<sup>2</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

In embodiments of formula (XIX) q is 0 to 5. In embodiments of formula (XIX) q is 1 to 5. In embodiments of formula (XIX) q is 2 to 5. In embodiments of formula (XIX) q is 3 to 5. In embodiments of formula (XIX) q is 4 to 5. Moreover, in embodiments, q is 0. In  
30 embodiments of formula (XIX) r is 0 to 10. In embodiments of formula (XIX) r is 1 to 10. In embodiments of formula (XIX) r is 2 to 10. In embodiments of formula (XIX) r is 3 to 10. In embodiments of formula (XIX) r is 4 to 10. In embodiments of formula (XIX) r is 5 to 10. In embodiments of formula (XIX) r is 6 to 10. In embodiments of formula (XIX) r is 7 to 10. In  
embodiments of formula (XIX) r is 8 to 10. In embodiments of formula (XIX) r is 9 to 10.

Moreover, in embodiments,  $r$  is 0. In embodiments of formula (XIX)  $p$  is 1 to 10. In  
embodiments of formula (XIX)  $p$  is 2 to 10. In embodiments of formula (XIX)  $p$  is 3 to 10. In  
embodiments of formula (XIX)  $p$  is 4 to 10. In embodiments of formula (XIX)  $p$  is 5 to 10. In  
embodiments of formula (XIX)  $p$  is 6 to 10. In embodiments of formula (XIX)  $p$  is 7 to 10. In  
embodiments of formula (XIX)  $p$  is 8 to 10. In embodiments of formula (XIX)  $p$  is 9 to 10.  $R^1$   
and  $R^2$  may be any of the embodiments described above (e.g.,  $R^1$  maybe linear unsubstituted  $C_1$ -  
 $C_6$  alkyl or hydrogen,  $R^2$  maybe linear unsubstituted  $C_1$ - $C_2$  alkyl).

In embodiments of formula (XIX)  $q$  is 0 to 4. In embodiments of formula (XIX)  $q$  is 1 to  
4. In embodiments of formula (XIX)  $q$  is 2 to 4. In embodiments of formula (XIX)  $q$  is 3 to 4.  
Moreover, in embodiments,  $q$  is 0. In embodiments of formula (XIX)  $r$  is 0 to 10. In  
embodiments of formula (XIX)  $r$  is 1 to 10. In embodiments of formula (XIX)  $r$  is 2 to 10. In  
embodiments of formula (XIX)  $r$  is 3 to 10. In embodiments of formula (XIX)  $r$  is 4 to 10. In  
embodiments of formula (XIX)  $r$  is 5 to 10. In embodiments of formula (XIX)  $r$  is 6 to 10. In  
embodiments of formula (XIX)  $r$  is 7 to 10. In embodiments of formula (XIX)  $r$  is 8 to 10. In  
embodiments of formula (XIX)  $r$  is 9 to 10. Moreover, in embodiments,  $r$  is 0. In embodiments  
of formula (XIX)  $p$  is 1 to 10. In embodiments of formula (XIX)  $p$  is 2 to 10. In embodiments  
of formula (XIX)  $p$  is 3 to 10. In embodiments of formula (XIX)  $p$  is 4 to 10. In embodiments  
of formula (XIX)  $p$  is 5 to 10. In embodiments of formula (XIX)  $p$  is 6 to 10. In embodiments  
of formula (XIX)  $p$  is 7 to 10. In embodiments of formula (XIX)  $p$  is 8 to 10. In embodiments  
of formula (XIX)  $p$  is 9 to 10.  $R^1$  and  $R^2$  may be any of the embodiments described above (e.g.,  
 $R^1$  maybe linear unsubstituted  $C_1$ - $C_6$  alkyl or hydrogen,  $R^2$  maybe linear unsubstituted  $C_1$ - $C_2$   
alkyl).

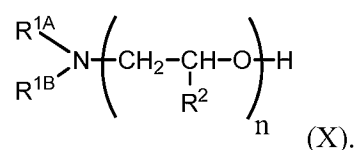
In embodiments of formula (XIX)  $q$  is 0 to 3. In embodiments of formula (XIX)  $q$  is 1 to  
3. In embodiments of formula (XIX)  $q$  is 2 to 3. Moreover, in embodiments,  $q$  is 0. In  
embodiments of formula (XIX)  $r$  is 0 to 10. In embodiments of formula (XIX)  $r$  is 1 to 10. In  
embodiments of formula (XIX)  $r$  is 2 to 10. In embodiments of formula (XIX)  $r$  is 3 to 10. In  
embodiments of formula (XIX)  $r$  is 4 to 10. In embodiments of formula (XIX)  $r$  is 5 to 10. In  
embodiments of formula (XIX)  $r$  is 6 to 10. In embodiments of formula (XIX)  $r$  is 7 to 10. In  
embodiments of formula (XIX)  $r$  is 8 to 10. In embodiments of formula (XIX)  $r$  is 9 to 10.  
Moreover, in embodiments,  $r$  is 0. In embodiments of formula (XIX)  $p$  is 1 to 10. In  
embodiments of formula (XIX)  $p$  is 2 to 10. In embodiments of formula (XIX)  $p$  is 3 to 10. In  
embodiments of formula (XIX)  $p$  is 4 to 10. In embodiments of formula (XIX)  $p$  is 5 to 10. In  
embodiments of formula (XIX)  $p$  is 6 to 10. In embodiments of formula (XIX)  $p$  is 7 to 10. In  
embodiments of formula (XIX)  $p$  is 8 to 10. In embodiments of formula (XIX)  $p$  is 9 to 10.  $R^1$

and R<sup>2</sup> may be any of the embodiments described above (e.g., R<sup>1</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl or hydrogen, R<sup>2</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

In embodiments of formula (XIX) q is 0 to 2. In embodiments of formula (XIX) q is 1 to 2. Moreover, in embodiments, q is 0. In embodiments of formula (XIX) r is 0 to 10. In  
 5 embodiments of formula (XIX) r is 1 to 10. In embodiments of formula (XIX) r is 2 to 10. In  
 embodiments of formula (XIX) r is 3 to 10. In embodiments of formula (XIX) r is 4 to 10. In  
 embodiments of formula (XIX) r is 5 to 10. In embodiments of formula (XIX) r is 6 to 10. In  
 embodiments of formula (XIX) r is 7 to 10. In embodiments of formula (XIX) r is 8 to 10. In  
 embodiments of formula (XIX) r is 9 to 10. Moreover, in embodiments, r is 0. In embodiments  
 10 of formula (XIX) p is 1 to 10. In embodiments of formula (XIX) p is 2 to 10. In embodiments  
 of formula (XIX) p is 3 to 10. In embodiments of formula (XIX) p is 4 to 10. In embodiments  
 of formula (XIX) p is 5 to 10. In embodiments of formula (XIX) p is 6 to 10. In embodiments  
 of formula (XIX) p is 7 to 10. In embodiments of formula (XIX) p is 8 to 10. In embodiments  
 of formula (XIX) p is 9 to 10. R<sup>1</sup> and R<sup>2</sup> may be any of the embodiments described above (e.g.,  
 15 R<sup>1</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl or hydrogen, R<sup>2</sup> maybe linear unsubstituted C<sub>1</sub>-C<sub>2</sub>  
 alkyl).

In embodiments, the co-solvent is present in an amount sufficient to increase the  
 solubility of the surfactant in the aqueous phase relative to the absence of the co-solvent. In  
 other words, in the presence of a sufficient amount of the co-solvent, the solubility of the  
 20 surfactant in the aqueous phase is higher than in the absence of the co-solvent. In embodiments,  
 the co-solvent is present in an amount sufficient to increase the solubility of the surfactant in the  
 aqueous phase relative to the absence of the co-solvent. Thus, in the presence of a sufficient  
 amount of the co-solvent the solubility of the surfactant in the aqueous phase is higher than in  
 the absence of the co-solvent. In embodiments, the co-solvent is present in an amount sufficient  
 25 to decrease the viscosity of the emulsion relative to the absence of the co-solvent.

The co-solvent may have the formula:



In formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently hydrogen, unsubstituted C<sub>1</sub>-C<sub>8</sub> alkyl,  
 unsubstituted cycloalkyl, unsubstituted heterocycloalkyl, unsubstituted aryl, unsubstituted

heteroaryl, C<sub>1</sub>-C<sub>6</sub> alkylamine or  
 30  $\left( \text{CH}_2 - \underset{\text{R}^3}{\text{CH}} - \text{O} \right)_m \text{H}$ . R<sup>2</sup> and R<sup>3</sup> are independently hydrogen or

unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl. The symbol n is an integer from 1 to 30 and m is an integer from 1 to 30.

In embodiments of formula (X) the symbol n is an integer from 1-30. In embodiments of formula (X) the symbol n is an integer from 1-28. In embodiments of formula (X) the symbol n is an integer from 1-26. In embodiments of formula (X) the symbol n is an integer from 1-24. In  
5       embodiments of formula (X) the symbol n is an integer from 1-22. In embodiments of formula (X) the symbol n is an integer from 1-20. In embodiments of formula (X) the symbol n is an integer from 1-18. In embodiments of formula (X) the symbol n is an integer from 1-16. In  
10       embodiments of formula (X) the symbol n is an integer from 1-14. In embodiments of formula (X) the symbol n is an integer from 1-12. In embodiments of formula (X) the symbol n is an integer from 1-10. In embodiments of formula (X) the symbol n is an integer from 1-8. In  
embodiments of formula (X) the symbol n is an integer from 1-6. In embodiments of formula (X) the symbol n is an integer from 1-4. In embodiments of formula (X) the symbol n is an integer from 1-3. In embodiments of formula (X) the symbol n is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11,  
15       12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, or 30. In embodiments of formula (X) the symbol n is 3. In embodiments of formula (X) the symbol n is 1. In  
embodiments of formula (X) the symbol n is 6.

In embodiments of formula (X) R<sup>2</sup> is hydrogen and n is as defined in an embodiment above (e.g., n is at least 1, or at least 10). Thus, in embodiments of formula (X) R<sup>2</sup> is hydrogen  
20       and n is 1. In embodiments of formula (X) R<sup>2</sup> is hydrogen and n is 3.

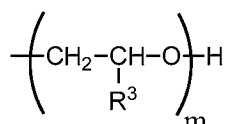
In embodiments of formula (X) the symbol m is an integer from 1-30. In embodiments of formula (X) the symbol m is an integer from 1-28. In embodiments of formula (X) the symbol m is an integer from 1-26. In embodiments of formula (X) the symbol m is an integer from 1-24. In embodiments of formula (X) the symbol m is an integer from 1-22. In  
25       embodiments of formula (X) the symbol m is an integer from 1-20. In embodiments of formula (X) the symbol m is an integer from 1-18. In embodiments of formula (X) the symbol m is an integer from 1-16. In embodiments of formula (X) the symbol m is an integer from 1-14. In  
embodiments of formula (X) the symbol m is an integer from 1-12. In embodiments of formula (X) the symbol m is an integer from 1-10. In embodiments of formula (X) the symbol m is an integer from 1-8. In embodiments of formula (X) the symbol m is an integer from 1-6. In  
30       embodiments of formula (X) the symbol m is an integer from 1-4. In embodiments of formula (X) the symbol m is an integer from 1-3. In embodiments of formula (X) the symbol m is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, or



30. In embodiments of formula (X) the symbol m is 3. In embodiments of formula (X) the symbol m is 1. In embodiments of formula (X) the symbol m is 6.

In embodiments of formula (X) R<sup>3</sup> is hydrogen and m is as defined in an embodiment above (e.g., n is at least 1, or at least 10). Thus, in embodiments of formula (X) R<sup>3</sup> is hydrogen and m is 1. In embodiments of formula (X) R<sup>3</sup> is hydrogen and m is 3.

As provided herein R<sup>1A</sup> and R<sup>1B</sup> may be independently hydrogen, unsubstituted C<sub>1</sub>-C<sub>8</sub> (e.g., C<sub>1</sub>-C<sub>4</sub>) alkyl, unsubstituted C<sub>3</sub>-C<sub>6</sub> (e.g., C<sub>6</sub>) cycloalkyl, unsubstituted 3 to 8 membered (e.g., 6 membered) heterocycloalkyl, C<sub>5</sub>-C<sub>8</sub> (e.g., C<sub>6</sub>) unsubstituted aryl, unsubstituted 5 to 8 membered (e.g., 5 to 6-membered) heteroaryl, C<sub>1</sub>-C<sub>6</sub> (e.g., C<sub>2</sub>-C<sub>4</sub>) alkylamine or



. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently unsubstituted C<sub>1</sub>-C<sub>8</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently unsubstituted C<sub>1</sub>-C<sub>4</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are unsubstituted C<sub>3</sub> alkyl. In embodiments of formula (X) the number of total carbon atoms within R<sup>1A</sup> and R<sup>1B</sup> combined does not exceed 8.

In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently branched or linear unsubstituted C<sub>1</sub>-C<sub>8</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently branched or linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently branched or linear unsubstituted C<sub>1</sub>-C<sub>4</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently branched or linear unsubstituted C<sub>3</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently linear unsubstituted C<sub>1</sub>-C<sub>8</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently branched unsubstituted C<sub>1</sub>-C<sub>8</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently linear unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently branched unsubstituted C<sub>1</sub>-C<sub>6</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently linear unsubstituted C<sub>1</sub>-C<sub>4</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently branched unsubstituted C<sub>1</sub>-C<sub>4</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are linear unsubstituted C<sub>3</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are branched unsubstituted C<sub>3</sub> alkyl. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are unsubstituted isopropyl.

As provided herein R<sup>1A</sup> and R<sup>1B</sup> may be independently hydrogen or C<sub>1</sub>-C<sub>6</sub> (e.g., C<sub>1</sub>-C<sub>4</sub>) alkylamine. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently hydrogen or C<sub>1</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently hydrogen or C<sub>2</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X) R<sup>1A</sup> and R<sup>1B</sup> are independently hydrogen or C<sub>3</sub>-C<sub>6</sub>

alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or C<sub>4</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or C<sub>4</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or C<sub>5</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or C<sub>6</sub> alkylamine.

In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or branched or linear C<sub>1</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or branched or linear C<sub>2</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or branched or linear C<sub>3</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or branched or linear C<sub>4</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or branched or linear C<sub>4</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or branched or linear C<sub>5</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or branched or linear C<sub>6</sub> alkylamine.

In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or linear C<sub>1</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or linear C<sub>2</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or linear C<sub>3</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or linear C<sub>4</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or linear C<sub>4</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or linear C<sub>5</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or linear C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or branched C<sub>1</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or branched C<sub>2</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or branched C<sub>3</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or branched C<sub>4</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or branched C<sub>4</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or branched C<sub>5</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or branched C<sub>6</sub> alkylamine.

In embodiments of formula (X)  $R^{1A}$  is hydrogen and  $R^{1B}$  is C<sub>4</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  is hydrogen and  $R^{1B}$  is branched or linear C<sub>4</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  is hydrogen and  $R^{1B}$  is linear C<sub>4</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  is hydrogen and  $R^{1B}$  is branched C<sub>4</sub>-C<sub>6</sub> alkylamine. In

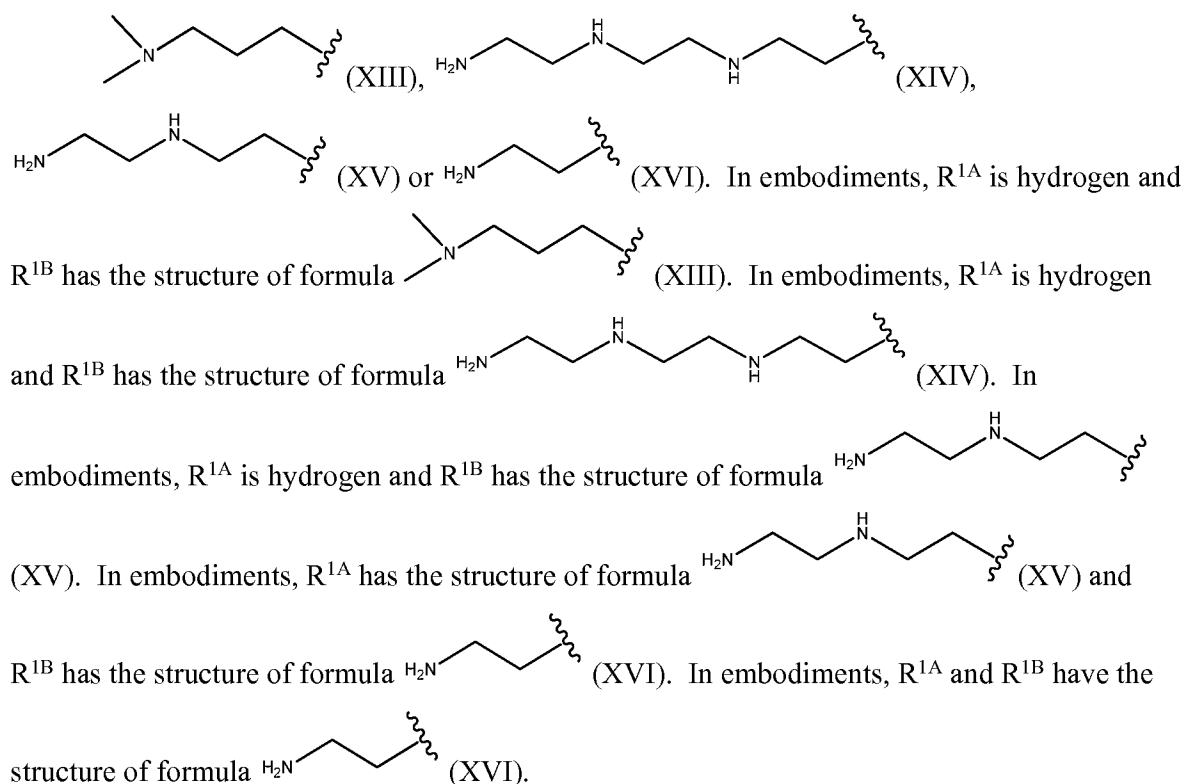
embodiments of formula (X)  $R^{1A}$  is hydrogen and  $R^{1B}$  is C<sub>4</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  is hydrogen and  $R^{1B}$  is linear C<sub>4</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  is hydrogen and  $R^{1B}$  is C<sub>5</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  is hydrogen and  $R^{1B}$  is linear C<sub>5</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  is hydrogen and  $R^{1B}$  is C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  is hydrogen and  $R^{1B}$  is linear C<sub>6</sub> alkylamine.

$R^{1A}$  and  $R^{1B}$  may be independently C<sub>1</sub>-C<sub>6</sub> (e.g., C<sub>1</sub>-C<sub>4</sub>) alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently C<sub>1</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently C<sub>2</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently C<sub>3</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently C<sub>4</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched or linear C<sub>1</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched or linear C<sub>2</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched or linear C<sub>3</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched or linear C<sub>4</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently linear C<sub>1</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently linear C<sub>2</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently linear C<sub>3</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently linear C<sub>4</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched C<sub>1</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched C<sub>2</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched C<sub>3</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched C<sub>4</sub>-C<sub>6</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently C<sub>2</sub> alkylamine or C<sub>4</sub> alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are C<sub>2</sub> alkylamine.

As described herein  $R^{1A}$  and  $R^{1B}$  may be an alkylpolyamine. Thus, in embodiments of formula (X) the alkylamine is an alkylpolyamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently C<sub>1</sub>-C<sub>6</sub> alkylpolyamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently C<sub>2</sub>-C<sub>6</sub> alkylpolyamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently C<sub>3</sub>-C<sub>6</sub> alkylpolyamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently C<sub>4</sub>-C<sub>6</sub> alkylpolyamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched or linear C<sub>1</sub>-C<sub>6</sub> alkylpolyamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched or linear C<sub>2</sub>-C<sub>6</sub> alkylpolyamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched or linear C<sub>3</sub>-C<sub>6</sub> alkylpolyamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched or linear C<sub>4</sub>-C<sub>6</sub> alkylpolyamine. In

embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently linear  $C_1$ - $C_6$  alkylpolyamine. In  
embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently linear  $C_2$ - $C_6$  alkylpolyamine. In  
embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently linear  $C_3$ - $C_6$  alkylpolyamine. In  
embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently linear  $C_4$ - $C_6$  alkylpolyamine. In  
5 embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched  $C_1$ - $C_6$  alkylpolyamine. In  
embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched  $C_2$ - $C_6$  alkylpolyamine. In  
embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched  $C_3$ - $C_6$  alkylpolyamine. In  
embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently branched  $C_4$ - $C_6$  alkylpolyamine. In  
embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently  $C_2$  alkylamine or  $C_4$   
10 alkylpolyamine.

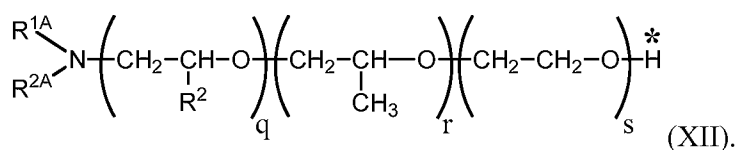
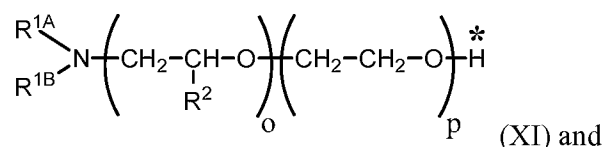
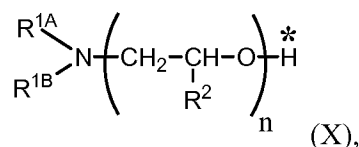
In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are independently hydrogen or  $C_1$ - $C_6$   
alkylamine. In embodiments of formula (X)  $R^{1A}$  and  $R^{1B}$  are  $C_1$ - $C_6$  alkylamine. In embodiments  
of formula (X)  $R^{1A}$  and  $R^{1B}$  are  $C_1$ - $C_6$  alkylpolyamine. In the embodiments provided herein  $R^{1A}$   
and  $R^{1B}$  may have the structure of formula:



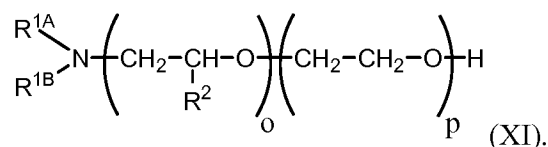
As provided herein  $R^{1A}$  and  $R^{1B}$  may be independently hydrogen, unsubstituted  $C_3$ - $C_6$   
(e.g.,  $C_6$ ) cycloalkyl or  $C_5$ - $C_8$  (e.g.,  $C_6$ ) unsubstituted aryl. Thus, in embodiments of formula (X)  
25  $R^{1A}$  is hydrogen and  $R^{1B}$  is unsubstituted (e.g.,  $C_3$ - $C_6$ ) cycloalkyl. In embodiments of formula  
(X)  $R^{1B}$  is unsubstituted 6 membered cycloalkyl. In embodiments of formula (X)  $R^{1A}$  is

hydrogen and R<sup>1B</sup> is (e.g., C<sub>5</sub>-C<sub>8</sub>) unsubstituted aryl. In embodiments of formula (X) R<sup>1B</sup> is phenyl.

As provided herein R<sup>2</sup> and R<sup>3</sup> of formula (X) may be independently hydrogen or unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl. Thus, in embodiments of formula (X) R<sup>2</sup> and R<sup>3</sup> are independently hydrogen, methyl or ethyl. In embodiments of formula (X) where multiple R<sup>2</sup> substituents are present and at least two R<sup>2</sup> substituents are different, R<sup>2</sup> substituents with the fewest number of carbons are present to the side of the compound, (XI), or (XII) bound to the hydrogen atom. In this embodiment, the compound, (XI), or (XII) will be increasingly hydrophilic in progressing from the nitrogen to the side of the compound, (XI), or (XII) bound to the hydrogen atom. The term “side of the compound, (XI), or (XII) bound to the hydrogen atom” refers to the side of the compound indicated by asterisk in the below structures:



In embodiments, the compound has the formula:



In formula (XI) R<sup>1A</sup> and R<sup>1B</sup> are defined as above (e.g., hydrogen, C<sub>3</sub> alkyl, or C<sub>1</sub>-C<sub>6</sub> alkylamine), R<sup>2</sup> is methyl or ethyl, o is an integer from 0 to 15 and p is an integer from 1 to 10. In embodiments of formula (XI) R<sup>2</sup> is hydrogen, o is 0 and p is 1 to 6.

In embodiments of formula (XI) o is 0 to 15. In embodiments of formula (XI) o is 0 to 12. In embodiments of formula (XI) o is 0 to 10. In embodiments of formula (XI) o is 0 to 8. In embodiments of formula (XI) o is 0 to 6. In embodiments of formula (XI) o is 0 to 4. In embodiments of formula (XI) o is 0 to 2. In embodiments of formula (XI) o is 0. In embodiments, p is 1 to 10. In embodiments of formula (XI) p is 1 to 8. In embodiments, p is 1 to 6. In embodiments of formula (XI) p is 1 to 4. In embodiments, p is 1 to 2. In embodiments, p is more than 1. In embodiments of formula (XI) p is 6. R<sup>1A</sup>, R<sup>1B</sup> and R<sup>2</sup> may be any of the

embodiments described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  $R^2$  maybe hydrogen or unsubstituted  $C_1$ - $C_2$  alkyl). Thus, in embodiments of formula (XI)  $R^{1A}$  and  $R^{1B}$  are isopropyl, o is 0 and p is 3.

In embodiments of formula (XI) o is 1 to 15. In embodiments of formula (XI) o is 1 to 12. In embodiments of formula (XI) o is 1 to 10. In embodiments of formula (XI) o is 1 to 8. In embodiments of formula (XI) o is 1 to 6. In embodiments of formula (XI) o is 1 to 4. In embodiments of formula (XI) o is 1 to 2. In embodiments, p is 1 to 10. In embodiments of formula (XI) p is 1 to 8. In embodiments, p is 1 to 6. In embodiments of formula (XI) p is 1 to 4. In embodiments of formula (XI) p is 1 to 2. In embodiments of formula (XI) p is more than 1.  $R^{1A}$ ,  $R^{1B}$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  $R^2$  maybe hydrogen or unsubstituted  $C_1$ - $C_2$  alkyl).

In embodiments of formula (XI) o is 2 to 15. In embodiments of formula (XI) o is 2 to 12. In embodiments of formula (XI) o is 2 to 10. In embodiments of formula (XI) o is 2 to 8. In embodiments of formula (XI) o is 2 to 6. In embodiments of formula (XI) o is 2 to 4. In embodiments of formula (XI) p is 1 to 10. In embodiments of formula (XI) p is 1 to 8. In embodiments of formula (XI) p is 1 to 6. In embodiments of formula (XI) p is 1 to 4. In embodiments of formula (XI) p is 1 to 2. In embodiments of formula (XI) p is more than 1.  $R^{1A}$ ,  $R^{1B}$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  $R^2$  maybe hydrogen or unsubstituted  $C_1$ - $C_2$  alkyl).

In embodiments of formula (XI) o is 4 to 15. In embodiments of formula (XI) o is 4 to 12. In embodiments of formula (XI) o is 4 to 10. In embodiments of formula (XI) o is 4 to 8. In embodiments of formula (XI) o is 4 to 6. In embodiments of formula (XI) p is 1 to 10. In embodiments of formula (XI) p is 1 to 8. In embodiments of formula (XI) p is 1 to 6. In embodiments of formula (XI) p is 1 to 4. In embodiments of formula (XI) p is 1 to 2. In embodiments of formula (XI) p is more than 1.  $R^{1A}$ ,  $R^{1B}$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  $R^2$  maybe hydrogen or unsubstituted  $C_1$ - $C_2$  alkyl).

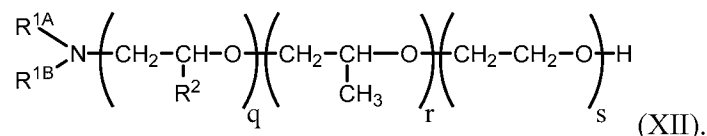
In embodiments of formula (XI) o is 6 to 15. In embodiments of formula (XI) o is 6 to 12. In embodiments of formula (XI) o is 6 to 10. In embodiments of formula (XI) o is 6 to 8. In embodiments of formula (XI) p is 1 to 10. In embodiments of formula (XI) p is 1 to 8. In embodiments of formula (XI) p is 1 to 6. In embodiments of formula (XI) p is 1 to 4. In embodiments of formula (XI) p is 1 to 2. In embodiments of formula (XI) p is more than 1.  $R^{1A}$ ,  $R^{1B}$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  $R^2$  maybe hydrogen or unsubstituted  $C_1$ - $C_2$  alkyl).

In embodiments of formula (XI) o is 8 to 15. In embodiments of formula (XI) o is 8 to 12. In embodiments of formula (XI) o is 8 to 10. In embodiments of formula (XI) p is 1 to 10. In embodiments of formula (XI) p is 1 to 8. In embodiments of formula (XI) p is 1 to 6. In  
 5 embodiments of formula (XI) p is 1 to 4. In embodiments of formula (XI) p is 1 to 2. In  
 embodiments of formula (XI) p is more than 1.  $R^{1A}$ ,  $R^{1B}$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  $R^2$  maybe hydrogen or unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

In embodiments of formula (XI) o is 10 to 15. In embodiments of formula (XI) o is 10 to 12. In embodiments of formula (XI) p is 1 to 10. In embodiments of formula (XI) p is 1 to 8. In  
 10 embodiments of formula (XI) p is 1 to 6. In embodiments of formula (XI) p is 1 to 4. In  
 embodiments of formula (XI) p is 1 to 2. In embodiments of formula (XI) p is more than 1.  $R^{1A}$ ,  $R^{1B}$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  $R^2$  maybe hydrogen or unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

In embodiments of formula (XI) o is 12 to 15. In embodiments of formula (XI) p is 1  
 15 to 10. In embodiments of formula (XI) p is 1 to 8. In embodiments of formula (XI) p is 1 to 6.  
 In embodiments of formula (XI) p is 1 to 4. In embodiments of formula (XI) p is 1 to 2. In  
 embodiments of formula (XI) p is more than 1.  $R^{1A}$ ,  $R^{1B}$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  $R^2$  maybe hydrogen or unsubstituted C<sub>1</sub>-C<sub>2</sub> alkyl).

20 In embodiments, the compound has the formula:



In formula (XII)  $R^2$  is ethyl, q is an integer from 0 to 10, r is an integer from 0 to 10 and s is an integer from 1 to 10.

In embodiments of formula (XII) q is 0 to 10. In embodiments of formula (XII) q is 1 to  
 25 10. In embodiments of formula (XII) q is 2 to 10. In embodiments of formula (XII) q is 3 to 10.  
 In embodiments of formula (XII) q is 4 to 10. In embodiments of formula (XII) q is 5 to 10. In  
 embodiments of formula (XII) q is 6 to 10. In embodiments of formula (XII) q is 7 to 10. In  
 embodiments of formula (XII) q is 8 to 10. In embodiments of formula (XII) q is 9 to 10.  
 Moreover, in embodiments of formula (XII) q is 0. In embodiments of formula (XII) r is 0 to 10.  
 30 In embodiments of formula (XII) r is 1 to 10. In embodiments of formula (XII) r is 2 to 10. In  
 embodiments of formula (XII) r is 3 to 10. In embodiments of formula (XII) r is 4 to 10. In  
 embodiments of formula (XII) r is 5 to 10. In embodiments of formula (XII) r is 6 to 10. In

embodiments of formula (XII) r is 7 to 10. In embodiments of formula (XII) r is 8 to 10. In  
embodiments of formula (XII) r is 9 to 10. Moreover, in embodiments of formula (XII) r is 0.  
In embodiments of formula (XII) s is 1 to 10. In embodiments of formula (XII) s is 2 to 10. In  
embodiments of formula (XII) s is 3 to 10. In embodiments of formula (XII) s is 4 to 10. In  
5 embodiments of formula (XII) s is 5 to 10. In embodiments of formula (XII) s is 6 to 10. In  
embodiments of formula (XII) s is 7 to 10. In embodiments of formula (XII) s is 8 to 10. In  
embodiments of formula (XII) s is 9 to 10.  $R^{1A}$ ,  $R^{1B}$  and  $R^2$  may be any of the embodiments  
described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  $R^2$  maybe hydrogen or unsubstituted  $C_1$ - $C_2$   
alkyl).

10 In embodiments of formula (XII) q is 0 to 9. In embodiments of formula (XII) q is 1 to 9.  
In embodiments of formula (XII) q is 2 to 9. In embodiments of formula (XII) q is 3 to 9. In  
embodiments of formula (XII) q is 4 to 9. In embodiments of formula (XII) q is 5 to 9. In  
embodiments of formula (XII) q is 6 to 9. In embodiments of formula (XII) q is 7 to 9. In  
embodiments of formula (XII) q is 8 to 9. Moreover, in embodiments of formula (XII) q is 0. In  
15 embodiments of formula (XII) r is 0 to 10. In embodiments of formula (XII) r is 1 to 10. In  
embodiments of formula (XII) r is 2 to 10. In embodiments of formula (XII) r is 3 to 10. In  
embodiments of formula (XII) r is 4 to 10. In embodiments of formula (XII) r is 5 to 10. In  
embodiments of formula (XII) r is 6 to 10. In embodiments of formula (XII) r is 7 to 10. In  
embodiments of formula (XII) r is 8 to 10. In embodiments of formula (XII) r is 9 to 10.  
20 Moreover, in embodiments of formula (XII) r is 0. In embodiments of formula (XII) s is 1 to 10.  
In embodiments of formula (XII) s is 2 to 10. In embodiments of formula (XII) s is 3 to 10. In  
embodiments of formula (XII) s is 4 to 10. In embodiments of formula (XII) s is 5 to 10. In  
embodiments of formula (XII) s is 6 to 10. In embodiments of formula (XII) s is 7 to 10. In  
embodiments of formula (XII) s is 8 to 10. In embodiments of formula (XII) s is 9 to 10.  $R^{1A}$ ,  
25  $R^{1B}$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  
 $R^2$  maybe hydrogen or unsubstituted  $C_1$ - $C_2$  alkyl).

In embodiments of formula (XII) q is 0 to 8. In embodiments of formula (XII) q is 1 to 8.  
In embodiments of formula (XII) q is 2 to 8. In embodiments of formula (XII) q is 3 to 8. In  
embodiments of formula (XII) q is 4 to 8. In embodiments of formula (XII) q is 5 to 8. In  
30 embodiments of formula (XII) q is 6 to 8. In embodiments of formula (XII) q is 7 to 8.  
Moreover, in embodiments of formula (XII) q is 0. In embodiments of formula (XII) r is 0 to 10.  
In embodiments of formula (XII) r is 1 to 10. In embodiments of formula (XII) r is 2 to 10. In  
embodiments of formula (XII) r is 3 to 10. In embodiments of formula (XII) r is 4 to 10. In  
embodiments of formula (XII) r is 5 to 10. In embodiments of formula (XII) r is 6 to 10. In



embodiments of formula (XII) r is 7 to 10. In embodiments of formula (XII) r is 8 to 10. In  
embodiments of formula (XII) r is 9 to 10. Moreover, in embodiments of formula (XII) r is 0.  
In embodiments of formula (XII) s is 1 to 10. In embodiments of formula (XII) s is 2 to 10. In  
embodiments of formula (XII) s is 3 to 10. In embodiments of formula (XII) s is 4 to 10. In  
5 embodiments of formula (XII) s is 5 to 10. In embodiments of formula (XII) s is 6 to 10. In  
embodiments of formula (XII) s is 7 to 10. In embodiments of formula (XII) s is 8 to 10. In  
embodiments of formula (XII) s is 9 to 10.  $R^{1A}$ ,  $R^{1B}$  and  $R^2$  may be any of the embodiments  
described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  $R^2$  maybe hydrogen or unsubstituted  $C_1$ - $C_2$   
alkyl).

10 In embodiments of formula (XII) q is 0 to 7. In embodiments of formula (XII) q is 1 to 7.  
In embodiments of formula (XII) q is 2 to 7. In embodiments of formula (XII) q is 3 to 7. In  
embodiments of formula (XII) q is 4 to 7. In embodiments of formula (XII) q is 5 to 7. In  
embodiments of formula (XII) q is 6 to 7. Moreover, in embodiments of formula (XII) q is 0. In  
embodiments of formula (XII) r is 0 to 10. In embodiments of formula (XII) r is 1 to 10. In  
15 embodiments of formula (XII) r is 2 to 10. In embodiments of formula (XII) r is 3 to 10. In  
embodiments of formula (XII) r is 4 to 10. In embodiments of formula (XII) r is 5 to 10. In  
embodiments of formula (XII) r is 6 to 10. In embodiments of formula (XII) r is 7 to 10. In  
embodiments of formula (XII) r is 8 to 10. In embodiments of formula (XII) r is 9 to 10.  
Moreover, in embodiments of formula (XII) r is 0. In embodiments of formula (XII) s is 1 to 10.  
20 In embodiments of formula (XII) s is 2 to 10. In embodiments of formula (XII) s is 3 to 10. In  
embodiments of formula (XII) s is 4 to 10. In embodiments of formula (XII) s is 5 to 10. In  
embodiments of formula (XII) s is 6 to 10. In embodiments of formula (XII) s is 7 to 10. In  
embodiments of formula (XII) s is 8 to 10. In embodiments of formula (XII) s is 9 to 10.  $R^{1A}$ ,  
 $R^{1B}$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  
25  $R^2$  maybe hydrogen or unsubstituted  $C_1$ - $C_2$  alkyl).

In embodiments of formula (XII) q is 0 to 6. In embodiments of formula (XII) q is 1 to 6.  
In embodiments of formula (XII) q is 2 to 6. In embodiments of formula (XII) q is 3 to 6. In  
embodiments of formula (XII) q is 4 to 6. In embodiments of formula (XII) q is 5 to 6.  
Moreover, in embodiments of formula (XII) q is 0. In embodiments of formula (XII) r is 0 to 10.  
30 In embodiments of formula (XII) r is 1 to 10. In embodiments of formula (XII) r is 2 to 10. In  
embodiments of formula (XII) r is 3 to 10. In embodiments of formula (XII) r is 4 to 10. In  
embodiments of formula (XII) r is 5 to 10. In embodiments of formula (XII) r is 6 to 10. In  
embodiments of formula (XII) r is 7 to 10. In embodiments of formula (XII) r is 8 to 10. In  
embodiments of formula (XII) r is 9 to 10. Moreover, in embodiments of formula (XII) r is 0.

In embodiments of formula (XII) s is 1 to 10. In embodiments of formula (XII) s is 2 to 10. In embodiments of formula (XII) s is 3 to 10. In embodiments of formula (XII) s is 4 to 10. In embodiments of formula (XII) s is 5 to 10. In embodiments of formula (XII) s is 6 to 10. In embodiments of formula (XII) s is 7 to 10. In embodiments of formula (XII) s is 8 to 10. In  
5 embodiments of formula (XII) s is 9 to 10.  $R^{1A}$ ,  $R^{1B}$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  $R^2$  maybe hydrogen or unsubstituted  $C_1$ - $C_2$  alkyl).

In embodiments of formula (XII) q is 0 to 5. In embodiments of formula (XII) q is 1 to 5. In embodiments of formula (XII) q is 2 to 5. In embodiments of formula (XII) q is 3 to 5. In  
10 embodiments of formula (XII) q is 4 to 5. Moreover, in embodiments of formula (XII) q is 0. In embodiments of formula (XII) r is 0 to 10. In embodiments of formula (XII) r is 1 to 10. In embodiments of formula (XII) r is 2 to 10. In embodiments of formula (XII) r is 3 to 10. In embodiments of formula (XII) r is 4 to 10. In embodiments of formula (XII) r is 5 to 10. In  
15 embodiments of formula (XII) r is 6 to 10. In embodiments of formula (XII) r is 7 to 10. In embodiments of formula (XII) r is 8 to 10. In embodiments of formula (XII) r is 9 to 10. Moreover, in embodiments of formula (XII) r is 0. In embodiments of formula (XII) s is 1 to 10. In embodiments of formula (XII) s is 2 to 10. In embodiments of formula (XII) s is 3 to 10. In  
20 embodiments of formula (XII) s is 4 to 10. In embodiments of formula (XII) s is 5 to 10. In embodiments of formula (XII) s is 6 to 10. In embodiments of formula (XII) s is 7 to 10. In embodiments of formula (XII) s is 8 to 10. In embodiments of formula (XII) s is 9 to 10.  $R^{1A}$ ,  $R^{1B}$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  $R^2$  maybe hydrogen or unsubstituted  $C_1$ - $C_2$  alkyl).

In embodiments of formula (XII) q is 0 to 4. In embodiments of formula (XII) q is 1 to 4. In embodiments of formula (XII) q is 2 to 4. In embodiments of formula (XII) q is 3 to 4.  
25 Moreover, in embodiments of formula (XII) q is 0. In embodiments of formula (XII) r is 0 to 10. In embodiments of formula (XII) r is 1 to 10. In embodiments of formula (XII) r is 2 to 10. In embodiments of formula (XII) r is 3 to 10. In embodiments of formula (XII) r is 4 to 10. In embodiments of formula (XII) r is 5 to 10. In embodiments of formula (XII) r is 6 to 10. In  
30 embodiments of formula (XII) r is 7 to 10. In embodiments of formula (XII) r is 8 to 10. In embodiments of formula (XII) r is 9 to 10. Moreover, in embodiments of formula (XII) r is 0. In embodiments of formula (XII) s is 1 to 10. In embodiments of formula (XII) s is 2 to 10. In embodiments of formula (XII) s is 3 to 10. In embodiments of formula (XII) s is 4 to 10. In  
embodiments of formula (XII) s is 5 to 10. In embodiments of formula (XII) s is 6 to 10. In  
embodiments of formula (XII) s is 7 to 10. In embodiments of formula (XII) s is 8 to 10. In

embodiments of formula (XII) s is 9 to 10.  $R^{1A}$ ,  $R^{1B}$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  $R^2$  maybe hydrogen or unsubstituted  $C_1$ - $C_2$  alkyl).

In embodiments of formula (XII) q is 0 to 3. In embodiments of formula (XII) q is 1 to 3.

In embodiments of formula (XII) q is 2 to 3. Moreover, in embodiments of formula (XII) q is 0.

In embodiments of formula (XII) r is 0 to 10. In embodiments of formula (XII) r is 1 to 10. In

embodiments of formula (XII) r is 2 to 10. In embodiments of formula (XII) r is 3 to 10. In

embodiments of formula (XII) r is 4 to 10. In embodiments of formula (XII) r is 5 to 10. In

embodiments of formula (XII) r is 6 to 10. In embodiments of formula (XII) r is 7 to 10. In

embodiments of formula (XII) r is 8 to 10. In embodiments of formula (XII) r is 9 to 10.

Moreover, in embodiments of formula (XII) r is 0. In embodiments of formula (XII) s is 1 to 10.

In embodiments of formula (XII) s is 2 to 10. In embodiments of formula (XII) s is 3 to 10. In

embodiments of formula (XII) s is 4 to 10. In embodiments of formula (XII) s is 5 to 10. In

embodiments of formula (XII) s is 6 to 10. In embodiments of formula (XII) s is 7 to 10. In

embodiments of formula (XII) s is 8 to 10. In embodiments of formula (XII) s is 9 to 10.  $R^{1A}$ ,

$R^{1B}$  and  $R^2$  may be any of the embodiments described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,

$R^2$  maybe hydrogen or unsubstituted  $C_1$ - $C_2$  alkyl).

In embodiments of formula (XII) q is 0 to 2. In embodiments of formula (XII) q is 1 to 2.

Moreover, in embodiments of formula (XII) q is 0. In embodiments of formula (XII) r is 0 to 10.

In embodiments of formula (XII) r is 1 to 10. In embodiments of formula (XII) r is 2 to 10. In

embodiments of formula (XII) r is 3 to 10. In embodiments of formula (XII) r is 4 to 10. In

embodiments of formula (XII) r is 5 to 10. In embodiments of formula (XII) r is 6 to 10. In

embodiments of formula (XII) r is 7 to 10. In embodiments of formula (XII) r is 8 to 10. In

embodiments of formula (XII) r is 9 to 10. Moreover, in embodiments of formula (XII) r is 0.

In embodiments of formula (XII) s is 1 to 10. In embodiments of formula (XII) s is 2 to 10. In

embodiments of formula (XII) s is 3 to 10. In embodiments of formula (XII) s is 4 to 10. In

embodiments of formula (XII) s is 5 to 10. In embodiments of formula (XII) s is 6 to 10. In

embodiments of formula (XII) s is 7 to 10. In embodiments of formula (XII) s is 8 to 10. In

embodiments of formula (XII) s is 9 to 10.  $R^{1A}$ ,  $R^{1B}$  and  $R^2$  may be any of the embodiments

described above (e.g.,  $R^{1A}$  and  $R^{1B}$  maybe isopropyl,  $R^2$  maybe hydrogen or unsubstituted  $C_1$ - $C_2$

alkyl).

In embodiments of the compound, or embodiments thereof provided herein, where  $R^{1A}$

and  $R^{1B}$  are isopropyl, and  $R^2$  is hydrogen, the symbol n is 1 or 3. In embodiments, where  $R^{1A}$  is

hydrogen,  $R^{1B}$  has the structure of formula (XIII) and  $R^2$  is hydrogen, the symbol n is 1 or 3. In

embodiments, where  $R^{1A}$  is hydrogen,  $R^{1B}$  has the structure of formula (XIV) and  $R^2$  is hydrogen, the symbol  $n$  is 1 or 3. In embodiments, where  $R^{1A}$  is hydrogen,  $R^{1B}$  has the structure of formula (XV) and  $R^2$  is hydrogen, the symbol  $n$  is 1 or 3. In embodiments, where  $R^{1A}$  has the formula of structure (XV),  $R^{1B}$  has the structure of formula (XVI) and  $R^2$  is hydrogen, the symbol  $n$  is 1 or 3. In embodiments, where  $R^{1A}$  and  $R^{1B}$  have the formula of structure (XVI) and  $R^2$  is hydrogen, the symbol  $n$  is 1 or 3. In embodiments, where  $R^{1A}$  is hydrogen,  $R^{1B}$  is phenyl and  $R^2$  is hydrogen, the symbol  $n$  is 1 or 3. In embodiments, where  $R^{1A}$  is hydrogen,  $R^{1B}$  is 6 membered cycloalkyl and  $R^2$  is hydrogen, the symbol  $n$  is 1 or 3.

The aqueous composition provided herein including embodiments thereof, may include seawater, or fresh water from an aquifer, river or lake. In embodiments, the aqueous composition includes hard brine water or soft brine water. In embodiments, the water is soft brine water. In soft brine water the ammonia compound provides for enhanced soap generation from the active oils, lower surfactant adsorption to the solid material (e.g., rock) in the reservoir and increased solubility of viscosity enhancing water soluble polymers.

In embodiments, the aqueous solution has a salinity of at least about 500 ppm to at least about 200,000 ppm. In embodiments, the aqueous solution has a salinity of at least about 2,000 ppm to at least about 150,000 ppm. In embodiments, the aqueous solution has a salinity of at least about 2,000 ppm to at least about 100,000 ppm. In embodiments, the aqueous solution has a salinity of at least about 2,000 ppm to at least about 50,000 ppm. In embodiments, the aqueous solution has a salinity of at least about 2,000 ppm to at least about 10,000 ppm. In embodiments, the aqueous solution has a salinity of at least about 2,000 ppm to at least about 5,000 ppm. In embodiments, the aqueous solution has a salinity of at least about 500 ppm. In embodiments, the aqueous solution has a salinity of at least about 2,000 ppm. In embodiments, the aqueous solution has a salinity of at least about 2500 ppm. In embodiments, the aqueous solution has a salinity of at least about 5,000 ppm. In embodiments, the aqueous solution has a salinity of at least about 10,000 ppm. In embodiments, the aqueous solution has a salinity of at least about 25,000 ppm. In embodiments, the aqueous solution has a salinity of at least about 50,000 ppm. In embodiments, the aqueous solution has a salinity of at least about 100,000 ppm. In embodiments, the aqueous solution has a salinity of at least about 150,000 ppm. In embodiments, the aqueous solution has a salinity of at least about 200,000 ppm.

In embodiments, ionic strength adjusting agent (i.e., a salt that is exogenous to the water that is added during formation, synthesis, or production of the compositions described herein, including embodiments thereof) halide salt, a sulfate salt, an acetate salt, or a nitrate salt. In embodiments, the ionic strength adjusting agent is sodium chloride (NaCl), potassium chloride

(KCl), sodium iodide (NaI), potassium iodide (KI), sodium acetate, potassium acetate, calcium chloride (CaCl<sub>2</sub>), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), sodium nitrate (NaNO<sub>3</sub>), or potassium nitrate (KNO<sub>3</sub>). In embodiments, the ionic strength adjusting agent may act as a chelating agent (i.e., a weak chelator of Ca or Mg). In embodiments, the ionic strength adjusting agent suppresses  
5 dissolution of a multivalent mineral cation by supplying excess ionic strength adjusting agent, thereby saturating the aqueous composition and preventing dissolution of the multivalent mineral cation. In embodiments, the ionic strength adjusting agent is not sodium sulfate.

In embodiments, the aqueous solution includes a chelating agent. The chelating agent may further increase wettability of the solution (i.e., the tendency of the aqueous solution to  
10 spread on or adhere to a solid material of e.g., a petroleum reservoir thereby displacing unrefined petroleum from the material). Thus, in embodiments, the chelating agent may be present in an amount sufficient to decrease the absorption of the surfactant to the solid material in a petroleum reservoir. In embodiments, the chelating agent is EDTA (e.g., tetrasodium EDTA).

In embodiments, the aqueous solution has a pH from about 8.5 to about 9.9. The  
15 aqueous solution may have a pH from about 9.0 to about 12.0. The aqueous solution may have a pH from about 10.0 to about 12.0. The aqueous solution may have a pH from about 11.0 to about 12.0. The aqueous solution may have a pH from about 10.0 to about 12.0. The aqueous solution may have a pH from about 10.0 to about 11.5. The aqueous solution may have a pH from about 10.0 to about 11.4. The aqueous solution may have a pH from about 10.0 to about  
20 11.3. The aqueous solution may have a pH from about 10.0 to about 11.2. The aqueous solution may have a pH from about 10.0 to about 11.1. The aqueous solution may have a pH from about 10.0 to about 11.0. In embodiments, the aqueous solution has a pH of at least about 9. In embodiments, the aqueous solution has a pH of at least about 10. In embodiments, the aqueous solution has a pH of at least about 11.

In embodiments, the aqueous solution has a pH of about 9. The aqueous solution may  
25 have a pH of about 9.5. The aqueous solution may have a pH of about 10. The aqueous solution may have a pH of about 10.1. The aqueous solution may have a pH of about 10.2. The aqueous solution may have a pH of about 10.3. The aqueous solution may have a pH of about 10.4. The aqueous solution may have a pH of about 10.5. The aqueous solution may have a pH of about  
30 10.6. The aqueous solution may have a pH of about 10.7. The aqueous solution may have a pH of about 10.8. The aqueous solution may have a pH of about 10.9. The aqueous solution may have a pH of about 11. The aqueous solution may have a pH of about 11.1. The aqueous solution may have a pH of about 11.2. The aqueous solution may have a pH of about 11.3. The aqueous solution may have a pH of about 11.4. The aqueous solution may have a pH of about

11.5. The aqueous solution may have a pH of about 11.6. The aqueous solution may have a pH of about 11.7. The aqueous solution may have a pH of about 11.8. The aqueous solution may have a pH of about 11.9. The aqueous solution may have a pH of about 12.

In another aspect is an aqueous composition that includes water (e.g., soft brine water), a hydrolyzed or partially hydrolyzed viscosity enhancing water soluble polymer and an ammonia compound at a pH of at least about 10. The ammonia compound is as described herein, including embodiments thereof. The hydrolyzed or partially hydrolyzed viscosity enhancing water soluble polymer may be hydrolyzed or partially hydrolyzed polyacrylamide. In embodiments, the aqueous compositions include the components, and amounts thereof, set forth above.

In embodiments, the aqueous compositions described herein include an alkali agent in addition to the ammonia compound described herein. The alkali agent may be an acetate, an amine, a carbonate, a silicate, or a borate. The alkali agent may be an acetate. The alkali agent may be an amine. The alkali agent may be a carbonate. The alkali agent may be a silicate. The alkali agent may be a borate. In embodiments, the alkali agent is borax, sodium acetate, potassium acetate, sodium metaborate, sodium silicate, or sodium orthosilicate.

## II. Emulsions

In another aspect, an emulsion composition is provided including an unrefined petroleum, water, a surfactant, an ammonia compound, and a multivalent mineral cation. In embodiments, the emulsion composition includes a co-solvent.

In another aspect, an emulsion composition is provided including an unrefined petroleum, water, a co-solvent, an ammonia compound, and a multivalent mineral cation. In embodiments, the emulsion composition includes a surfactant. The ammonia compound is as described herein, including embodiments thereof.

In embodiments, the emulsion compositions include the components, and amounts thereof, set forth above in the description of the aqueous compositions above. The emulsion composition provided herein may include a combination of one or more surfactants (i.e., a surfactant blend including for example, a first, a second and a third surfactant). For example, in embodiments the emulsion composition includes an alkoxy sulfonate surfactant and an internal olefin sulfonate surfactant. In embodiments, the ammonia compound is present in an amount sufficient to increase the solubility of the surfactant in the aqueous phase relative to the absence of the ammonia compound. In other words, in the presence of a sufficient amount of the ammonia compound, the solubility of the surfactant in the emulsion composition is higher than in the absence of the ammonia compound. In embodiments, the ammonia compound is present

in an amount sufficient to increase the solubility of the surfactant in the emulsion composition (e.g., in the aqueous phase) relative to the absence of the ammonia compound. Thus, in the presence of a sufficient amount of the ammonia compound the solubility of the surfactant in the emulsion composition is higher than in the absence of the ammonia compound (e.g., the surfactant does not precipitate out of the emulsion or aqueous phase).

The emulsion provided herein includes the aqueous composition provided herein including embodiments thereof (e.g., an aqueous composition including an alkoxy sulfate surfactant, wherein the alkoxy sulfate surfactant is C<sub>13</sub>-13PO-sulfate present, an olefin sulfonate surfactant, wherein the olefin sulfonate surfactant is C<sub>19</sub>-C<sub>23</sub> IOS, a co-solvent, wherein the co-solvent is isobutyl alcohol, sodium metaborate, a polymer, wherein the polymer is 3330S Flopaam and a sulfate mineral, wherein the sulfate mineral is gypsum). In embodiments, the emulsion composition is within a petroleum reservoir. In embodiments, the sulfate mineral is gypsum.

In embodiments, the ammonia compound is present in an amount sufficient to decrease the adsorption of the surfactant to the solid material in a petroleum reservoir relative to the absence of the ammonia compound. In other words, in the presence of a sufficient amount of the ammonia compound, the adsorption of the surfactant to the solid material in a petroleum reservoir is lower than in the absence of the ammonia compound. In embodiments, the ammonia compound is present in an amount sufficient to decrease the adsorption of the surfactant to the solid material in a petroleum reservoir relative to the absence of the ammonia compound. Thus, in the presence of a sufficient amount of the ammonia compound the adsorption of the surfactant to the solid material in a petroleum reservoir is lower than in the absence of the ammonia compound. In embodiments, the ammonia compound (e.g., ammonium hydroxide) is present at a concentration of at least 0.5% w/w.

In embodiments, the surfactant is an anionic surfactant, a non-ionic surfactant, a zwitterionic surfactant or a cationic surfactant. In embodiments, the anionic surfactant is an alkoxy carboxylate surfactant, an alkoxy sulfate surfactant, an alkoxy sulfonate surfactant, an alkyl sulfonate surfactant, an aryl sulfonate surfactant or an olefin sulfonate surfactant. In embodiments, the surfactant is present at a concentration of at least 0.1% w/w (e.g., 0.4% w/w, 0.6% w/w). In embodiments, the surfactant is present at a concentration of at least 0.05 % w/w.

In embodiments, the emulsion composition includes a viscosity enhancing water soluble polymer. In embodiments, the viscosity enhancing water soluble polymer is polyacrylamide or a co-polymer of polyacrylamide. In embodiments, the ammonia compound is present in an amount sufficient to increase the solubility of the viscosity enhancing water soluble polymer.

In embodiments, the emulsion composition includes a co-solvent. In embodiments, the co-solvent is an alcohol, alcohol ethoxylate, glycol ether, glycols, or glycerol. In embodiments, the emulsion composition includes unrefined petroleum, water, a surfactant, ammonia compound, a multivalent mineral cation (e.g., gypsum) and a co-solvent. As described above for the aqueous composition the emulsion compositions provided herein may include more than one co-solvent. Thus, in embodiments, the emulsion composition includes a plurality of different co-solvents. In embodiments, the co-solvent is IBA (isobutyl alcohol). In embodiments, IBA is present at a concentration of about 0.25%. In embodiments, IBA is present at a concentration of about 1%. In embodiments, the emulsion composition includes a gas. In embodiments, the water is soft brine water. In embodiments, the emulsion composition includes a gas, as described herein above for the aqueous compositions.

In embodiments, the emulsion composition is a microemulsion. A "microemulsion" as referred to herein is a thermodynamically stable mixture of oil, water and surfactants that may also include additional components such as the compounds provided herein including embodiments thereof, electrolytes, alkali and polymers. In contrast, a "macroemulsion" as referred to herein is a thermodynamically unstable mixture of oil and water that may also include additional components. The emulsion composition provided herein may be an oil-in-water emulsion, wherein the surfactant forms aggregates (e.g., micelles) where the hydrophilic part of the surfactant molecule contacts the aqueous phase of the emulsion and the lipophilic part contacts the oil phase of the emulsion. Thus, in embodiments, the surfactant forms part of the aqueous part of the emulsion. In embodiments, the surfactant forms part of the oil phase of the emulsion. In embodiments, the surfactant forms part of an interface between the aqueous phase and the oil phase of the emulsion.

The emulsions may have the same pH as set forth above in the context of the aqueous compositions provided herein. Thus, in embodiments, the pH of the emulsion is at least about 9. In embodiments, the pH of the emulsion is at least about 10. In embodiments, the pH of the emulsion is at least about 11. Where an emulsion has a pH, it is understood that the pH is within the hydrophilic (e.g., aqueous) portion. In embodiments, the water (e.g., aqueous phase) is soft brine water as described herein.

In embodiments, the oil and water solubilization ratios are insensitive to the combined concentration of multivalent mineral cations (e.g.,  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ ) within the emulsion composition. In embodiments, the oil and water solubilization ratios are insensitive to the salinity of the water or to all of the specific electrolytes contained in the water. The term "insensitive" used in the context of this paragraph means that the solubilization ratio tends not to



change (e.g., tends to remain approximately constant) as the concentration of multivalent mineral cations and/or salinity of water changes. In embodiments, the change in the solubilization ratios are less than 5%, 10%, 20%, 30%, 40%, or 50% over a multivalent mineral cation (e.g., divalent metal cation) concentration range of 10 ppm, 100 ppm, 1000 ppm or 10,000 ppm. In  
5      embodiments, the change in the solubilization ratios are less than 5%, 10%, 20%, 30%, 40%, or 50% over a salinity concentration range of 10 ppm, 100 ppm, 1000 ppm or 10,000 ppm.

In embodiments, the pH of the emulsion composition is insensitive to the combined concentration of multivalent mineral cations (e.g.,  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ ) within the emulsion composition. In embodiments, the pH is insensitive to the concentration of multivalent mineral  
10      cation (e.g., derived or dissolved from gypsum) contained in the emulsion composition. The term “insensitive” used in the context of this paragraph means that the pH tends not to change (e.g., tends to remain approximately constant) as the concentration of multivalent metal cations (e.g., derived or dissolved from a sulfate mineral) changes. In embodiments, the change in the pH is less than 5%, 10%, 20%, 30%, 40%, or 50% over a divalent metal cation concentration  
15      range of 10 ppm, 100 ppm, 1000 ppm or 10,000 ppm. In embodiments, the change in pH is less than 5%, 10%, 20%, 30%, 40%, or 50% over a concentration range of 10 ppm, 100 ppm, 1000 ppm or 10,000 ppm of multivalent mineral cation.

### III. Methods

In another aspect, a method of displacing an unrefined petroleum material in contact with  
20      a solid material is provided. The method includes contacting an unrefined petroleum material with an aqueous composition as provided herein. The unrefined petroleum material is in contact with a solid material comprising a mineral, wherein water dissolves multivalent mineral cations from the mineral. The unrefined petroleum material is allowed to separate from the solid material thereby displacing the unrefined petroleum material in contact with the solid material.

25      In embodiments, the aqueous composition includes the components, and amounts thereof, set forth above in the description of the aqueous solution (e.g., an aqueous composition including an alkoxy sulfate surfactant, wherein the alkoxy sulfate surfactant is  $\text{C}_{13}$ -13PO-sulfate, an olefin sulfonate surfactant, wherein the olefin sulfonate surfactant is  $\text{C}_{19}$ - $\text{C}_{23}$  IOS, a co-solvent, wherein the co-solvent is isobutyl alcohol, sodium metaborate, a viscosity enhancing  
30      water soluble polymer, wherein the polymer is 3330S Flopaam and a multivalent mineral cation derived or dissolved from a sulfate mineral, wherein the sulfate mineral is gypsum ( $\text{Ca}^{2+}$ ). Thus, in embodiments, the surfactant is an anionic surfactant, a non-ionic surfactant, a zwitterionic surfactant or a cationic surfactant. In embodiments, the anionic surfactant is an alkoxy carboxylate surfactant, an alkoxy sulfate surfactant, an alkoxy sulfonate surfactant, an alkyl

sulfonate surfactant, an aryl sulfonate surfactant or an olefin sulfonate surfactant. In  
embodiments, the surfactant is present at a concentration of at least 0.1% w/w (e.g., 0.4% w/w,  
0.6% w/w). As described above the ammonia compound may be present in the aqueous  
composition (or emulsion composition) in an amount sufficient to increase the solubility of the  
5 surfactant. In embodiments, the ammonia compound is present in an amount sufficient to  
increase the solubility of the surfactant in the emulsion composition relative to the absence of the  
ammonia compound. In embodiments, the ammonia compound is present in an amount  
sufficient to decrease the adsorption of the surfactant to the solid material in a petroleum  
reservoir relative to the absence of the ammonia compound. In embodiments, the ammonia  
10 compound (e.g., ammonium hydroxide) is present at a concentration of at least 0.1% w/w (e.g.,  
3.75% w/w).

In embodiments, the aqueous composition includes a viscosity enhancing water soluble  
polymer. In embodiments, the aqueous composition includes a co-solvent. In embodiments, the  
aqueous composition includes a gas. In embodiments, the water is soft brine water.

15 In embodiments, the method includes contacting the solid material with the ammonia  
compound and ammonium hydroxide. In embodiments, the solid material is a endogenous (also  
referred to herein as “natural”) solid material (i.e., a solid found in nature such as rock). In  
embodiments, the natural solid material is rock or regolith. The natural solid material may be a  
geological formation such as clastics or carbonates. The natural solid material may be either  
20 consolidated or unconsolidated material or mixtures thereof. The unrefined petroleum material  
may be trapped or confined by “bedrock” above or below the natural solid material. The  
unrefined petroleum material may be found in fractured bedrock or porous natural solid material.  
In embodiments, the regolith is soil. In embodiments, the rock includes a sulfate mineral. In  
embodiments, the sulfate mineral is gypsum.

25 In embodiments, the solid material is a natural solid material in a petroleum reservoir. In  
embodiments, the method is an enhanced oil recovery method. Enhanced oil recovery methods  
are well known in the art. A general treatise on enhanced oil recovery methods is *Basic  
Concepts in Enhanced Oil Recovery Processes* edited by M. Baviere (published for SCI by  
Elsevier Applied Science, London and New York, 1991). For example, in an enhanced oil  
30 recovery method, the displacing of the unrefined petroleum in contact with the solid material is  
accomplished by contacting the unrefined petroleum with an aqueous composition provided  
herein (e.g., an aqueous composition including an alkoxy sulfate surfactant, wherein the alkoxy  
sulfate surfactant is C<sub>13</sub>-13PO-sulfate, an olefin sulfonate surfactant, wherein the olefin sulfonate  
surfactant is C<sub>19</sub>-C<sub>23</sub> IOS, a co-solvent, wherein the co-solvent is isobutyl alcohol, sodium

metaborate, a polymer, wherein the polymer is 3330S Flopaam and a multivalent mineral cation derived or dissolved from a sulfate mineral, wherein the sulfate mineral is gypsum), wherein the unrefined petroleum is in contact with the solid material. The unrefined petroleum may be in an oil reservoir. The aqueous composition provided herein is pumped into the reservoir in accordance with known enhanced oil recovery parameters. The aqueous composition provided herein may be pumped into the reservoir and, upon contacting the unrefined petroleum, form an emulsion composition provided herein.

In embodiments, an emulsion forms after the contacting. The emulsion thus formed may be the emulsion composition as described above. In embodiments, the method includes allowing an unrefined petroleum acid within the unrefined petroleum material to enter into the emulsion (e.g., emulsion composition), thereby converting the unrefined petroleum acid into a surfactant. In other words, where the unrefined petroleum acid converts into a surfactant it is mobilized and therefore separates from the solid material. In embodiments, the multivalent mineral cation forms part of the emulsion. In embodiments, the multivalent mineral cation is dissolved or derived from gypsum, anhydrite, barite, or magnesium sulfate. In embodiments, the multivalent mineral cation is dissolved or derived from gypsum.

In another aspect, a method of converting an unrefined petroleum acid into a surfactant is provided. The method includes contacting a petroleum material with an aqueous composition as provided herein, thereby forming an emulsion in contact with the petroleum material. The unrefined petroleum acid within the unrefined petroleum material is allowed to enter into the emulsion, thereby converting the unrefined petroleum acid into a surfactant. The aqueous composition may be, e.g., an aqueous composition including an alkoxy sulfate surfactant, wherein the alkoxy sulfate surfactant is C<sub>13</sub>-13PO-sulfate present, an olefin sulfonate surfactant, wherein the olefin sulfonate surfactant is C<sub>19</sub>-C<sub>23</sub> IOS, a co-solvent, wherein the co-solvent is isobutyl alcohol, sodium metaborate, a polymer, wherein the polymer is 3330S Flopaam and a multivalent mineral cation derived or dissolved from a sulfate mineral, wherein the sulfate mineral is gypsum. In embodiments, the reactive petroleum material is in a petroleum reservoir. In embodiments of the methods and compositions provided herein, as described above and as is generally known in the art, the unrefined petroleum acid is a naphthenic acid. In embodiments, as described above and as is generally known in the art, the unrefined petroleum acid is a mixture of naphthenic acids.

### EXAMPLES

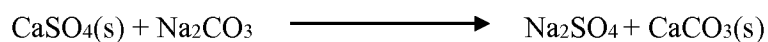
The presence of gypsum or anhydrite in oil reservoirs limits the application of alkali-surfactant-polymer (ASP) flooding using conventional alkalis such as sodium carbonate

( $\text{Na}_2\text{CO}_3$ ) because these alkalis precipitate in the presence of gypsum leading to high alkalinity loss and permeability damage. Sodium metaborate ( $\text{NaBO}_2$ ) and Ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) were investigated as possible alternatives to  $\text{Na}_2\text{CO}_3$ . Batch mixing experiments were performed with these alkalis in the presence of excess anhydrite, single phase brine-alkali transport experiments were performed in sandstone and carbonate cores containing anhydrite, and ASP corefloods were performed in outcrop and reservoirs cores (containing anhydrite). Effluent pH and ion concentrations including boron, calcium and sulfate were measured using an ion chromatograph (IC) and inductively coupled plasma (ICP). The residence times in injection experiments were increased up to 15 days to study the effect of reaction kinetics.  $\text{NaBO}_2$  and  $\text{NH}_4\text{OH}$  were found to maintain and propagate a high pH of more than 10 in the batch and transport experiments without significant permeability changes. Gypsum dissolution was not increased by  $\text{NH}_4\text{OH}$  (over that of the brine itself) in batch or transport experiments. It, however, increased during  $\text{NaBO}_2$  injection depending on the flow rate. High oil recoveries were obtained in the ASP corefloods along with low surfactant retention due to the high pH propagation.

Enhanced oil recovery (EOR) techniques are needed to produce the oil left behind after waterflood in known reservoirs. ASP flooding is a common chemical EOR technique where surfactant reduces oil-water interfacial tension and mobilizes oil, polymer increases sweep efficiency and alkali reduces surfactant adsorption and produces in situ surfactant if the oil is active. Typically, the use of alkali, by itself, is not effective in improving oil recovery since the microemulsion viscosity is high, leading to high pressure drops, and the optimum salinity is very low. Nelson et al. (1984) suggested the use of a suitable surfactant with the alkali to increase the optimum salinity to a desirable value which marked the origin of a much more versatile co-surfactant EOR process (or ASP). Cosolvents are used to reduce microemulsion viscosity and equilibration time (Sahni et al., 2010). Fortenberry et al. (2013) have developed effective alkali-cosolvent-polymer (ACP) processes for sufficiently active viscous oils. Anionic surfactants are commonly used for EOR because they yield ultralow interfacial tension (IFT) and do not adsorb much on silica surfaces. The clay edges are often positively charged at neutral pH and become negatively charged around pH of 9 (Hirasaki et al., 2008). The surface properties of carbonate rocks have been studied by Hirasaki et al. (2004) who observed that these rocks become negatively charged at pH more than 9. The surfactant adsorption can be minimized by raising the pH with the alkali.

While including an alkali in surfactant formulations has many advantages, it can also react with certain rock minerals. This is especially serious when gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or anhydrite ( $\text{CaSO}_4$ ) is present in the reservoir. Gypsum and anhydrite differ in the water of

hydration and the transition from gypsum to anhydrite takes place around 45 °C. Here we use both the terms interchangeably. Gypsum is fairly soluble in water as a result of which the calcium concentration of brine in equilibrium with gypsum can be as high as 2,000 ppm. Na<sub>2</sub>CO<sub>3</sub> is a commonly used alkali in ASP flooding; however, it cannot be used in the presence of gypsum or anhydrite because it loses its alkalinity rapidly by precipitation of calcium carbonate as follows:



The precipitation reaction goes to near completion since the solubility of gypsum is high compared to that of calcium carbonate. Besides loss of alkalinity, the precipitation of calcium carbonate can cause permeability damage. Other alkalis like sodium hydroxide, potassium hydroxide and sodium silicate behave similarly, besides having other drawbacks due to their high reactivity with the minerals commonly found in petroleum reservoirs.

The use of alkali for improving oil recovery is not a new practice, in fact, one of the earliest patents on the use of alkalis for increasing oil recovery is from Atkinson (1927). However, most of the studies related to the role of alkali in improving oil recovery were performed from mid-seventies to mid-eighties. Mechanisms such as emulsification, entrainment, and wettability reversal (oil-wet to water-wet or the opposite) were proposed for improvements in oil recovery due to alkali (Johnson, 1976). Jennings et al. (1974) attributed the increase in oil recovery to generation of in-situ soap, due to the reaction of alkali with surface-active organic acids present in oil, and the resulting decrease in IFT. Further, they emphasized the importance of estimating alkali consumption for a successful field operation. deZabala et al.(1982) introduced a model to take into account the in-situ surfactant generation and sodium/hydrogen exchange. They concluded that alkaline flooding should be done at high pH to overpower the chromatographic ion-exchange retardation of the hydroxide. Bunge et al.(1985) developed mass action equilibrium model to study the effects of pH, salinity and temperature on hydroxide uptake during sodium-hydrogen exchange and sodium-calcium exchange and proposed three mechanisms of hydroxide consumption: (1) Reversible rock adsorption or ion exchange, (2) Congruent and incongruent dissolution, and (3) Precipitation of insoluble hydroxides. Novosad et al.(1984)performed experiments to calculate cation exchange capacity(CEC) and hydrogen exchange capacity(HEC) of Berea sandstone by monitoring the sodium concentration in effluent. Their experiments also showed that mineral dissolution is a slow process where as ion-exchange is fast. Southwick (1985) performed batch-mixing experiments to study quartz dissolution in sodium hydroxide and sodium silicate and its effect on the alkalinity. They also proposed alternate methods to estimate alkalinity loss. Mohnot et al.(1987) performed batch experiments

of sodium hydroxide with commonly occurring reservoir rock minerals and observed that, under high alkali concentration and temperature, kaolinite consumes more hydroxide than montmorillonite. Contrary results were obtained at mild conditions. Huang et al.(1986) studied consumption of sodium hydroxide and orthosilicate by clays and found it was highest for montmorillonite.

Most of the chemical EOR studies in the past were performed for sandstone reservoirs. Only recently a few studies have been performed on carbonate reservoirs. Mohnot et al.(1989) performed alkali consumption studies of sodium hydroxide with carbonates and observed that useful alkalinity loss was greatest for gypsum, high for dolomite and insignificant for calcite. Precipitation/ dissolution mechanism was responsible for alkalinity consumption in the case of dolomite and gypsum. Lopez-salinas et al.(2011) performed simulations to show that with 1% Na<sub>2</sub>CO<sub>3</sub> as an alkali, even 0.1% anhydrite retards alkali breakthrough by 0.7 pore volume. Many alternate alkalis have been investigated recently for their interaction with gypsum and divalent ions, in general. Flatten et al.(2008) suggested the use of NaBO<sub>2</sub> in the presence of divalent ions. Burger et al.(2006) suggested using an organic alkali in ASP formulations that is able to tolerate high TDS and hardness. Kazempour et al.(2011) performed single phase alkali injection experiments with NaOH, Na<sub>2</sub>CO<sub>3</sub> and NaBO<sub>2</sub> in Berea and Minnelusa cores (containing gypsum) and observed little pH change and permeability damage on NaBO<sub>2</sub> injection in Minnelusa core. Levitt et al. (2011) discussed various challenges encountered in carbonate reservoirs for ASP flooding, in particular, the uncertainty about presence of anhydrite or gypsum which limits the use of conventional alkalis. They further ruled out the possibility of using chelating agents like EDTA in the presence of anhydrite. ShamsiJazeyi et al. (2013) used sacrificial agent to reduce surfactant adsorption in gypsum containing reservoirs. Panthi et al. (2013) used NaBO<sub>2</sub> as the alkali in performing ASP corefloods in carbonate cores and observed low surfactant retention. Recently alkali was also shown to stabilize sulfate surfactants at high temperatures for long period (Adkins et al. 2011).

Unlike other alkalis, little information is available on the use of NH<sub>4</sub>OH in alkaline flooding (Cooke et al., 1974; Jennings, 1975; Mayer et al., 1983; Martin et al., 1985). Nelson et al. (1984) found NH<sub>4</sub>OH to be equally effective in their oil displacement experiments. They also recommended using NH<sub>4</sub>OH to reduce co-surfactant requirements. Pursley et al. (1973) used the combination of Na<sub>2</sub>CO<sub>3</sub> and (less expensive) NH<sub>4</sub>OH to reduce divalent ions in the formation brine and satisfy rock consumption during their surfactant flooding pilot test at Loudon, Illinois.

Herein, various alkalis were tested in the presence of gypsum. Batch mixing experiments were performed to screen alkalis based on their consumption in the presence of gypsum. Single

phase alkali transport experiments were then performed at various injection rates with these alkalis in sandstone and carbonate cores containing gypsum. Oil displacement experiments by ASP corefloods were then conducted in outcrop and reservoir (containing gypsum) cores.

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**Table 1:** Experimental design.

<b>Batch experiments</b>	
B1	(a) 0.58 M Na <sub>2</sub> CO <sub>3</sub> , (b) 0.58 M NaBO <sub>2</sub> , (c) 0.58 M NH <sub>4</sub> OH, (d) 0.58 M Na <sub>2</sub> SiO <sub>3</sub> (e) 0.19 M NaBO <sub>2</sub> in the presence of excess gypsum at 53 °C.
B2	(a) NaBO <sub>2</sub> , (b) NH <sub>4</sub> OH in the presence of varying amount of calcium chloride at 53 °C.
<b>Alkali transport experiments</b>	
D1	1 wt % NH <sub>4</sub> OH in 1 wt % NaCl brine injection in carbonate core containing gypsum at 0.25 ft/d at 25 °C.
D2	(a) 3.5 wt % Na <sub>2</sub> CO <sub>3</sub> , (b) 1 wt % NaBO <sub>2</sub> in 3 wt % NaCl brine injection at 0.25 ft/d in a carbonate core with gypsum at 50 °C.
D3	3 wt % NaBO <sub>2</sub> in 1 wt % NaCl brine injection in carbonate core with gypsum at varying flow rates.
D4	3 wt % NaBO <sub>2</sub> in 8 wt % NaCl brine injection in sandstone core containing gypsum at 1 ft/d at 55 °C.
<b>Phase behavior experiments</b>	
P1	Phase behavior experiments with crude oil 1 to identify ultra low IFT surfactant formulation using NaBO <sub>2</sub> as the alkali.
P2	Phase behavior experiments with crude oil 2 to identify ultra-low IFT surfactant formulation using NH <sub>4</sub> OH as the alkali.
<b>Oil recovery experiments</b>	
R1	ASP coreflood in sandstone core containing gypsum using formulation P1 at 55 °C at 1 ft/d.
R2	ASP coreflood in sandstone core containing gypsum using formulation P1 at 55 °C at 0.20 ft/d.
R3	ASP coreflood in Berea sandstone using formulation P2 at 60 °C at 1 ft/d.

## Methodology

**Materials:** Chemical agents used in these experiments consist of commercially available alkali, polymers and surfactants. 98.5% pure NaBO<sub>2</sub>·4H<sub>2</sub>O powder was obtained from Arcos Organic. NH<sub>4</sub>OH solution (ACS grade) having 30 wt% NH<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, sodium silicate, sodium chloride, calcium sulfate, and calcium chloride were obtained from Fisher Scientific. Polymers Floppam 3630S and Floppam 3330S were obtained from SNF Floerger (Cedex, France) in a powder form. Surfactant A was C<sub>12-13</sub>-13PO-SO<sub>4</sub>; surfactants B and C were internal olefin sulfonates C<sub>19-23</sub>-IOS and C<sub>15-18</sub>-IOS. Surfactants were obtained from Shell chemicals.

**Batch experiments:** To screen potential alkalis that could be used in the presence of gypsum, batch experiments B1 (b), B1 (c), B1 (d), and B1 (e) were performed with Na<sub>2</sub>CO<sub>3</sub>, NaBO<sub>2</sub>, NH<sub>4</sub>OH and sodium silicate, respectively (Table 3). B1 (a) was performed without any alkali and B1 (f) was performed with a lower concentration of NaBO<sub>2</sub>. Both lab grade calcium sulfate and crushed selenite (a mineral form of calcium sulfate) were used in these tests. Equal moles of alkalis were mixed in 1.25 wt% NaCl brine and excess of gypsum. Plastic containers

were used, instead of glass, to avoid any contamination by glass dissolution at high pH. The samples were mixed from time to time and also weighted to account for any water loss at 53 °C. pH and ionic concentration of the supernatants were measured to estimate alkali consumption. The pH of these samples were measured using Oakton pH meter, calcium and sulfate concentrations using dionex ICS-3000 ion chromatograph, and total boron concentration using Agilent 7500ce inductively coupled plasma. The sulfate concentration and the difference in calcium and sulfate concentration (in mol/g) was used to estimate gypsum dissolution and alkali precipitation (as calcium salt), respectively. Since gypsum is only sparingly soluble in water, almost all of the gypsum powder that was initially mixed settled down in the bottles. This made it impossible to differentiate reaction precipitates, which may have formed, from the initially present powder. Experiment B2 (a) and B2 (b) were therefore performed similarly, except calcium chloride was used instead of calcium sulfate. NaBO<sub>2</sub> and NH<sub>4</sub>OH were used in experiment B2 (a) and B2 (b), respectively.

Alkali transport experiments: Single phase alkali corefloods were performed in sandstone and carbonate cores containing gypsum with NH<sub>4</sub>OH, NaBO<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>. The presence of gypsum in these cores was confirmed by analyzing effluent calcium and sulfate concentrations as described by Lopez-Salinas et al. (2011). 10,000 ppm NaCl brine was injected through the core at slow flow rate to ensure that the local equilibrium was achieved. The effluent samples were analyzed for Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> by ion chromatograph.

In experiment D1, 1 wt% NH<sub>4</sub>OH in 1 wt% NaCl brine was injected at 0.25 ft/d in a carbonate core (Table 2) containing gypsum and the effluent pH, salinity, NH<sub>4</sub>OH, calcium and sulfate concentrations were measured. The effluent samples were collected in sealed tubes to avoid any NH<sub>3</sub> loss from the samples. The NH<sub>4</sub>OH concentration was measured by titrating with a standard solution of potassium hydrogen phthalate (KHP) and phenolphthalein was used as an indicator.

To compare Na<sub>2</sub>CO<sub>3</sub> and NaBO<sub>2</sub>, experiment D2 (a) and D2 (b) were performed. In experiment D2 (a), 1 wt% NaBO<sub>2</sub> (in 30,000 ppm NaCl brine) was injected in a carbonate core containing gypsum (Table 2) at 50 °C. The core was then cleaned by flowing many pore volumes of 30,000 ppm NaCl brine and experiment D2 (b) was performed. In this experiment, 3.5 wt% Na<sub>2</sub>CO<sub>3</sub> (in 30,000 ppm NaCl brine) was injected in the same core at 50 °C. Both the experiments were performed at 0.015 mL/min corresponding to a residence time of 1 day in the 1.5" x 3" core. The effluent pH, calcium, and sulfate concentrations were measured.

Experiment D3 was performed with NaBO<sub>2</sub> in a 1.5" x 8" carbonate core (Table 2) containing gypsum at 55 °C to study the effects of injection rate on gypsum dissolution. The core



was saturated with the formation brine and then left for two days for equilibration with gypsum to be established. The alkali solution was then injected, continuously, at varying flow rates and the effluent samples were collected using an automatic fractional collector. The samples were capped soon after collection. For ion analysis, the samples were acidified with nitric acid to dissolve any solids that may have formed, but not visible, although some precipitate was observed in effluent samples collected during slow injection rate experiments. The pressure drop data was not very reliable at slow flow rates; therefore, the alkali solution was injected at higher flow rates for permeability measurement at the end of the experiment. Experiment D4 was similarly performed with 3 wt% NaBO<sub>2</sub> in 8 wt% brine at 0.9 ft/d in a sandstone core containing gypsum at 55 °C. The effluent pH and the pressure drop across the core were monitored.

Surfactant phase behavior experiments: Surfactant phase behavior was optimized by varying the ratio of surfactants according to their hydrophobic and hydrophilic properties. Salinity scans were performed to determine upper (CSEU) and lower (CSEL) salinity boundaries of the Winsor type III region at the chosen surfactants concentration. NaBO<sub>2</sub> was used for performing salinity scans in experiment P1. NaCl was used in experiment P2 and NH<sub>4</sub>OH concentration was fixed to 3 wt%. The reason for not using NH<sub>4</sub>OH by itself for salinity scans, just like NaBO<sub>2</sub> in the case of P1, is that NH<sub>4</sub>OH by itself does not add much to salinity. Aqueous stability experiments were simultaneously performed at appropriate temperatures to check the stability of the surfactant blends with polymers. HPAM 3330S was used for P1, and HPAM 3630S was used for P2.

Oil recovery experiments: These experiments were performed using the same oil and cores from the same reservoir block. Before each experiment, gypsum presence was ensured by the procedure mentioned previously. Experiments R1 and R2 were performed using NaBO<sub>2</sub> as the alkali. Experiment R3 was performed in the same core as coreflood R1 using NH<sub>4</sub>OH as the alkali. The temperature was the reservoir temperature, 55 °C in all three experiments. Surfactant formulations from experiments P1 were used for experiments R1 and R2, while surfactant formulation from experiment P2 was used for experiment R3. For performing an oil recovery experiment, the core was placed in a coreholder and saturated with formation brine. The core was then saturated with the crude oil at a pressure of about 300 psi. A water flood was performed using injection brine. Then the surfactant slug containing the surfactants, the co-solvent, the alkali and the polymer was injected followed by a polymer drive. A negative salinity gradient was maintained in these corefloods to reduce surfactant retention and increase robustness. Produced effluent was collected in graduated test tubes and analyzed for oil cut (visually), surfactant (by HPLC), dissolved solids (by refractometer), dissolved ions (by ion

chromatograph), viscosity (by rheometer) and pH (by potentiometer). The presence of gypsum in the cores that were used for experiments R1, R2 and R3 was determined by analyzing effluent calcium and sulfate concentrations. In experiment R1, a 0.40 PV ASP slug having 1 wt% mixture of surfactants A and B, 1wt% IBA-3EO (Isobutyl alcohol-3ethoxylate), 3.75 wt% NaBO<sub>2</sub> followed by 0.2 PV polymer drive 1 and 1.4 PV polymer drive 2 (Table 4) were injected in a sandstone core containing gypsum at a frontal rate of 1 ft/d. In experiment R2, a 0.25 PV ASP slug having 1 wt% surfactants (same as R1), 0.5 wt% IBA, 2.4 wt% NaBO<sub>2</sub> followed by 1.8 PV polymer drive (Table 4) were injected in another sandstone core from the same reservoir that also contained gypsum. The residence time in experiment R2 was about 5 days. In experiment R3, a 0.40 PV ASP slug having 1.0 wt % mixture of surfactants A and B, 0.5 wt% IBA-3EO, 3 wt% NH<sub>4</sub>OH and polymer was injected at 1 ft/d. This was followed by a polymer drive (Table 4).

**Table 2:** Properties of the carbonate cores used in experiments D1, D2 and D3.

	Experiment D1	Experiments D2 (a) and D2 (b)	Experiment D3
Diameter x Length	1.5" x 29.56"	1.5" x 3"	1.485" x 7.93"
Porosity	19.5 %	24.1 %	19.31 %
Permeability	453 md	101 md	68 md
Formation Brine	80,000 ppm NaCl	30,000 ppm NaCl	10,000 ppm
Injection Brine	10,000 ppm NaCl+1 wt% NH <sub>4</sub> OH	3 wt% Alkali in 30,000 ppm NaCl	30,000 ppm NaBO <sub>2</sub> in 10,000 ppm NaCl

Batch experiments: The results of the batch experiment B1 are shown in Table 3. The boron concentration here corresponds to the total boron concentration present in the supernatant solution. Note that no calcium or sulfate ions were separately added in making these samples and the presence of these ions in the supernatant solutions is due to gypsum dissolution in these alkalis. Also note that NH<sub>4</sub>OH solution contained 30 wt% NH<sub>3</sub>, therefore, 1 wt% NH<sub>4</sub>OH is equivalent to 0.3 wt% NH<sub>3</sub>.

**Table 3:** pH and ion concentration of various alkalis in the presence of excess gypsum at 53°C.

Experiment	Alkali	wt% Alkali	Day 2				Day 25		
			pH	Ca(ppm)	B(ppm)	SO <sub>4</sub> (ppm)	pH	Ca(ppm)	SO <sub>4</sub> (ppm)
B1 (a)	No Alkali	-	6.8	1,082	-	2,560			
B1 (b)	Na <sub>2</sub> CO <sub>3</sub>	6.11	8.1	441	-	53,302	8.3	n.a.	52,692
B1 (c)	NaBO <sub>2</sub>	3.84	10.9	1,489	2,490	26,551	10.9	1,497	22,105
B1 (d)	NH <sub>4</sub> OH	2.0	11.1	1,312	-	2,584			
B1 (e)	Na <sub>2</sub> SiO <sub>3</sub>	3.52%							
	+ Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	+ 5.82%	11.4	695		64,146			
B1 (f)	NaBO <sub>2</sub>	1.28	10.4	1,604	1,594	7,974	10.3	1,324	6,934

The sulfate concentrations given in Table 3, suggest that gypsum dissolution was high for Na<sub>2</sub>CO<sub>3</sub> and sodium silicate-borax mixture, moderate for NaBO<sub>2</sub> and almost insignificant for NH<sub>4</sub>OH. In experiment B1 (b), the total boron concentration changed from 6400 ppm to about 2490 ppm suggesting that some boron was lost due to this interaction. Also note that for the lower initial concentration of NaBO<sub>2</sub>, experiment B1 (e), gypsum dissolution was lesser. The calcium and sulfate concentrations for NH<sub>4</sub>OH in the presence of gypsum correspond to that of just NaCl brine (Blank), suggesting that no extra gypsum dissolution took place in presence of NH<sub>4</sub>OH. Both NaBO<sub>2</sub> and NH<sub>4</sub>OH were able to maintain high pH while the pH dropped to about 8.1 for Na<sub>2</sub>CO<sub>3</sub> within a day. Experiment B2 was performed similar to experiment B1 except calcium sulfate was replaced with calcium chloride. The results of experiment B2 are shown in Figures 2 and 3. NaBO<sub>2</sub> showed precipitation in the presence of calcium but was able to maintain a pH of more than 10.5. Interestingly, NH<sub>4</sub>OH was able to tolerate high amount of calcium without showing any precipitation and was able to maintain a pH about 10.5 (Figure 1). Figures 2 and 3 show that even in the presence of excess NaBO<sub>2</sub>, not all the calcium was consumed. This suggests that the precipitate that forms on mixing NaBO<sub>2</sub> and calcium is somewhat soluble in water (unlike calcium carbonate that forms when Na<sub>2</sub>CO<sub>3</sub> reacts with gypsum). Also the extent of calcium precipitation is dependent on the amount of NaBO<sub>2</sub> added. Similar results were observed for seawater in the presence of borax by Vo et al. (2012). Based on this result, it is possible that NaBO<sub>2</sub> consumption in the presence of gypsum can be minimized with a lower NaBO<sub>2</sub> concentration. It can also be seen from Table 3 that for 1.28 wt% NaBO<sub>2</sub>, the total boron changes from 2100 ppm (present initially) to about 1600 ppm while for 3.84 wt% NaBO<sub>2</sub>, the total boron changes from 6400 ppm to 2490 ppm.

Alkali transport experiments: Based on the batch experiments, NH<sub>4</sub>OH and NaBO<sub>2</sub> were chosen for single-phase transport studies. In experiment D1, 1 wt% NH<sub>4</sub>OH was injected in a

1.5x12 inch carbonate core (Table 2) containing gypsum which was initially saturated with 80,000 ppm NaCl brine at 0.25 ft/d. The effluent pH, NH<sub>4</sub>OH concentration and ion concentrations are shown in Figures 4 and 5. It can be seen from Figure 4 that the effluent pH is more than 10 after 1.2 PV injection. This pH is sufficient to reduce anionic surfactant adsorption<sup>4</sup>. The breakthrough for NH<sub>4</sub>OH was around 1.1 PV. Figure 5 shows the effluent calcium and sulfate concentrations in mM. It can be seen that the molar concentrations of calcium and sulfate are almost equal suggesting that no precipitation took place inside the core after NH<sub>4</sub>OH injection at 0.25 ft/d. It is interesting to note the decrease in both calcium and sulfate concentration after 0.8 PV in Figure 5. The gypsum dissolution was higher when 80,000 ppm NaCl brine was present in the core, initially, and decreased when 1 wt% NH<sub>4</sub>OH in 10,000 ppm NaCl brine was injected. This decrease seems to be the effect of salinity on gypsum dissolution.

To understand the transport of Na<sub>2</sub>CO<sub>3</sub> and NaBO<sub>2</sub>, experiments D2 (a) and D2 (b) were performed. Aqueous solutions with 1 wt% NaBO<sub>2</sub> or 3.5 wt% Na<sub>2</sub>CO<sub>3</sub> in 30,000 NaCl brine were injected in a carbonate core (Table 2) with gypsum at 50 °C. The injection was performed at 0.015 mL/min corresponding to a residence time of 1 day in the 1.5x3 inch core. The effluent pH and sulfate concentrations are shown in Figure 6. The pH data shows that a steady pH value was achieved after about 1.5 PV injection in the case of NaBO<sub>2</sub>, but not in the case of Na<sub>2</sub>CO<sub>3</sub>. The effluent sulfate data shows that gypsum dissolution was much higher in the case of Na<sub>2</sub>CO<sub>3</sub>, compared with NaBO<sub>2</sub>. The effluent calcium concentration was about 100 ppm for NaBO<sub>2</sub> injection and about 26,000 ppm for Na<sub>2</sub>CO<sub>3</sub>. The sulfate molar concentration was much higher than the calcium during Na<sub>2</sub>CO<sub>3</sub> injection implying a large amount of precipitation inside the core on Na<sub>2</sub>CO<sub>3</sub> injection. For NaBO<sub>2</sub> injection, the molar concentration of sulfate was slightly higher than the calcium implying a small amount of precipitation.

Figure 7 shows the effluent pH and pressure drop data for experiment D4 where 3 wt% NaBO<sub>2</sub> solution was injected in a sandstone core with anhydrite at 55 °C at 0.89 ft/d. This experiment was conducted after a waterflood with a residual oil saturation of 0.18. Note that the pH after 1 PV injection is about 9.5 and the pressure drop was steady.

In experiment D3, 3 wt% NaBO<sub>2</sub> solution was injected at different rates in a carbonate core containing gypsum (Table 2) to study the effects of flow rate on its interaction with gypsum. The effluent pH and ion concentration for injection at 0.67 ft/d are given in Figure 8. Note that the pH after 1 PV was about 10.4, high enough to form in-situ soap with naphthenic acids.

The calcium concentration changed from about 1,000 ppm, the equilibrium value with formation brine, to about 300 ppm while sulfate changed from about 2,100 ppm to 1,000 ppm. Note that these are the steady state values obtained for this flow rate and need not be the equilibrium values. In molar terms, the steady state value of effluent calcium is about 7.5 mM and that of sulfate is about 10.4 mM. The calcium concentration is slightly less than the sulfate concentration suggesting some calcium was precipitated inside the core. The total boron concentration followed the salinity curve without any noticeable delays. The alkali injection rate was then varied in experiment D3; effluent pH and ionic concentration were monitored. The effluent sulfate concentration was found to be a function of injection rate. As shown in Figure 9, the effluent sulfate was higher at a low flow rate (~3,500 ppm at 0.1 ft/d) and decreased as the flow rate was increased (~1,000 ppm at 0.67 ft/d, Figure 8). The velocity was further reduced to 0.044 ft/d, corresponding to 15 days residence time in the core, and the effluent sulfate was found to be about 52 mM (or 5,000 ppm). The effluent pH was about 10 for this case. The effluent calcium concentration did not change much with injection rate, unlike sulfate, and stayed near 250 ppm. The plot of effluent sulfate concentration as a function of residence time inside the core is given in Figure 10. From this figure it can be seen that the apparent equilibrium value for effluent sulfate is around 5,200 ppm. Overall in this experiment, 12 PV of NaBO<sub>2</sub> was injected over two months. The permeability at the end of the experiment was almost the same (56.5 md compared to the initial permeability of 68 md).

The extent of reaction from lab experiments can be estimated in order to scale these results to field scale as the residence times are much longer in the field. When ammonium hydroxide was injected at 0.25 ft/d in experiment D1, the steady state value corresponded to the equilibrium value and therefore this result could be scaled up with reliability. However, in case of sodium metaborate, the reaction was found to be dependent on the injection rate suggesting that this reaction is a slow reaction. In such a case, it is important to perform lab experiments with much longer residence times in order to estimate the extent of reaction and loss of alkalinity in the field. Low permeability cores have larger surface area compared to high permeability cores and can have more interaction with alkali. The alkali transport experiments were conducted in cores of different permeabilities from 430 md to 68 md, but similar behavior was observed. The pH front moved through the core in about 1 PV for NaBO<sub>2</sub> and NH<sub>4</sub>OH, but not for Na<sub>2</sub>CO<sub>3</sub>. Significant calcium precipitation was observed on injection of Na<sub>2</sub>CO<sub>3</sub>.

Phase behavior experiments: Surfactants A and B were mixed in different proportions in experiment P1 to obtain ultralow IFT surfactant formulation with crude oil 1. Along with the surfactants, 1 wt% IBA-3EO and 0.5 wt% IBA were used as cosolvents in experiments P1 (a)

and P1 (b), respectively. NaBO<sub>2</sub> was used as the alkali in these experiments. The solubilization plots obtained from experiments P1 (a) and P1 (b) are shown in Figures 11 and 12. The solubilization ratios in both cases at their respective optimum salinities were more than 15, corresponding to the IFT of less than 0.001 dynes/cm as per the Chun-Huh equation.<sup>33</sup> IFT reduction was observed as the cosolvent amount was reduced from 1 wt % IBA-3EO in experiment P1 (a) to 0.5 wt% IBA in experiment P1 (b). The surfactant formulation obtained from experiment P1 (a) was aqueous stable (clear solution) up to the optimum salinity at 55 °C. The surfactant formulation obtained from experiment P1 (b) was aqueous stable up to 25,619 ppm at 55 °C while the optimum salinity was slightly higher than that. This formulation was injected at 25,619 ppm (Table 4) and since the formation brine salinity was much higher, type III region was encountered in the coreflood. In experiment P2, surfactants A and C were mixed in different proportions to obtain a low IFT surfactant formulation. Along with the surfactants, 0.5 wt% IBA-3EO and NH<sub>4</sub>OH were used as the cosolvent and the alkali, respectively. The solubilization ratio (Figure 13) at optimum salinity of about 65,000 ppm was about 11 and the formulation was aqueous stable up to 55,000 ppm at 55 °C. Since NH<sub>4</sub>OH does not precipitate calcium ions, another salinity scan was performed using the same surfactants in the presence of 1,000 ppm calcium ions (Figure 14) as the injection slug is expected to pick up some calcium ions from the core itself. The surfactant formulation gave ultra low IFT even in the presence of 1,000 ppm calcium ions. Note that C19-23-IOS was replaced by C15-18-IOS in this formulation as the original formulation does not give ultralow IFT in presence of calcium ions. The optimum salinity decreased to about 45,000 ppm on addition of 1,000 ppm calcium ions. It is therefore necessary to account for the shift in optimum salinity due to gypsum dissolution in order to design a robust ASP coreflood using ammonium hydroxide. Surfactant formulations from experiments P1 (a), P1 (b) and P2 were used for ASP coreflood R1, R2, and R3, respectively. Note that in experiment P2, NaCl was used for salinity scan and NH<sub>4</sub>OH concentration was fixed to 3 wt% because NH<sub>4</sub>OH by itself does not contribute much to the salinity. Figure 16 compares the conductance values of NH<sub>4</sub>OH and sodium chloride solutions as a function of their concentrations. For sodium chloride solution, the conductance increases from zero to about 80,000 μS as its concentration changes from zero to 5 wt%. For the same amount of NH<sub>4</sub>OH, the conductance values increase from zero to only about 1,150 μS showing that NH<sub>4</sub>OH by itself does not add much to salinity. The plausible explanation for this is that NH<sub>4</sub>OH does not dissociate completely to ions when it is mixed in water, unlike NaCl.

Oil recovery experiments: After performing waterflood with brine having a total salinity of 147,507 ppm and hardness of 2,144 ppm (same as the formation brine in corefloods R1, R2

and R3), tertiary ASP floods were conducted in coreflood R1 and R2 using NaBO<sub>2</sub>. ASP slug and polymer drive compositions are listed in Table 4. In coreflood R1, the ASP slug size was 0.4 PV; the fluids were injected at 1 ft/d. Oil recovery, pH, pressure data, salinity data and surfactant recovery of coreflood R1 are presented in Figures 17 and 18. The oil bank arrived at about 0.4 PV, the oil cut increased to a maximum of 0.4. About 99% of the water flood residual oil was recovered in the coreflood R1, which corresponds to a residual oil saturation of 0.01 after the chemical flood. The surfactant arrived at the outlet end at about 1 PV along with the high pH front. Approximately 45% of the injected surfactant was recovered. About 0.197 mg of surfactant per gram of rock was retained. The most likely reasons for the low surfactant retention are the high pH, the low mobility ratio, the uniform nature of the core and the good microemulsion phase behavior.

In the core flood R2, the residence time was increased from 1 day (used in R1) to 5 days to observe the effect of gypsum in contact with NaBO<sub>2</sub> in the porous media for a longer period of time. The residence time was increased by alternately injecting at 1 ft/d for 6 hours followed by a shutdown of 18 hours. The ASP slug size was reduced to 0.25 PV in coreflood R2 because the first coreflood had excess surfactant production. Oil recovery, pH, salinity and surfactant recovery are presented in Figure 19. The oil bank arrived at the outlet at 0.4 PV; the oil cut increased to 0.4 before decreasing slowly, similar to coreflood R1. After the chemical flood, about 94% of the water flood residual oil was recovered, which corresponds to a residual oil saturation of 0.02. Surfactant broke through at about 0.9 PV. Approximately 19% of the injected surfactant was recovered. Only 0.231 mg of surfactant per gram of rock was retained. The pH measurements shown in Figure 19 indicate that NaBO<sub>2</sub> did propagate with the surfactant in a single front in the core containing gypsum. However, the pH did not reach the injected pH of 10.3 even after 2 PV indicating that some of the metaborate was consumed after 5 days in contact with gypsum. The pH of 9.8 after 1.5 PV is high enough to ensure low surfactant adsorption. Ion chromatography was used to measure ion concentration of the effluent to evaluate the geochemical interactions inside the core flood (Figure 19). The effluent calcium concentration decreased around 1 PV, while the sulfate concentration increased, similar to the observations in the single phase experiments. The effluent sulfate concentration after 1 PV was about 2,200 ppm, while the calcium was around 100 ppm.

**Table 4:** Summary of R1 and R2 core floods results

Experiment (Core)		R1	R2	Units
SP Slug	Surfactant A	5,000	5,000	ppm
	Surfactant B	5,000	5,000	
	Co-solvent	10,000	5,000	
	NaBO <sub>2</sub>	37,500	24,000	
	FP3330	2,500	2,750	
	Size	0.40 PV	0.25 PV	
	pH	10.58	10.50	
Polymer Drive 1	NaBO <sub>2</sub>	10,000	10,000	ppm
	FP3330	2,000	2,500	
	Size	0.20 PV	1.8 PV	
	pH	10.17	10.3	
Polymer Drive 2	NaBO <sub>2</sub>	-	-	ppm
	FP3330	1,000		
	Size	1.4 PV		
	pH	8.42		
Oil Saturation After Chemical Flood (Sor <sub>c</sub> )		1	1	%
Oil Recovery		99	94	%
Surfactant Retention		0.197	0.231	mg of surfactant/g of rock

ASP coreflood R3 was performed with the surfactant formulation developed in experiment P2. A 0.40 PV ASP slug, having 3 wt% NH<sub>4</sub>OH, was injected at 1 ft/d followed by a 2.0 PV polymer drive. Along with the required amount of NaCl, 10,000 ppm of sodium sulfate was added to the ASP slug as well as the polymer drive to reduce calcium uptake from gypsum present in the core. About 71.2 % of the remaining oil after waterflood was recovered by the ASP flood. The recovery is 87.5 % OOIP including the waterflood. The residual oil saturation at the end of the coreflood was about 0.084 (Figure 21). The surfactant retention in this coreflood was about 0.25 mg/g rock. Somewhat high surfactant retention was observed in this experiment possibly because surfactant was trapped in the residual oil. The details of the coreflood are given in Table 4.

A high oil cut of about 50% was observed in the oil bank and the pH increased to about 10.2 on 1 PV injection. The effluent viscosity data confirmed that a favorable mobility ratio was



maintained during the coreflood. The AN125 polymer maintained its stability in the presence of calcium ions dissolved from the gypsum.

Very few ASP studies have been conducted in the past for cores containing gypsum. This study identified two alternative alkalis ( $\text{NaBO}_2$  and  $\text{NH}_4\text{OH}$ ) for gypsum-containing reservoirs where  $\text{Na}_2\text{CO}_3$  cannot be used.  $\text{NaBO}_2$  can be used with softened injection brine.  $\text{NH}_4\text{OH}$  has the potential to be used with hard injection brine. Further experiments are being performed in gypsum containing sandstone and carbonate cores to understand and optimize ASP processes with  $\text{NH}_4\text{OH}$ .

## Example 2

The use of an alkali in an alkali-surfactant-polymer (ASP), alkali-surfactant(AS), alkali-co-solvent-polymer(ACP) or alkali-co-solvent(AC) is many folds. First, the alkali reacts with the acidic components of oil to generate in-situ surfactants hence reducing the requirements of the injected surfactant. Second, because of the high pH, it reduces the adsorption of anionic surfactants on oil bearing rocks. Anionic surfactants are the most effective in providing ultra-low IFT with oil, hence making the process economical.

The conventional alkalis such as  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{Na}_2\text{SiO}_3$  cannot be used in case the reservoir contains gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or anhydrite ( $\text{CaSO}_4$ ), which are fairly soluble in water, because of the precipitation of the Calcium compounds of these alkalis, for example, precipitation of  $\text{CaCO}_3$  in case of  $\text{Na}_2\text{CO}_3$ . This precipitation reaction causes the excessive consumption of alkalis as well as may reduce the reservoir permeability. This is especially serious in the case of carbonate reservoirs where there is always a lingering uncertainty about the presence of gypsum or anhydrite. In this study, we found out that  $\text{NH}_4\text{OH}$  (or  $\text{NH}_3$ ) could be a possible solution to this problem. This alkali was found to give a  $\text{pH} > 11$  (requirement for ASP/AS/AC/ACP processes), do not cause calcium precipitation, forms in-situ soaps with acidic components of oil and give good surfactant phase behavior like other alkalis.

Numerous batch experiments showed that ammonia is able to maintain high pH in the presence of calcium without precipitating it. The batch experiment results given below compare the pH and aqueous ionic concentrations on adding different alkalis in the presence of excess gypsum. From the results, it can be seen that  $\text{NH}_4\text{OH}$  is able to give a high pH without significant dissolution of gypsum. Note that in other cases (except for base case, that is, case 2), sulfate concentration is much higher than calcium concentration suggesting the precipitation of calcium with these alkalis.

**Table 5:** Interaction of different alkalis in presence of excess gypsum in batch tests.

Sample	Alkali	pH after 21 hours	Ion measurement after 2 days	
			Sulfate	Calcium
1	0.45M Na <sub>2</sub> CO <sub>3</sub> in 10000ppm NaCl	8.3	53302.2	441.06
2	10,000ppm NaCl (Blank)	7.85	2572.64	886.82
3	0.225M Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O- 0.225M Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O in 10,000ppm NaCl	11.4	64146.5	695.14
4	0.45M NH <sub>4</sub> OH in 10,000ppm NaCl	11.1	2584.46	1073.8

Following this experiment, a number of surfactant phase behavior experiments were performed in order to study the effect of NH<sub>4</sub>OH in making low IFT formulations. A number of low IFT formulations were obtained using only NH<sub>4</sub>OH and a co-solvent, making it clear that just like conventional alkalis, NH<sub>4</sub>OH is able to form in-situ soaps from the acidic components of oil and hence also making it suitable for ACP/AC type EOR processes. Following this, a number of phase behavior experiments were performed with non-active oils and using conventional surfactant, both in the presence and absence of calcium in the brine. The first observation from these experiments was that there was no precipitation of the aqueous surfactant samples even on addition of 1500 ppm calcium in the presence of NH<sub>4</sub>OH. On mixing this aqueous solution with oil in different proportions, low IFT formulations were obtained that are suitable for ASP processes. The figure shown below is the solubilization ratio plot of one such surfactant formulation and oil in the presence of various proportions of calcium.

Following this experiment, single phase NH<sub>4</sub>OH injection was performed in a carbonate core with gypsum. The purpose of this experiment was to test if it was able to propagate a high pH through the core. The single phase results presented below shows that the pH is able to propagate in the presence of gypsum without any precipitation of calcium. The coreflood results shown below are for injection of 1% ammonium hydroxide in a carbonate core with gypsum. The pore volume of this core was about 67 mL. The injection was done at 0.25 ft/day corresponding to 4 day residence time in the 1 ft long core that was used in this experiment. The samples were sealed while being collected and afterwards in order to avoid any ammonia loss from them. The effluent ammonium hydroxide concentration was calculated by titrating with Potassium hydrogen phalate (KHP) and using phenolphthalein as an indicator.

Based on these results, it can be seen that ammonium hydroxide can be used for performing ASP flooding in the presence of gypsum in the reservoir. The effluent pH after 1 PV injection is already more than 9.5 which makes it suitable for ASP and related corefloods. Based on the effluent ion concentration data, it can be seen that molar effluent calcium and sulfate are

almost equal suggesting that there is not precipitation of calcium in the core. These makes this alkali superior than the conventionally used alkalis for reservoirs that have gypsum.

In summary, various alkalis were tested in the presence of gypsum and  $\text{NaBO}_2$  and  $\text{NH}_4\text{OH}$  were able to maintain high pH in the presence of gypsum in both batch and transport experiments. In addition, in batch experiments,  $\text{Na}_2\text{CO}_3$  solution pH dropped to 8.1 in the presence of gypsum within a day and the sulfate concentration in the supernatant was very high. In alkali transport experiments with  $\text{Na}_2\text{CO}_3$ , in the presence of gypsum, effluent sulfate concentration was very high compared to calcium suggesting large gypsum dissolution and  $\text{CaCO}_3$  precipitation inside the core. Also, in batch experiments, gypsum dissolution with  $\text{NaBO}_2$  was dependent on its initial concentration. Also, higher calcium loss was observed with increasing amount of  $\text{NaBO}_2$  in the presence of fixed amount of calcium chloride in the solution. In alkali transport experiments with  $\text{NaBO}_2$ , in the presence of gypsum, the effluent sulfate concentration was dependent on injection rate showing the importance of reaction kinetics in scaling up from lab to field scale. It was discovered that no additional gypsum dissolved with  $\text{NH}_4\text{OH}$  in batch or transport experiments.  $\text{NH}_4\text{OH}$  was able to transport through Berea and carbonate core, having gypsum, without significant delay or loss. Successful ASP corefloods were performed with  $\text{NaBO}_2$  as alkali in the presence of gypsum at 1 ft/d and 0.25 ft/d without noticeable permeability damage. The surfactant retentions were very low in both the cases. Methods were developed to perform phase behavior experiments with  $\text{NH}_4\text{OH}$  and a low IFT formulation was developed. High tertiary oil recovery was obtained with this ASP formulation in a Berea sandstone core.

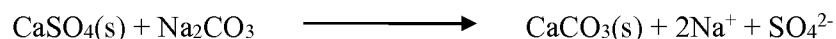
### Example 3

In alkali surfactant polymer (ASP) floods, alkali reduces surfactant adsorption and forms in situ surfactant with active oils, thus reducing synthetic surfactant requirement. Many reservoirs, especially carbonates, contain gypsum or anhydrite. In such cases, a conventional alkali like sodium carbonate cannot be used in ASP formulations because it precipitates as calcite. However, in this example, it was found that the calcium concentration in the presence of gypsum can be as high as 2000 ppm without causing any precipitation when ammonia is used as the alkali. Ultralow IFT surfactant formulations were obtained in the presence of up to 1200 ppm  $\text{Ca}^{2+}$ . Propagation of high pH, good oil recovery and low surfactant retention were observed in an ASP coreflood performed in a carbonate core containing gypsum. The Phreeqc geochemical simulator was used for reactive transport modeling and was found to be an effective

tool for designing these corefloods. A good match was observed between the measured concentration of the effluent ions from a coreflood experiment and the Phreeqc simulations.

After primary and secondary recovery in oil reservoirs, a large amount of residual oil is unrecovered due to trapping in the pores of the reservoir rock by capillary forces. Surfactants are able to mobilize this trapped oil by lowering the interfacial tension. Surfactants are retained in the reservoir by various mechanisms such as adsorption on mineral surfaces and phase trapping (Solairaj et al., 2012). Since a limited amount of surfactant can be used for an economical flood, the surfactant retention needs to be minimized. One of the ways of doing this is by incorporating an alkali into the surfactant formulation to increase the pH, which reduces the adsorption of anionic surfactants by making the surface charge negative (Somasundaran, 1979; Hirasaki et al., 2008). Alkali also helps in minimizing the amount of surfactant needed for oils that contain organic acids by generating soap.

Many carbonate reservoirs contain either gypsum or anhydrite. Levitt et al. (2011) discuss various challenges encountered in the application of chemical EOR in carbonate reservoirs, especially in the presence of gypsum. Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or anhydrite ( $\text{CaSO}_4$ ) differ in the water of hydration. The transition from gypsum to anhydrite takes place around  $45^\circ\text{C}$ . Gypsum (or anhydrite depending on the temperature, but for convenience we refer to gypsum unless we are describing a specific instance of anhydrite) is commonly present in carbonate reservoirs, especially dolomite formations as well as some sandstones, but it is less common in sandstone reservoirs. Under these circumstances, a conventional alkali such as sodium carbonate cannot be used because of precipitation of calcite by the reaction,



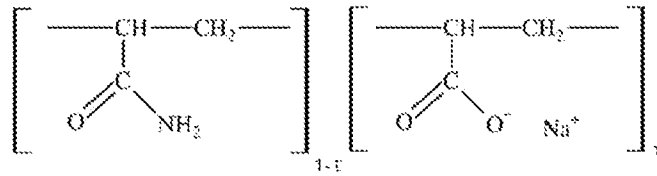
This  $\text{CaCO}_3$  precipitation consumes alkali, retards pH propagation and may cause a decrease in the permeability.

Lopez-salinas et al. (2011), through simulations, predicted that even 0.1 wt% anhydrite can delay the pH front by 0.7 pore volumes on injection of 1 wt%  $\text{Na}_2\text{CO}_3$ . Many attempts have been made to solve this problem (Kazempour et al., 2011; ShamsiJazeyi et al., 2013; Sharma et al., 2014). Sharma et al. (2014) recently tested metaborate alkali and observed high pH propagation, good oil recovery and low surfactant retention in sandstone cores containing gypsum. They observed limited calcium precipitation on injecting sodium metaborate in a gypsum containing core by a slow reaction, but little change in permeability was observed. ShamsiJazeyi et al. (2013) used a sacrificial agent to reduce surfactant adsorption in gypsum containing reservoirs.

Southwick et al. (2014) observed ammonia to be as effective as sodium carbonate in reducing surfactant adsorption in sandstone cores. They found a combination of ammonia and sodium carbonate to be more effective, in terms of handling at offshore locations and economics, than sodium carbonate alone. Sharma et al. (2014) performed single phase alkali transport experiments with ammonia in cores containing gypsum and observed high pH propagation without calcium precipitation. However, since ammonia does not precipitate calcium ions dissolved from gypsum and gives a pH of about 11, the surfactant and polymers should be tolerant to hardness.

Addition of ethylene oxide (EO) and propylene oxide (PO) groups increases the tolerance of anionic surfactants to divalent cations and improves surfactant phase behavior. EO/PO numbers can be tailored as per the requirement. New surfactants have been developed that are able to perform under harsh conditions such as oils with high equivalent alkane carbon number (EACN) numbers, high salinity, high hardness and high temperature (Adkins et al., 2010; Liyanage et al., 2012; Lu et al., 2014;). Alkoxy sulfate surfactants can be stabilized at temperatures greater than 65 °C with the use of an alkali (Adkins et al., 2010). However, in the presence of anhydrite, a conventional alkali such as sodium carbonate cannot be used for increasing the pH (Levitt et al., 2006; Levitt et al., 2011, Lu et al, 2014).

Polymers are used to increase the viscosity of surfactant solutions so that the displacement of the oil bank will be stable. Hydrolyzed polyacrylamide (HPAM) polymers are commonly used in chemical EOR. These polymers are shown to undergo precipitation in the presence of divalent cations such as calcium depending on the degree of hydrolysis ( $\tau$ ). Previous studies on HPAM suggest that these polymers are susceptible to precipitation in presence of calcium ions when  $\tau > 0.35$ , but it also depends on the calcium concentration, temperature and salinity (Zaitoun et.al, 1983; Levitt and Pope, 2008). The degree of hydrolysis of HPAM becomes a crucial parameter in deciding if it can be used for chemical flooding in the presence of divalent ions. HPAM hydrolysis is faster under acidic or alkaline conditions, compared to the neutral pH. Levitt et al (2011) studied HPAM hydrolysis in detail and observed significant hydrolysis within 1-2 months in the presence of  $\text{Na}_2\text{CO}_3$  at room temperature. Levitt and Pope (2008) performed experiments with extensively hydrolyzed PAM and recommended using HPAM when calcium concentration is lower than 400 ppm at high salinity at 23 °C but the critical calcium concentration is also a function of temperature.



Replacing some acrylate moieties with monomer units such as 2-acrylamide-2-methylpropane sulfonic acid (AMPS) or N-vinyl pyrrolidones (NVP) is found to increase the calcium tolerance. Levitt and Pope (2008) observed a fourfold increase in calcium tolerance on using AMPS substituted PAM. The ter-polymers of NVP, AMPS and AM moieties are found to be even more tolerant to divalent ions and showed good transport properties in porous media (Vermolen et al, 2011; Kulawardana et al, 2012). In this work, experiments were performed to study the effect of calcium ions dissolved from gypsum on various aspects of ASP flooding in such reservoirs, for example, surfactant phase behavior and polymer stability when ammonia was used as the alkali. Simulations were performed in a geochemical simulator, Phreeqc, to test various ways to design a robust ASP coreflood and the results of the coreflood were compared with Phreeqc simulations. A list of experiments and simulations performed in this work is given in Table 6.

**Table 6:** List of experiments and simulations

Ammonia for active oils	
A1	Alkali-cosolvent formulations with an active oils using ammonia as alkali. Effect of calcium on IFT.
Surfactant selection and phase behavior experiments	
B1	Phase behavior using alkoxy sulfate + IOS blend and effect of calcium ions on IFT, optimal salinity and aqueous stability at 25 °C
B2	Phase behavior experiments using alkoxy carboxylate + IOS blend and effect of calcium ions on IFT, optimal salinity and aqueous stability at 59 °C
Polymer selection	
C1	HPAM, AMPS, NVP stability experiments at pH of 11 with 1000-1500 ppm calcium at 59 °C
Oil recovery experiments	
D1	ASP coreflood a Berea sandstone core in the absence of anhydrite at 59 °C
D2	ASP coreflood in a carbonate core containing anhydrite at 59 °C
PHREEQC Simulations	
E1	Phreeqc simulations to design coreflood D2
E2	Comparison of Phreeqc predictions obtained from simulation E1 with effluent ions obtained from coreflood D2

## Methodology

**Materials:** Chemical agents used in these experiments consist of commercially available alkali, polymers and surfactants. NH<sub>4</sub>OH solution (ACS grade having 30 wt% NH<sub>3</sub>), sodium chloride, sodium sulfate, and calcium chloride were obtained from Fisher Scientific. Polymers Floppam 3630S, Floppam 3330S, AN 125, Superpusher SAV 550 were obtained from SNF

Floerger (Cedex, France) in powdered form. Alkoxy sulfate surfactants and internal olefin sulfonate (IOS) surfactants were obtained from Shell Chemical Co. and Stepan Chemical Co.; alkoxy carboxylate surfactants were synthesized at the University of Texas at Austin. Cosolvents were obtained from Huntsman Chemical. Oils 1 and 2 were active oils with acid numbers of about 2 mg KOH/g oil and 5 mg KOH/g oil, respectively. Oil 3 and oil 4 were inactive oils. The viscosities of oil 1, oil 2, and oil 4 were 14 cP, 113 cP and 8.3 cP, respectively at 59°C. The viscosity of oil 3 was about 5 cP at 25°C.

Ammonia for active oils: One of the important uses of adding an alkali in chemical EOR is that it reacts with active acids present in the oil, especially viscous to heavy oils, to form soap. Experiment A1 was performed at 59 °C to study if ammonia is able to form soap with oils known to contain acidic components. Oils 1 and 2 were used for phase behavior experiments and no surfactant was externally added to these formulations. Cosolvents were used in these formulations to reduce equilibration time and microemulsion viscosity. Using a fixed oil-aqueous phase ratio and a fixed amount of ammonia (about 0.6 wt%), a NaCl salinity scan was performed. IFT of these samples were observed visually by the emulsion test and in some cases also measured using a spinning drop tensiometer. In another experiment, about 1000 ppm of calcium was added to these formulations to study its effect on phase behavior.

Surfactant selection and phase behavior experiments: It is well known that for a robust ASP flooding, the salinity ahead of the ASP slug should be in type II region and the salinity behind the ASP slug (the polymer drive) should be in type I region. During an ASP coreflood, in presence of gypsum, the salinity range for types I, II and III change as a result of gypsum dissolution and it is important to consider these changes for a robust ASP coreflood. Experiments were therefore performed to identify surfactant formulations that give ultralow IFT values in the presence of calcium ions as well as exhibit a clear single phase solution in the absence of oil. The calcium concentration was varied systematically in these experiments to identify changes in optimum salinity and the type III window with ultra-low IFT, which ideally should not shift too much with changes in calcium concentration. A fixed amount of ammonia was added during surfactant phase behavior experiments and salinity scans were performed with NaCl. In experiment B1, a surfactant formulation was developed with crude oil#3 using alkoxy sulfate and IOS blend at 25°C. In experiment B2, a surfactant formulation was developed with crude oil#4 using alkoxy carboxylate and IOS blend at 59°C. Calcium was added, as CaCl<sub>2</sub>, systematically during phase behavior experiments to study its effects on optimal salinity, IFT and aqueous stability.

Polymer selection: The purpose of these experiments was to identify polymers that could be used for gypsum containing reservoirs; however this also depends on other parameters such as reservoir temperature, permeability, salinity and so forth. Experiments C1 were performed with different polymers in the presence of ammonia and up to 1500 ppm Ca at 59°C. Aqueous solutions containing fixed NaCl concentration, 0.6% NH<sub>3</sub>, up to 3000 ppm polymer and up to 1500 ppm Ca were prepared in glass ampules and kept at 59 °C. These samples were observed visually for any signs of chemical degradation and viscosity measurements were performed from time to time using the TI ARG2 rheometer. The detailed procedure for preparing these ampules is given in Levitt and Pope (2008). Floppam 3630S, Floppam 3330S, AN-125 and Superpusher SAV 550 were used in these experiments.

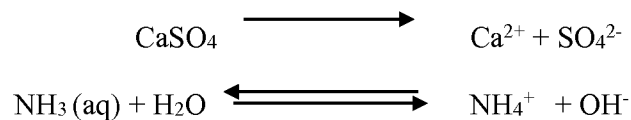
Oil Recovery experiments: After selecting an ultralow IFT surfactant formulation, developed previously, and suitable polymers, oil recovery experiments were performed with crude oil#4 at 59°C. The core properties are listed in Table 7. The cores were initially saturated with formation brine. The oil was injected at a constant pressure of about 200 psi to displace the brine and obtain initial oil saturation. When no more brine was produced, oil was injected at varying flow rates to obtain oil relative permeability at residual water saturation. A waterflood was then performed using the injection brine and effluent samples were collected in graduated tubes to obtain residual oil saturation after waterflood. The water relative permeability at residual oil saturation was obtained from the pressure drop data. A fixed amount of ASP slug was then injected in the core followed by the polymer solution. A negative salinity gradient was maintained in these corefloods to reduce surfactant retention and increase robustness. Produced effluent was collected in graduated test tubes and analyzed for oil cut, surfactant (by HPLC), dissolved solids (by refractometer), dissolved ions (by ion chromatograph), viscosity (by rheometer) and pH (by potentiometer).

Experiment D1 was performed in a Berea sandstone core (no gypsum present) to test the formulation and experiment D2 was then performed in a carbonate core containing gypsum. The presence of gypsum in the carbonate core was confirmed by analyzing effluent calcium and sulfate concentrations by an ion chromatograph. In experiment D1, 0.4 PV of ASP slug was injected followed by the polymer drive. Floppam 3630S was used both in the ASP slug and the polymer drive since the core did not have gypsum. 0.9% NH<sub>3</sub> was added to the ASP slug and 0.45% NH<sub>3</sub> was added to the polymer drive in this experiment. The salinity of the ASP slug was about 80,000 ppm and the salinity of the polymer drive was about 60,000 ppm. Coreflood D2 was performed in a carbonate core containing gypsum. At the end of the waterflood in coreflood D2, the core was allowed to equilibrate for one day after which the presence of gypsum was



confirmed once again. In experiment D2, 0.4 PV of ASP slug was injected followed by two polymer drives of decreasing salinities. 1.35 wt% surfactant, 0.5 wt% NH<sub>3</sub> and 5,500 ppm AN-125 were used in the ASP slug. The polymer drives were made using Floppam 3630S and no alkali was added to them. 10,000 ppm sodium sulfate was added to the ASP slug as well as the polymer drives to reduce calcium uptake from gypsum for the purpose of enhanced polymer stability. The salinity of the formation brine was 90,000 ppm (NaCl only). The salinity of the ASP slug, polymer drive-I and polymer drive-II (including 10,000ppm Na<sub>2</sub>SO<sub>4</sub>) was about 80,000 ppm, 50,000 ppm and 35,000 ppm, respectively. These experiments were performed at 59 °C.

PHREEQC Simulations: Simulations were performed in Phreeqc (version 3), the USGS program for geochemical calculations, to estimate effluent ion concentrations on injection of ammonia in a gypsum containing core. These values were first compared with those from experiments conducted by Sharma et al. (2014) to determine whether equilibrium was reached during these experiments. Pitzer.dat database was used in these calculations. Two of the most important geochemical reactions used are as follows.



Simulations E1 were performed to estimate the calcium concentration in the ASP slug and polymer drive due to gypsum dissolution. Phreeqc was used to explore different ways to maintain ultralow IFT, a good salinity gradient and enhanced polymer stability. For example, the benefit of adding sodium sulfate to minimize calcium uptake from gypsum was estimated. Based on these simulations and the phase behavior results, the salinities of the ASP slug and polymer drives were chosen for coreflood D2. In simulation E2, Phreeqc simulation results were compared with the effluent ions that were obtained from coreflood D2.

**Table 7:** Properties of the cores used in experiments D1 and D2

	Experiment D1	Experiment D2
Diameter (cm) x Length (cm)	3.77 x 29.6	3.76 x 29.6
Porosity	0.20	0.20
Permeability (md)	409	480
Gypsum Present	No	Yes

## Results

Ammonia-active oil interaction: The results of phase behavior experiments A1 performed with two active oils are discussed here. No surfactant was used in these experiments. Alkali was used to generate soap and co-solvent was used to promote formation of microemulsions. The results of the experiment with oil#1 are shown in Figure 28. Classical phase behavior was observed when ammonia was used as the alkali, going from Windsor type I to type III to type II on increasing salinity. Note that the ammonia concentration was fixed and NaCl concentration was varied for the salinity scan. Similarly another formulation was developed using ammonia as the alkali with oil#2. The results of this experiment are given in Figure 29. A spinning drop tensiometer was used to measure the IFT values of phase behavior samples shown in Figure 29. The IFT for type III samples was about 0.01 dyne/cm. The phase behavior changed to type II when 1000 ppm calcium was added.

Surfactant selection and phase behavior experiments: Surfactant phase behavior experiments were performed to obtain ultralow IFT surfactant formulations taking gypsum dissolution into account. For oil#3, surfactant formulations were developed using alkoxy sulfate and IOS combinations at 25°C using ammonia as the alkali. Some formulations showed ultralow IFT even in the presence of about 1000 ppm calcium ions, but were not found to be aqueous stable at optimal salinity. Some formulations were aqueous stable, but the IFT was not ultra-low with this oil. A combination of propoxy sulfate (C12-13-7PO-SO<sub>4</sub>), propoxy ethoxy sulfate (C12-13-35PO-30EO-SO<sub>4</sub>) and internal olefin sulfonate (C20-24-IOS) gave ultralow IFT in the presence of calcium as well as better aqueous stability. The solubilization plots obtained with this formulation in the presence of 800 ppm Ca and 1200 ppm calcium are given in Figures 30 and 31. A solubilization ratio of more than 20 at optimum salinity was observed with this surfactant formulation even in the presence of 1200 ppm calcium ions. A decrease in the optimal salinity by about 5000 ppm was observed on increasing calcium concentration from 800 ppm to 1200 ppm. The formulation did not show phase separation up to the optimal salinity at 25 °C in the presence of 1200 ppm calcium and 2000 ppm Floppam 3630S polymer, but was slightly hazy.

A surfactant formulation was also developed with a mixture of alkoxy carboxylate (C28-25PO-45EO-carboxylate) and IOS (C15-18-IOS; C19-23 IOS) surfactants with crude oil#4 using ammonia as alkali. This formulation was found to give ultra-low IFT with crude oil even in the presence of 1000 ppm calcium and was aqueous stable at 59 °C. From the solubilization plots shown in Figures 32 and 33, it can be seen that a solubilization ratio at optimum salinity of more than 10 was observed with up to 1000 ppm Ca<sup>2+</sup>. The solutions were also aqueous stable at 59 °C

in the presence of 1500 ppm calcium with or without polymer. The optimal salinity decreased by about 10,000 ppm on addition of about 1000 ppm calcium ions.

Polymer selection: Some initial surfactant aqueous stability samples containing 1500 ppm  $\text{Ca}^{2+}$ , ammonia, polymer and NaCl brine, showed precipitation after a few hours of mixing when HPAM polymer was used and were clear in the absence of it. This precipitation was attributed to the polymer and therefore aqueous stability experiments were performed with polymers alone to identify polymers that can be used in lab experiments to test these surfactant formulations. Aqueous stability samples prepared using Floppam 3630S and Floppam 3330S in 1500 ppm  $\text{Ca}^{2+}$  and ammonia (pH~10.5) showed mixed results. Some samples showed precipitation after a few hours of mixing while some stayed clear for many days. This difference is possibly due to different degree of hydrolysis of the polymer stock solutions.

Similar samples prepared using Superpusher SAV 550, a terpolymer containing NVP, and AN-125, a copolymer containing AMPS, were found to be clear even after 50 days of mixing at 59 °C. NVP ter-polymers are known to tolerate high calcium concentrations, but since the calcium concentration was limited to 2000 ppm in these experiments, AN-125 polymer was tested. The results of AN-125 samples prepared by mixing 3000 ppm polymer, 1000 ppm  $\text{Ca}^{2+}$  and 40,000 ppm NaCl at 59 °C is given in Figure 34. The pH of these samples was about 10. AN-125 was found to maintain most of its viscosity for at least one month. Small quantity of oxygen was detected in the last sample which may have affected the result. The solutions stayed clear for this duration and no precipitation was observed. Based on these results, AN-125 was used in the ASP coreflood with gypsum in the core. The polymer concentrations were chosen taking into account expected increases in calcium concentration due to dissolution of gypsum.

Oil recovery experiments and Phreeqc simulations: The surfactant formulation developed from experiment B2 was used to perform a coreflood experiment (D1) in Berea sandstone to test the formulation before performing a coreflood in the reservoir carbonate core containing gypsum. The oil recovery for the Berea coreflood is summarized in Table 8 and Figure 35. About 80% of the oil left after waterflood was recovered by injecting 0.4 PV of ASP slug and about 1 PV of polymer drive. A high oil cut of about 50% was reached and the oil saturation decreased to about 7% from about 34%. A pH of 10.5 was observed after 1 PV injection. The overall oil recovery, including waterflood recovery, was about 88%. No surfactant was observed in the coreflood effluent. The most likely reason for the high surfactant retention is that the effective salinity of the polymer drive was not low enough to give type I phase behavior.

Before performing an ASP coreflood using ammonia in a carbonate core containing gypsum, some preliminary simulations were performed using Phreeqc to get an idea of the

expected calcium concentrations during the coreflood at experimental conditions. This was critical for designing a robust salinity gradient because the surfactant phase behavior was dependent on calcium ions. It was especially important to make sure that the type-I region was going to be encountered in the coreflood during the polymer drive. Phreeqc simulations were first performed to match with the experimental results obtained by Sharma et al. (2014) on aqueous phase ammonia transport in a core containing gypsum at 25 °C. The results of the simulations are shown in Figure 36. Phreeqc results matched the experimental results very well. Note that the default database, Pitzer.dat, was used for performing these calculations. One interesting observation from Figure 36 is that gypsum dissolution was dependent on salinity. At high salinity, more gypsum dissolution is observed leading to higher calcium ion concentrations. This nature of gypsum dissolution is favorable for performing ASP floods as it provides an additional salinity gradient. In negative salinity gradient design, high salinity is maintained ahead of the ASP slug. This means that, if gypsum is present, higher amount of calcium would exist ahead of the ASP slug which would further drive the process into type-II phase behavior. As the salinity decreases towards the polymer drive, lower calcium concentration would give type-I phase behavior.

Phreeqc simulations were performed to test the addition of sodium sulfate to reduce gypsum dissolution (Figure 37). Figure 37 shows dissolved calcium ions from gypsum at two different salinities and two different temperatures with increasing  $\text{Na}_2\text{SO}_4$  concentration. From this figure, it can be seen that there is a sharp decrease in calcium uptake on adding up to 10,000 ppm  $\text{Na}_2\text{SO}_4$  at both salinities and temperatures. About 50% reduction in calcium concentration was observed on adding only 10,000 ppm  $\text{Na}_2\text{SO}_4$  to the injection slugs. Not much reduction in calcium uptake is observed on adding  $\text{Na}_2\text{SO}_4$  beyond 10,000 ppm based on the simulation results. Another important observation is that gypsum dissolution is less at higher temperatures which is favorable as many carbonate reservoirs are at high temperature.

Based on surfactant phase behavior experiments, polymer stability experiments and Phreeqc simulations, an improved design was developed for ASP corefloods in carbonate cores containing gypsum. The formation brine salinity was about 90,000 ppm (NaCl only) with about 2000 ppm calcium ions expected due to gypsum dissolution. 10,000 ppm  $\text{Na}_2\text{SO}_4$  was added to the ASP slug and the polymer drives to reduce calcium uptake from gypsum. AN-125 polymer was used in the ASP slug and FP 3630 S was used in the polymer drives. 0.5%  $\text{NH}_3$  was added only to the ASP slug. Further details of the coreflood D2 are given in Table 8. A second polymer drive was used to ensure that type-I phase behavior was encountered during the polymer drive. The oil recovery, effluent surfactant concentration, and effluent ion concentrations are shown in

Figures 38-40. About 81% of the oil left after waterflood was recovered due to the 0.4 PV ASP slug and 1.6 PV of polymer drive and the oil saturation was decreased from about 29% to 5.5%. The overall oil recovery, including waterflood recovery, was about 91%. A maximum pressure drop of about 4.5 psi/ft was observed which stabilized around 2 psi/ft at the end of the coreflood. No plugging was observed during the experiment. Emulsion breakthrough was observed around 0.8 PV and the maximum surfactant concentration (measured by HPLC) was about 50% of the injected concentration. The surfactant retention in this coreflood was about 0.246 mg/g rock and about 43% of the injected surfactant was recovered. The effluent pH at 1 PV was about 10. From Figures 39 and 14, it can be seen that high pH and surfactant propagated together.

The effluent calcium data (Figure 40) shows that calcium concentration decreased from about 1700 ppm, when 90,000 NaCl formation brine was present, to about 400 ppm at the end of the coreflood. Note that sodium sulfate was not present in the formation brine. Addition of Na<sub>2</sub>SO<sub>4</sub> to the ASP slug and polymer drives significantly decreased the calcium ion uptake from gypsum. The reduction in Ca<sup>2+</sup> was also helpful in increasing polymer stability and the robustness of the ASP coreflood. The sulfate concentration was about 5400 ppm in the formation brine, due to gypsum dissolution, and increased to a steady value about 8600 ppm during the coreflood.

**Table 8:** Summary of D1 and D2 core floods results

Experiment (Core)		D1	D2	Units
ASP Slug	Surfactant A	6500	6500	ppm
	Surfactant B	4500	4500	
	Surfactant C	2500	2500	
	Co-solvent	10,000	10,000	
	NH <sub>3</sub>	9000	5000	
	Polymer	3500 ppm	5500 ppm AN-125	
	Size	0.4 PV	0.4 PV	
	pH	11.1	11.5	
Polymer Drive 1	NH <sub>3</sub>	4500	-	ppm
	FP3630	3500	2,500	
	Size	1.5 PV	0.5 PV	
	pH	10.9	7.7	
Polymer Drive 2	NH <sub>3</sub>	-	-	ppm
	FP3630	-	2500	
	Size	-	1.2 PV	
	pH	-	7.8	
Oil Saturation After Chemical Flood (Sor <sub>c</sub> )		7	5.5	%
Overall Oil Recovery		88	91	%
Surfactant Retention		-	0.246	mg of surfactant/g of rock

The effluent calcium data are compared with a Phreeqc simulation in Figure 41. Phreeqc results closely match the experimental results using the Pitzer.dat database in this case. Note that since no oil was considered in these simulations, the injection schedule of the simulations was rescaled based on the average oil saturation inside the core. Dispersion was not included in Phreeqc simulations but doing so would be expected to improve the match. However, the match without including dispersion also seems reasonable and, more importantly, shows that Phreeqc is able to predict calcium concentration very well during ASP corefloods in gypsum containing cores when ammonia is used as alkali. Since the effluents obtained during the ASP coreflood at 1 ft/d correspond to the equilibrium values, these results are scalable to the field.

## Discussion

This example shows an ASP process using ammonia in reservoirs containing gypsum. The calcium concentration can be about 2000 ppm in the presence of gypsum, depending on the salinity and temperature, which significantly affects polymer stability, surfactant phase behavior and salinity gradient design. Use of sodium sulfate was simulated with Phreeqc to reduce the gypsum dissolution and enhance polymer stability. Adding sodium sulfate is also helpful in designing a robust coreflood since the optimal salinity does not change much as a result on gypsum dissolution. It is also expected to enhance polymer stability. Sodium sulfate may not be used in some reservoirs due to their mineralogy. However, in those cases, the effects of gypsum dissolution may be taken into account and the coreflood designed accordingly. The spatial variation of gypsum in the reservoir may also affect the salinity gradient design.

Phreeqc simulations showed that adding up to 10,000 ppm  $\text{Na}_2\text{SO}_4$  can reduce gypsum dissolution by 50%, decreasing the calcium concentration to less than 1000 ppm. The calcium concentration was less than 500 ppm at low salinities. The surfactants and polymers should have tolerance to calcium ion concentration that is expected from gypsum. It is, however, not clear if the ASP slug should be aqueous stable after calcium ions dissolve from gypsum. Use of alkoxy sulfate surfactant may be feasible at high temperature for reservoirs containing gypsum with the use of ammonia.

In the coreflood experiment, AN-125 polymer was used in the ASP slug and Floppam 3630S in the polymer drive. No alkali was added to the polymer drive which could increase surfactant retention at the trailing end of the ASP slug. Adding sodium sulfate is likely to cost less than using expensive polymers. However, long term stability of these polymers needs to be ensured.

## Summary

- Ammonia was found to react with acidic components of oil to form soap.
- Ultra-low IFT surfactant formulations with good aqueous stability were obtained with ammonia in the presence of up to 1200 ppm calcium ions with the use of large-hydrophobe alkoxy carboxylate and large-hydrophobe alkoxy sulfate surfactants with high ethylene oxide content.
- Phreeqc simulations were found to be accurate in predicting gypsum dissolution in presence of ammonia. It was found to be a very helpful tool in designing the ASP corefloods. The effluent ion concentrations from the experiment matched well with the Phreeqc simulations.
- High pH propagation, good oil recovery and low surfactant retention was observed by using ammonia in the ASP coreflood in a carbonate core containing gypsum.

**Nomenclature**

	ASP	Alkaline-surfactant-polymer
	CaCO <sub>3</sub>	Calcium carbonate
5	CaSO <sub>4</sub>	Calcium sulfate (Anhydrite)
	CaSO <sub>4</sub> .2H <sub>2</sub> O	Calcium sulfate dehydrate (Gypsum)
	HPAM	Hydrolyzed polyacryamide
	AMPS	2-Acrylamide-2-methylpropane sulfonic acid (AMPS)
	NVP	N-vinyl pyrrolidones
10	HPLC	High performance liquid chromatography
	IC	Ion chromatograph
	IFT	Interfacial Tension
	md	Millidarcy
	NH <sub>3</sub>	Ammonia
15	NaCl	Sodium chloride
	Na <sub>2</sub> CO <sub>3</sub>	Sodium carbonate
	OOIP	Original oil in place
	ppm	Parts per million
	PV	Pore volume
20	TDS	Total dissolved solids
	TEGBE	Triethylene glycol monobutyl ether
	wt%	Percentage by weight

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**CLAIMS**

What is claimed is:

1. An aqueous composition comprising water, a surfactant, an ammonia compound, an ionic strength adjusting agent, and a multivalent mineral cation;  
wherein said ammonia compound is  $R^3H_2N$ ,  $(R^3)_2HN$ ,  $(R^3)_3N$ , or  $NH_3$ , wherein  $R^3$  is independently unsubstituted C<sub>1</sub>-C<sub>5</sub> alkyl.
2. The aqueous composition of claim 1, further comprising a co-solvent.
3. An aqueous composition comprising water, a co-solvent, an ammonia compound, an ionic strength adjusting agent and a multivalent mineral cation;  
wherein said ammonia compound is  $R^3H_2N$ ,  $(R^3)_2HN$ ,  $(R^3)_3N$ , or  $NH_3$ , wherein  $R^3$  is independently unsubstituted C<sub>1</sub>-C<sub>5</sub> alkyl.
4. The aqueous composition of claim 3, further comprising a surfactant.
5. The aqueous composition of one of claims 1 to 4, wherein  $R^3$  is independently methyl or ethyl.
6. The aqueous composition of one of claims 1 to 4, wherein said ammonia compound is  $NH_3$ .
7. The aqueous composition of one of claims 1 to 6, wherein said ionic strength adjusting agent is sodium chloride, potassium chloride, sodium iodide, potassium iodide, sodium acetate, potassium acetate, calcium chloride, sodium sulfate, sodium nitrate, or potassium nitrate.
8. The aqueous composition of one of claims 1 to 7, wherein said aqueous composition is within a petroleum reservoir.
9. The aqueous composition of one of claims 1 to 8, wherein said aqueous composition has a pH of at least about 10.
10. The aqueous composition of one of claims 1 to 9, wherein said aqueous composition is in contact with a mineral, wherein water dissolves said multivalent mineral cation from said mineral.
11. The aqueous composition of claim 10, wherein said mineral is a sulfate mineral.
12. The aqueous composition of one of claims 1 to 11, wherein said mineral is gypsum, anhydrite, barite or magnesium sulfate.
13. The aqueous composition of one of claims 1 to 12, wherein said aqueous composition further comprises Borax, sodium acetate, or potassium acetate.

14. The aqueous composition of one of claims 1 to 12, wherein said multivalent mineral cation is an alkaline earth metal cation.
15. The aqueous composition of one of claims 1 to 14, wherein said multivalent mineral cation is  $\text{Ca}^{2+}$ .
16. The aqueous composition of one of claims 1 to 15, wherein said multivalent mineral cation is derived from  $\text{CaCl}_2$ .
17. The aqueous composition of one of claims 1, 2, or 4 to 16, wherein said surfactant is an anionic surfactant, a non-ionic surfactant, a zwitterionic surfactant or a cationic surfactant.
18. The aqueous composition of one of claims 1, 2, or 4 to 17, wherein said anionic surfactant is an alkoxy carboxylate surfactant, an alkoxy sulfate surfactant, an alkoxy sulfonate surfactant, an alkyl sulfonate surfactant, an aryl sulfonate surfactant or an olefin sulfonate surfactant.
19. The aqueous composition of one of claims 1, 2, or 4 to 18, wherein said surfactant is present at a concentration of at least 0.05% w/w.
20. The aqueous composition of one of claims 1 to 21, wherein the ammonia compound is present at a concentration of at least about 0.3% w/w.
21. The aqueous composition of one of claims 1 to 20, wherein said aqueous composition comprises an alkali agent in addition to ammonia.
22. The aqueous composition of one of claims 1 to 21, wherein said alkali agent comprises an acetate, amine, carbonate, silicate or borate.
23. The aqueous composition of claim 22, wherein said alkali agent is Borax, sodium acetate, potassium acetate, sodium metaborate, sodium silicate, or sodium orthosilicate.
24. The aqueous composition of one of claims 1 to 23, further comprising a viscosity enhancing water soluble polymer.
25. The aqueous composition of claim 24, wherein said viscosity enhancing water soluble polymer is polyacrylamide or a co-polymer of polyacrylamide.
26. The aqueous composition of claim 24, wherein said viscosity enhancing water soluble polymer is a hydrolyzed polyacrylamide polymer.
27. The aqueous composition of claim 24, wherein said viscosity enhancing water soluble polymer is a biopolymer.
28. The aqueous composition of claim 27, wherein said biopolymer is xanthan gum or scleroglucan.

29. The aqueous composition of one of claims 1 to 28, further comprising a chelating agent.
30. The aqueous composition of claim 29, wherein said chelating agent is EDTA.
31. The aqueous composition of one of claims 1 to 30, further comprising a gas.
32. The aqueous composition of one of claims 1 to 31, wherein said water is soft brine water.
33. The aqueous composition of one of claims 1 to 32, having a salinity of at least 5,000 ppm.
34. The aqueous composition of one of claims 1 to 32, having a salinity of at least 10,000 ppm.
35. The aqueous composition of one of claims 1 to 32, having a salinity of at least 50,000 ppm.
36. The aqueous composition of one of claims 1 to 32, having a salinity of at least 100,000 ppm.
37. The aqueous composition of one of claims 1 to 32, having a salinity of at least 150,000 ppm.
38. The aqueous composition of one of claims 1 to 37, having a pH of about 10 to about 11.5.
39. The aqueous composition of one of claims 1 to 37, having a pH of about 10.5.
40. An aqueous composition comprising water, a hydrolyzed or partially hydrolyzed viscosity enhancing water soluble polymer and an ammonia compound at a pH of at least about 10,  
wherein said ammonia compound is  $R^3H_2N$ ,  $(R^3)_2HN$ ,  $(R^3)_3N$ , or  $NH_3$ , wherein  $R^3$  is independently unsubstituted C<sub>1</sub>-C<sub>5</sub> alkyl.
41. The aqueous composition of claim 40, wherein said hydrolyzed viscosity enhancing water soluble polymer is a hydrolyzed or partially hydrolyzed polyacrylamide.
42. The aqueous composition of one of claims 40 to 41, wherein said ammonia compound is  $NH_3$ .
43. An emulsion composition comprising an unrefined petroleum, water, a surfactant, an ammonia compound and a multivalent mineral cation,  
wherein said ammonia compound is  $R^3H_2N$ ,  $(R^3)_2HN$ ,  $(R^3)_3N$ , or  $NH_3$ , wherein  $R^3$  is independently unsubstituted C<sub>1</sub>-C<sub>5</sub> alkyl.
44. The emulsion of claim 43, further comprising a co-solvent.

45. An emulsion composition comprising an unrefined petroleum, water, a co-solvent, an ammonia compound and a multivalent mineral cation,  
wherein said ammonia compound is  $R^3H_2N$ ,  $(R^3)_2HN$ ,  $(R^3)_3N$ , or  $NH_3$ , wherein  $R^3$  is independently unsubstituted  $C_1$ - $C_5$  alkyl.
46. The emulsion of claim 44, further comprising a surfactant.
47. The emulsion composition of one of claims 43 to 46, wherein  $R^3$  is independently methyl or ethyl.
48. The emulsion composition of one of claims 43 to 46, wherein said ammonia compound is  $NH_3$ .
49. The emulsion of one of claims 43 to 48, wherein said emulsion is within a petroleum reservoir.
50. The emulsion of one of claims 43 to 49, wherein said emulsion has a pH of at least about 9.
51. The emulsion of one of claims 43 to 49, wherein said emulsion is in contact with a mineral, wherein water dissolves said multivalent mineral cation from said mineral.
52. The emulsion of claim 51, wherein said mineral is a sulfate mineral.
53. The emulsion of claim 51, wherein said mineral is gypsum, anhydrite, barite or magnesium sulfate.
54. The emulsion of one of claims 43 to 53, wherein said emulsion further comprises sodium silicate.
55. The emulsion of one of claims 43 to 47, wherein said multivalent mineral cation is an alkaline earth metal cation.
56. The emulsion of one of claims 43, 44, or 46 to 55, wherein said surfactant is an anionic surfactant, a non-ionic surfactant, a zwitterionic surfactant or a cationic surfactant.
57. The emulsion of one of claims 43, 44, or 46 to 56, wherein said anionic surfactant is an alkoxy carboxylate surfactant, an alkoxy sulfate surfactant, an alkoxy sulfonate surfactant, an alkyl sulfonate surfactant, an aryl sulfonate surfactant or an olefin sulfonate surfactant.
58. The emulsion of one of claims 43, 44, or 46 to 57, wherein said surfactant is present at a concentration of at least 0.05% w/w.
59. The emulsion of one of claims 43, 44, or 46 to 58, wherein the ammonia compound is present in an amount sufficient to increase the solubility of said surfactant in said emulsion composition relative to the absence of the ammonia.



60. The emulsion of one of claims 43 to 59, wherein the ammonia compound is present at a concentration of at least 0.3% w/w.

61. The emulsion of one of claims 43 to 60, further comprising a viscosity enhancing water soluble polymer.

62. The emulsion composition of claim 61, wherein said viscosity enhancing water soluble polymer is polyacrylamide or a co-polymer of polyacrylamide.

63. The emulsion composition of claim 61, wherein said viscosity enhancing water soluble polymer is a hydrolyzed polyacrylamide polymer.

64. The emulsion of one of claims 44 to 62, further comprising a co-solvent.

65. The emulsion of one of claims 43 to 64, further comprising a gas.

66. The emulsion of one of claims 43 to 65, wherein said water is soft brine water.

67. The emulsion of one of claims 43 to 66, wherein the emulsion composition is a microemulsion.

68. A method of displacing an unrefined petroleum material in contact with a solid material, said method comprising:

(i) contacting an unrefined petroleum material with an aqueous composition as in any one of claims 1-42, wherein said unrefined petroleum material is in contact with a solid material comprising a mineral, wherein water dissolves multivalent mineral cations from said mineral;

(ii) allowing said unrefined petroleum material to separate from said solid material thereby displacing said unrefined petroleum material in contact with said solid material.

69. The method of claim 68, further comprising contacting said solid material with ammonia and ammonium hydroxide.

70. The method of claim 68, wherein said solid material is an endogenous solid material in a petroleum reservoir.

71. The method of claim 68, wherein said method is an enhanced oil recovery method.

72. The method of claim 68, wherein an emulsion forms after said contacting.

73. The method of claim 68, wherein said mineral is gypsum, anhydrite, barite or magnesium sulfate.

74. A method of converting an unrefined petroleum acid into a surfactant, said method comprising:

(i) contacting a petroleum material with an aqueous composition as in any one of claims 1-42, thereby forming an emulsion in contact with said petroleum material;

- (ii) allowing an unrefined petroleum acid within said unrefined petroleum material to enter into said emulsion, thereby converting said unrefined petroleum acid into a surfactant.

75. The method of claim 74, wherein said reactive petroleum material is in a petroleum reservoir.

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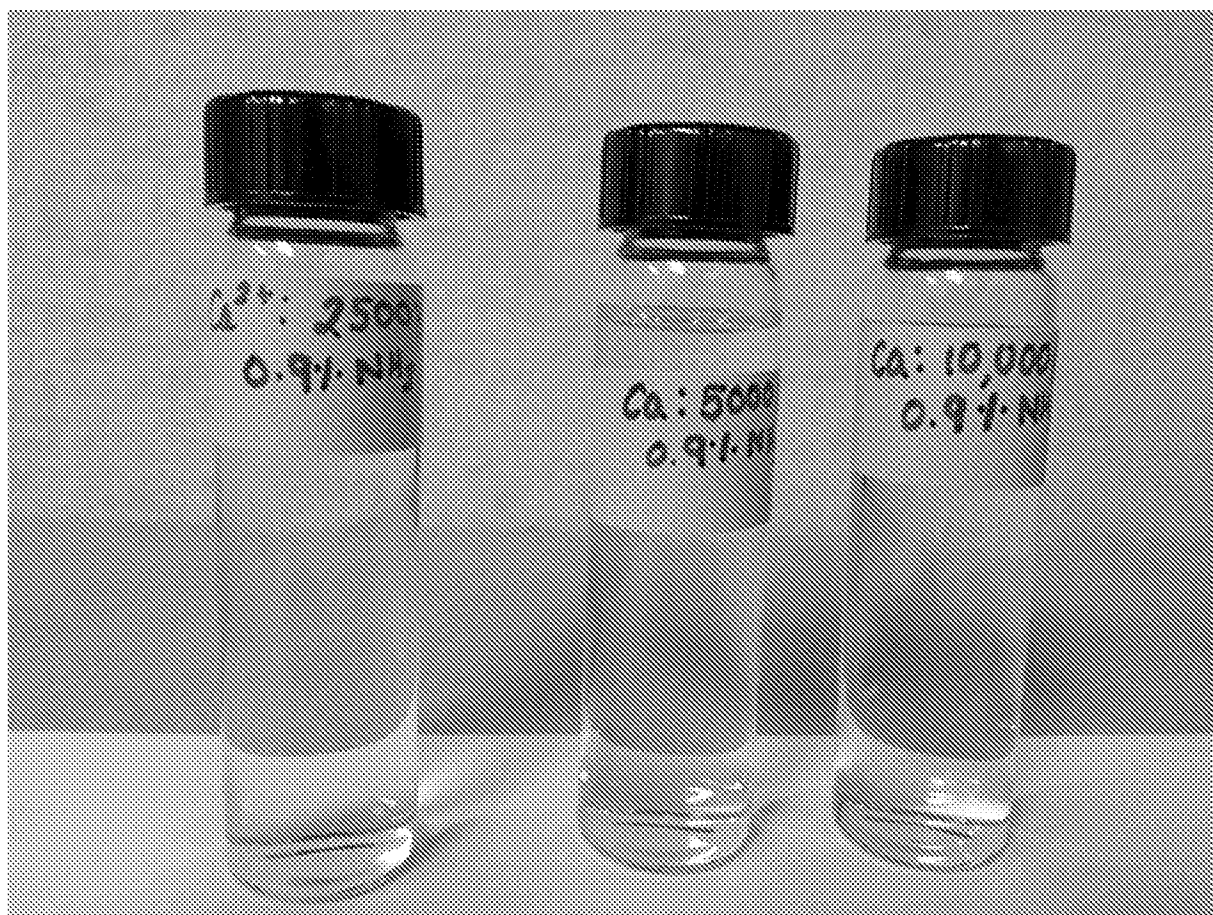


Figure 1

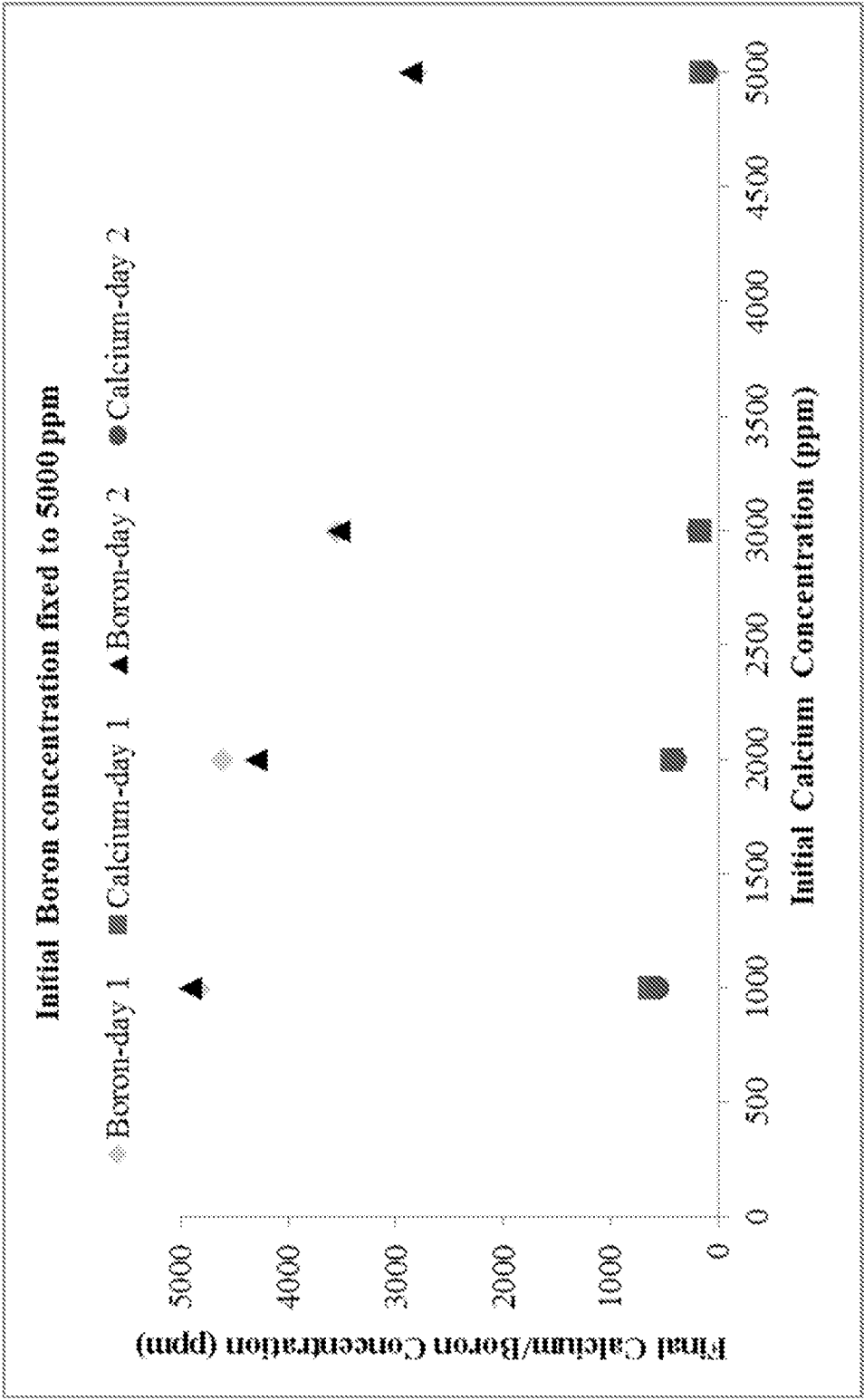


Figure 2

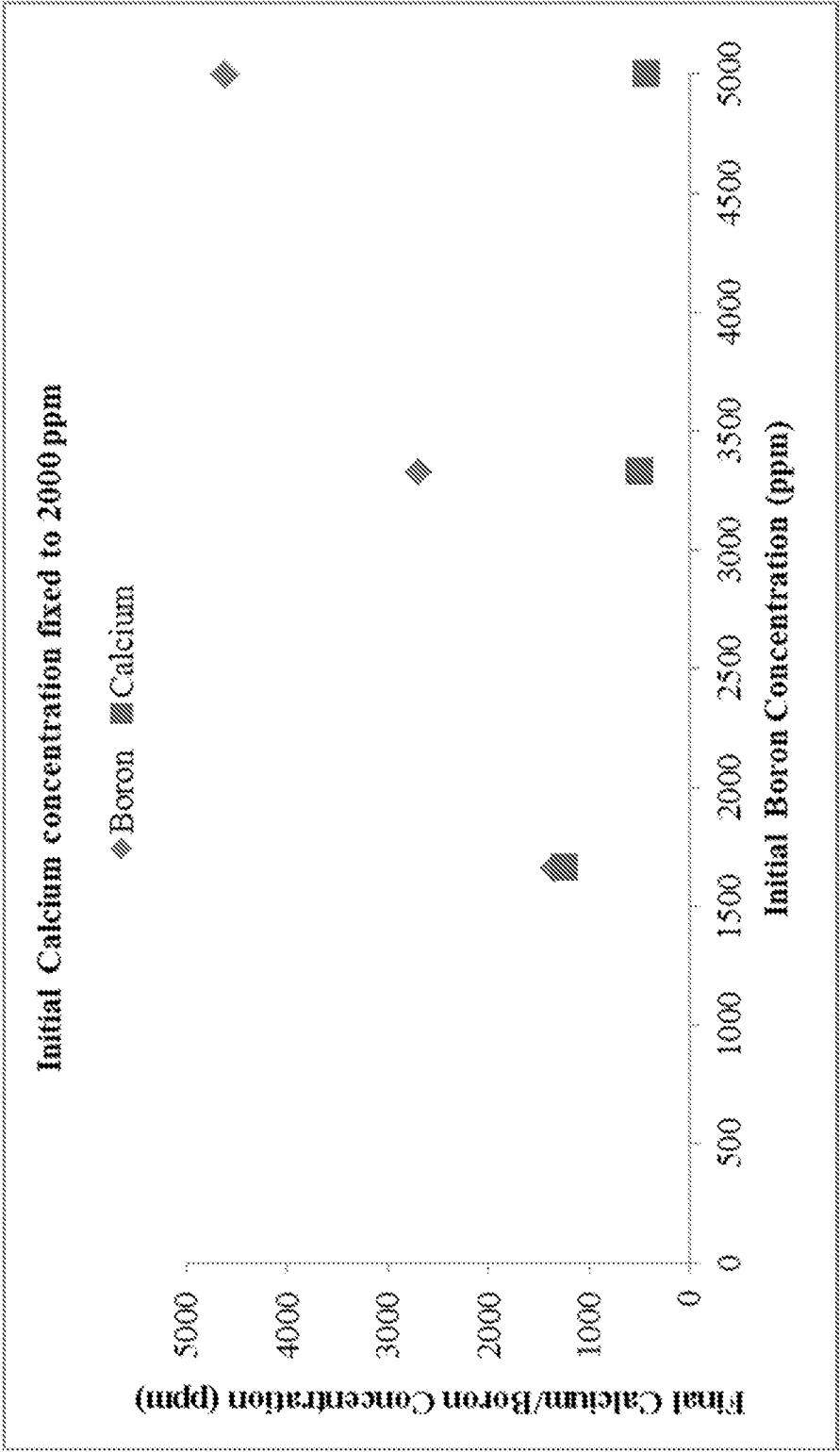


Figure 3

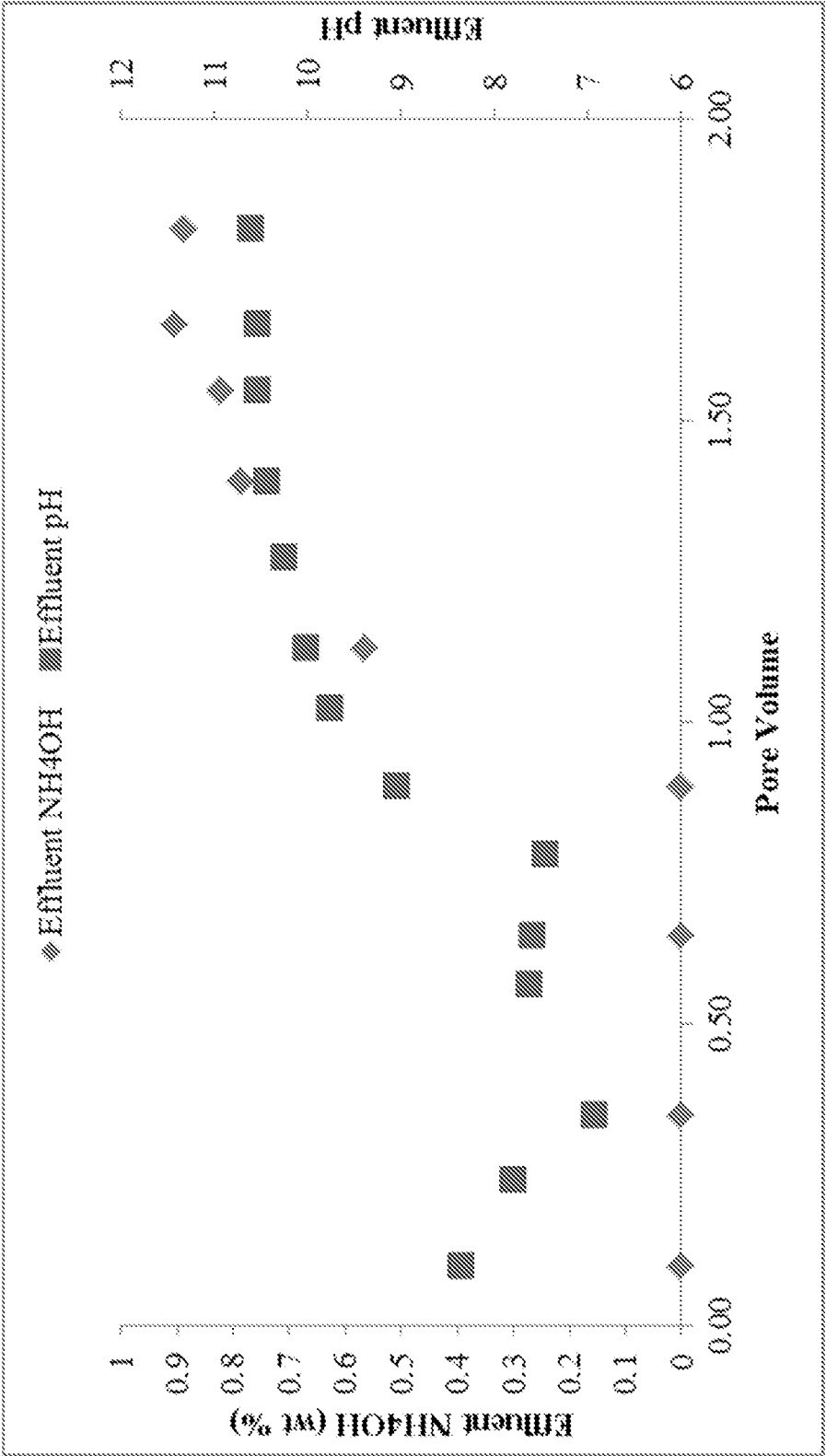


Figure 4

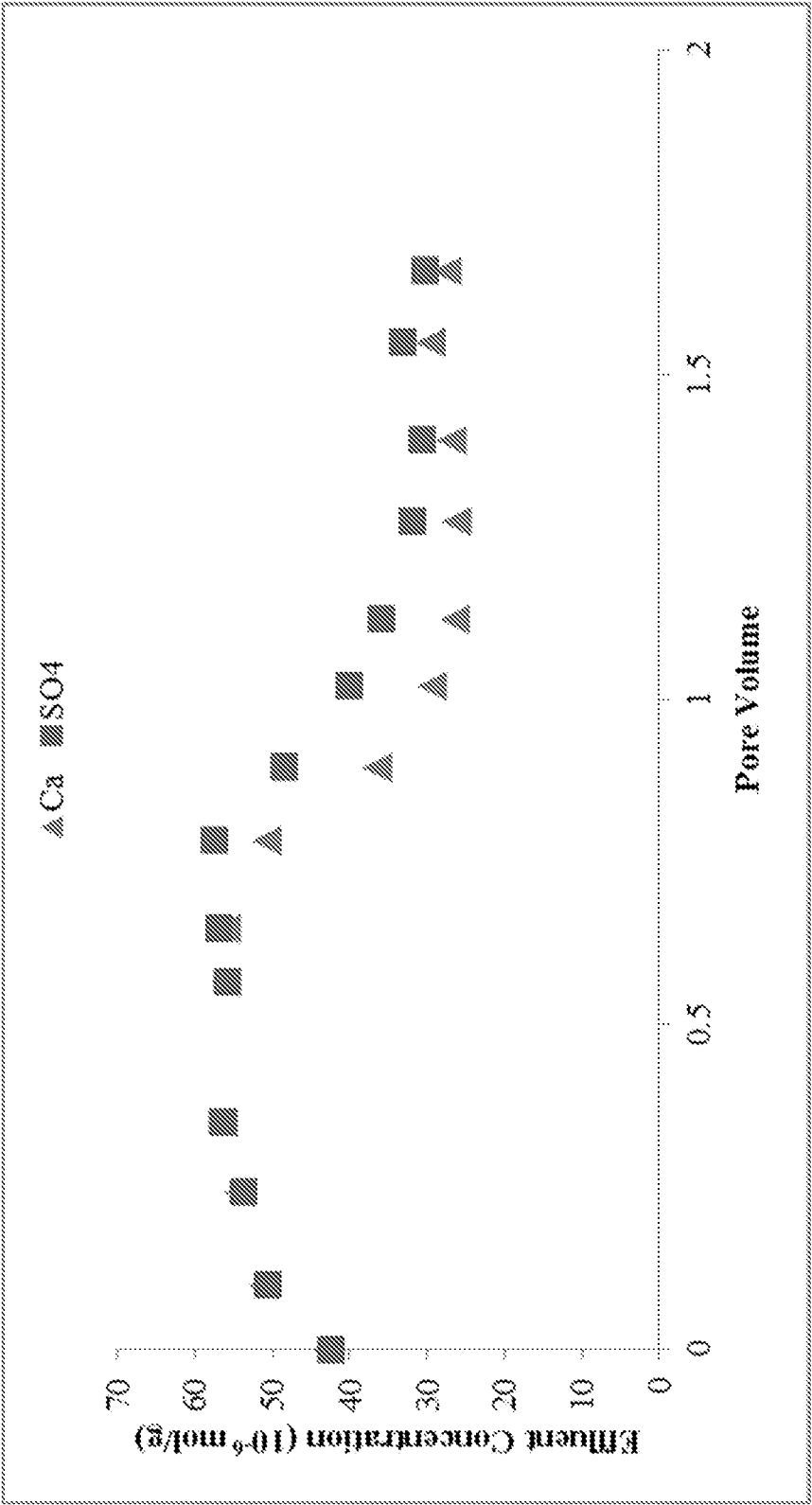


Figure 5

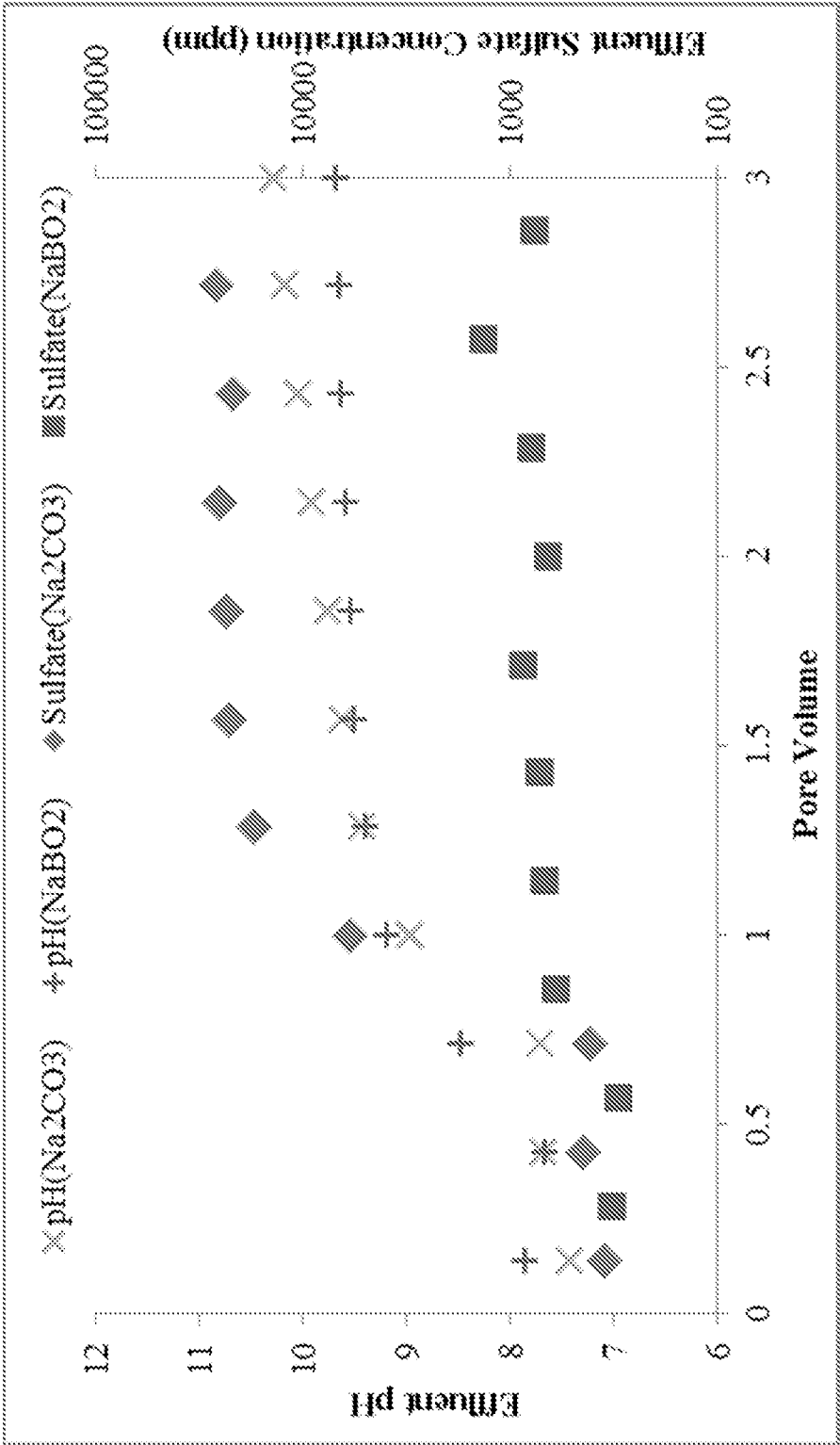


Figure 6



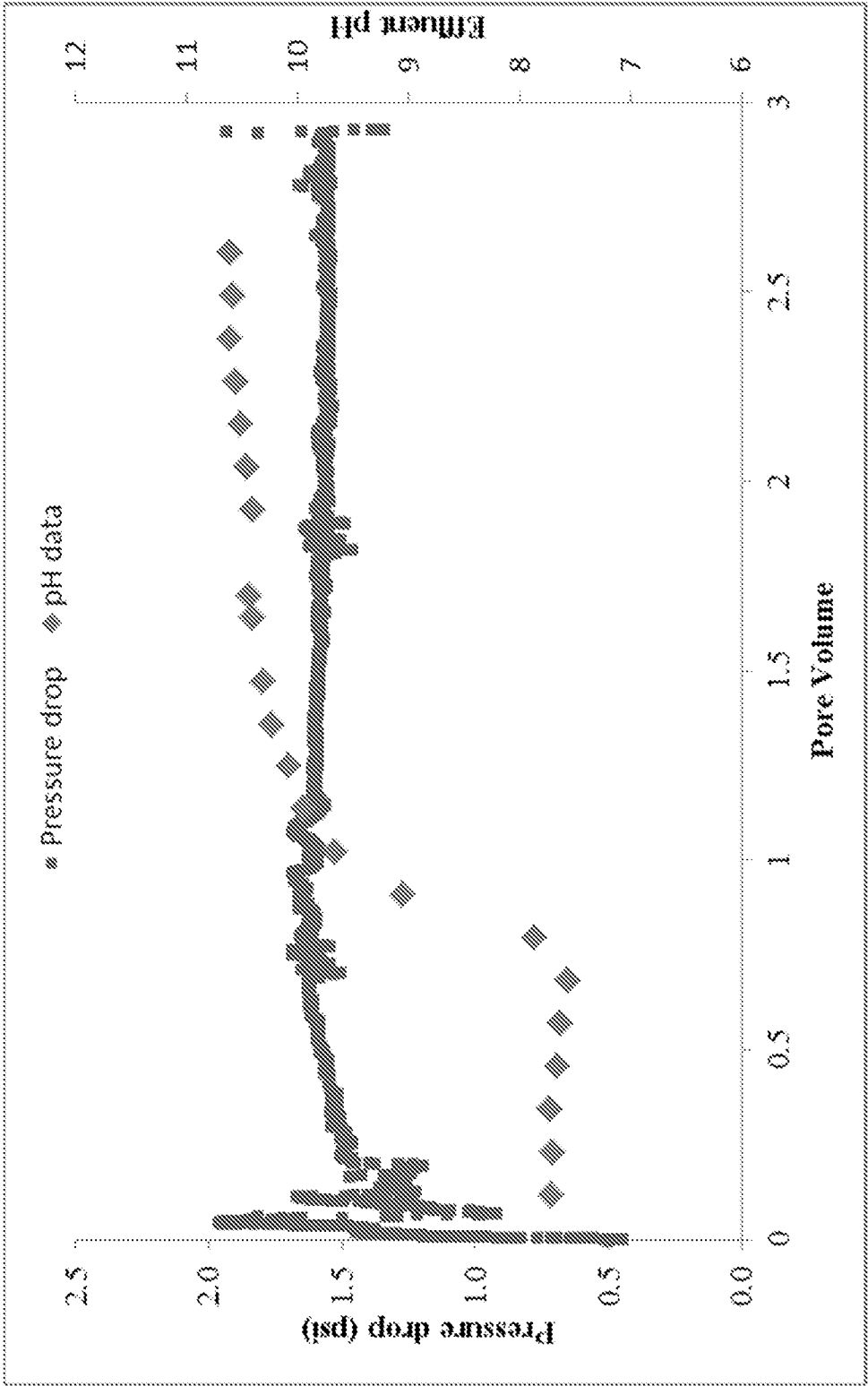


Figure 7

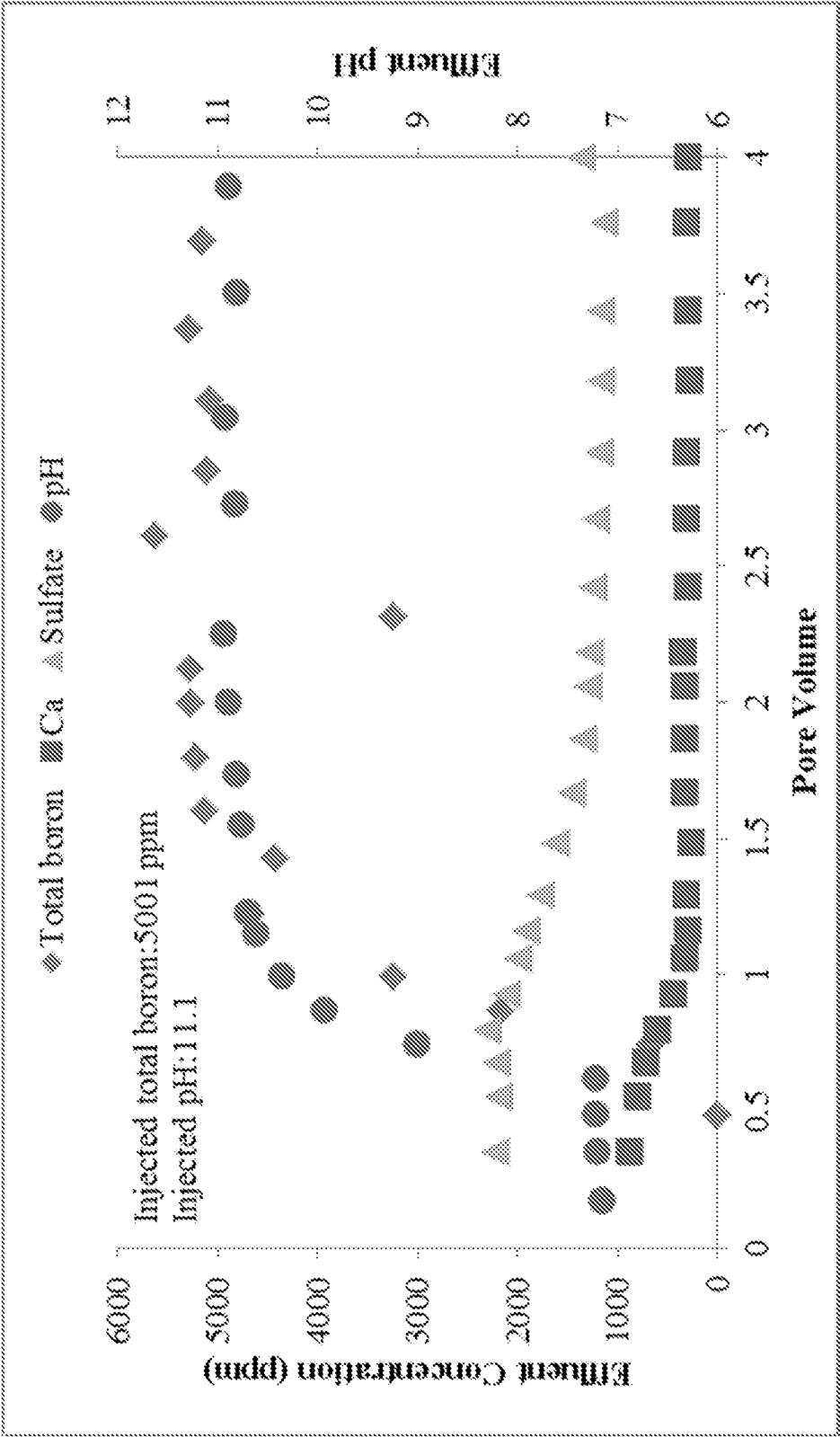


Figure 8

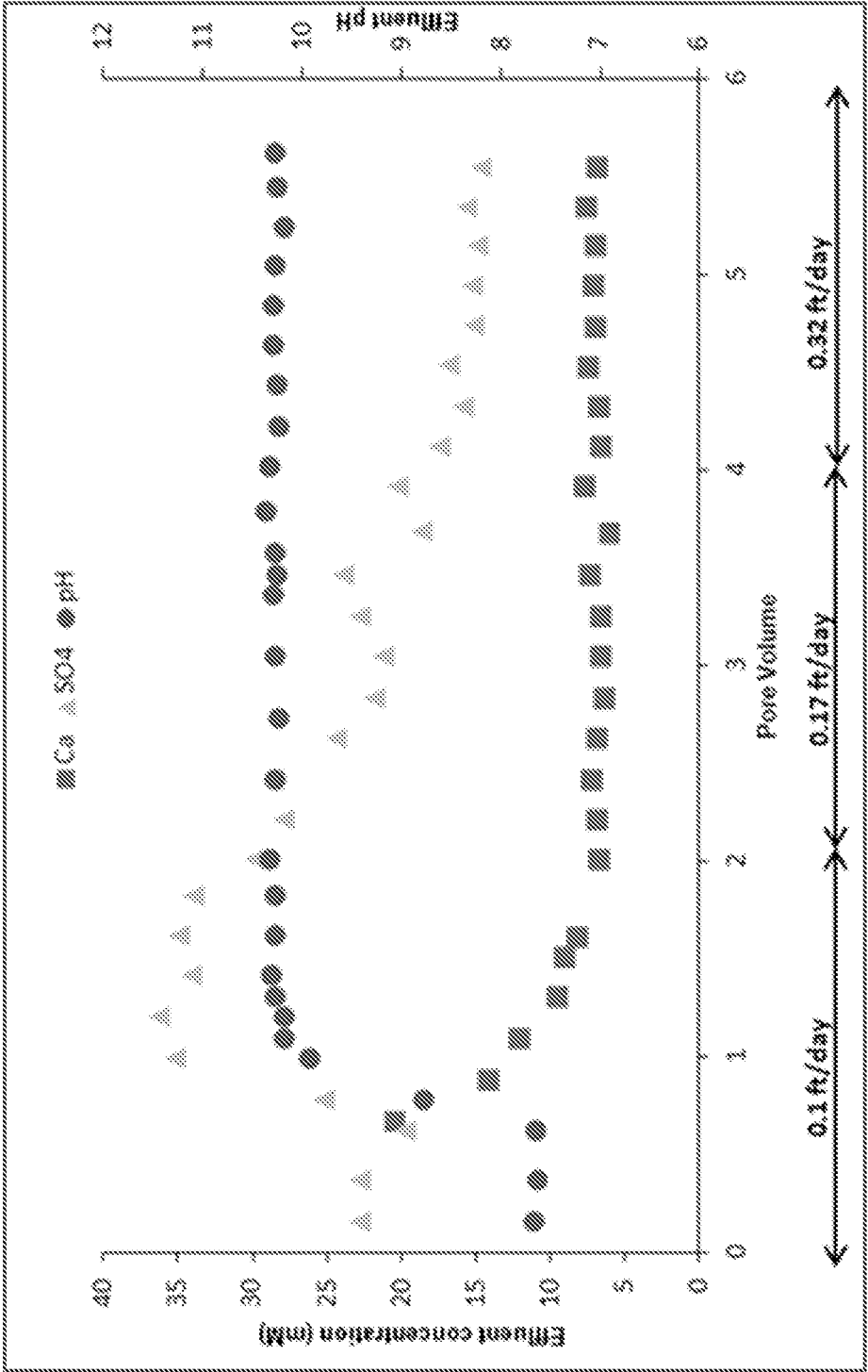


Figure 9

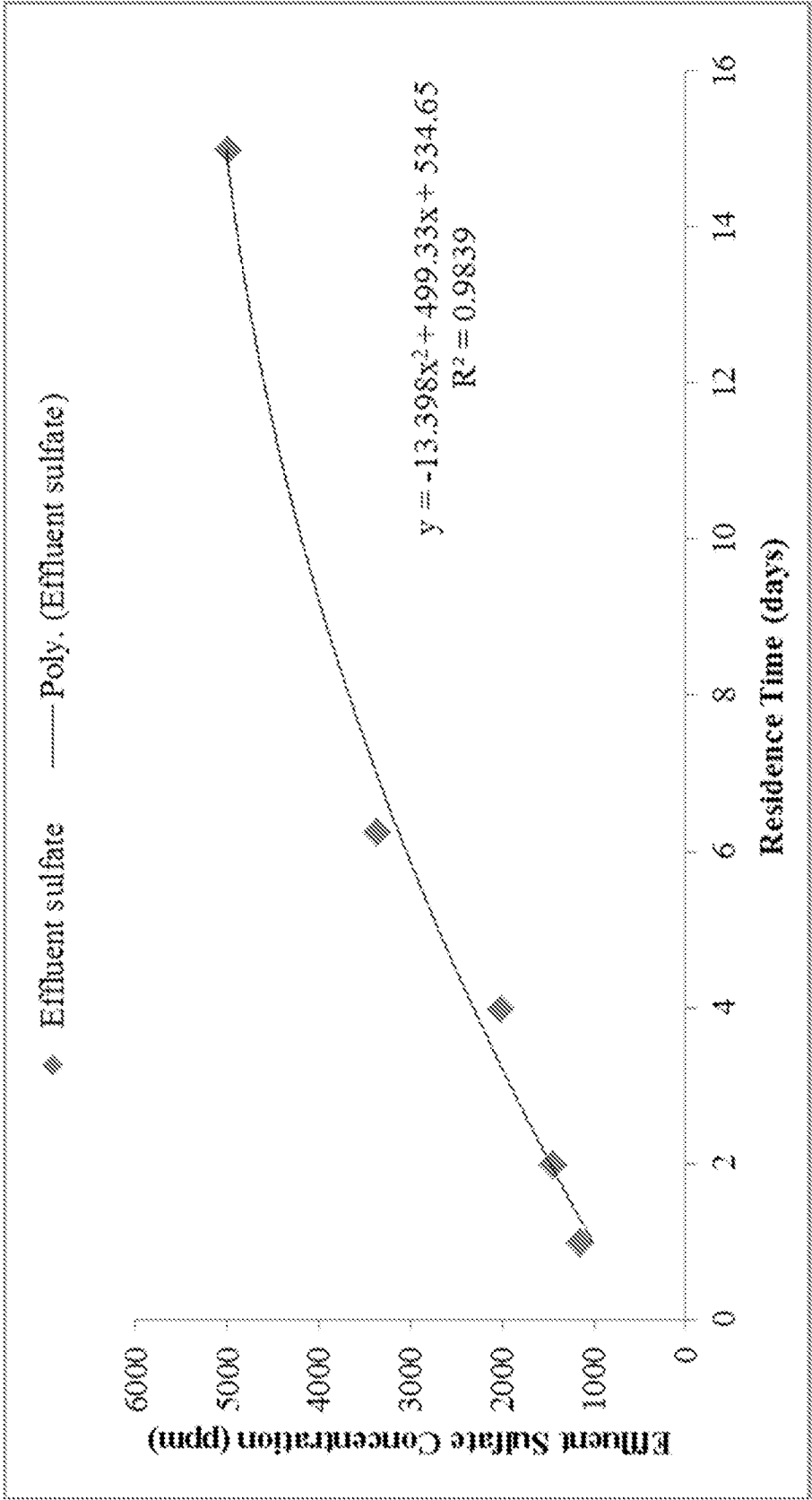


Figure 10

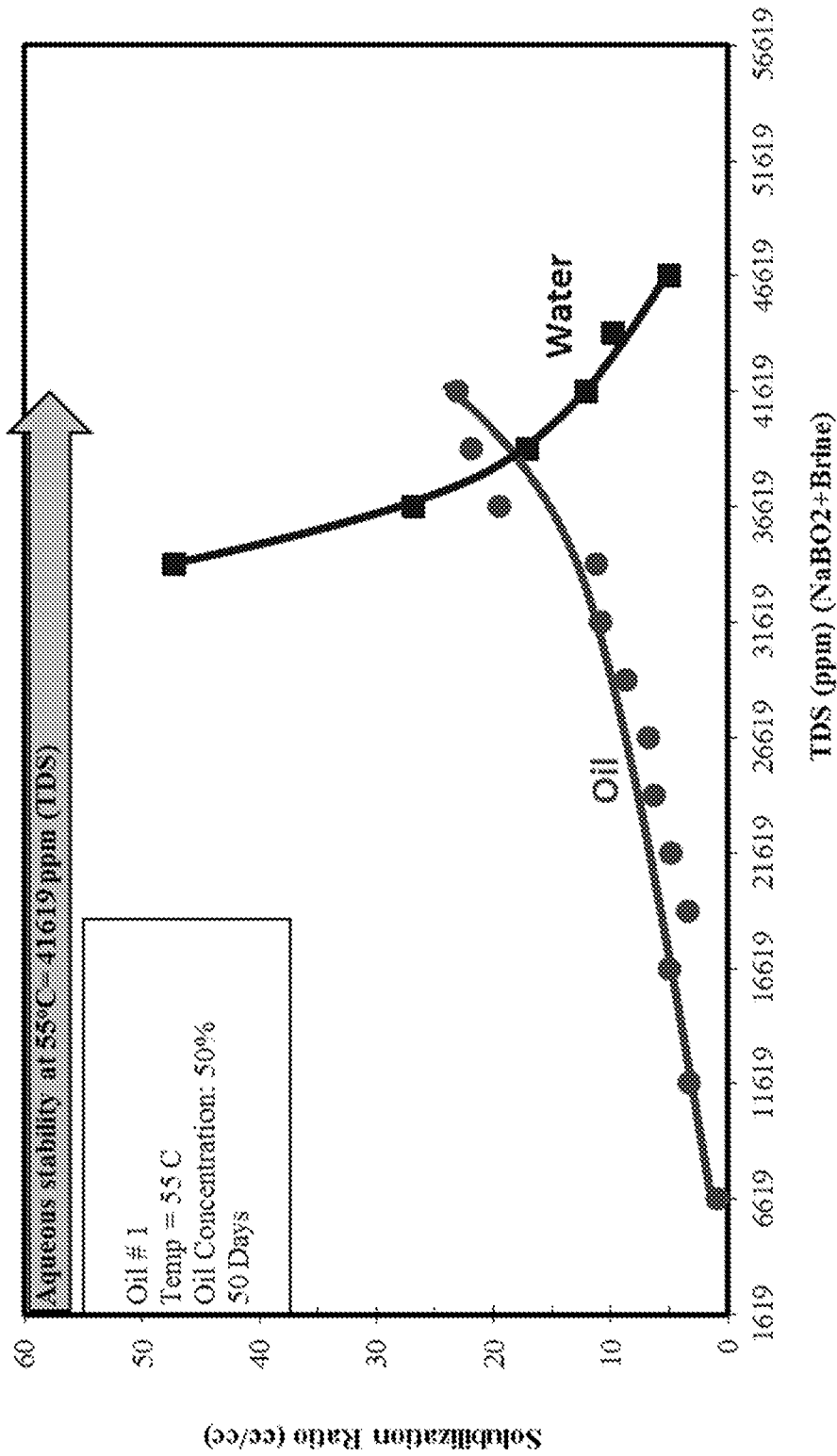


Figure 11

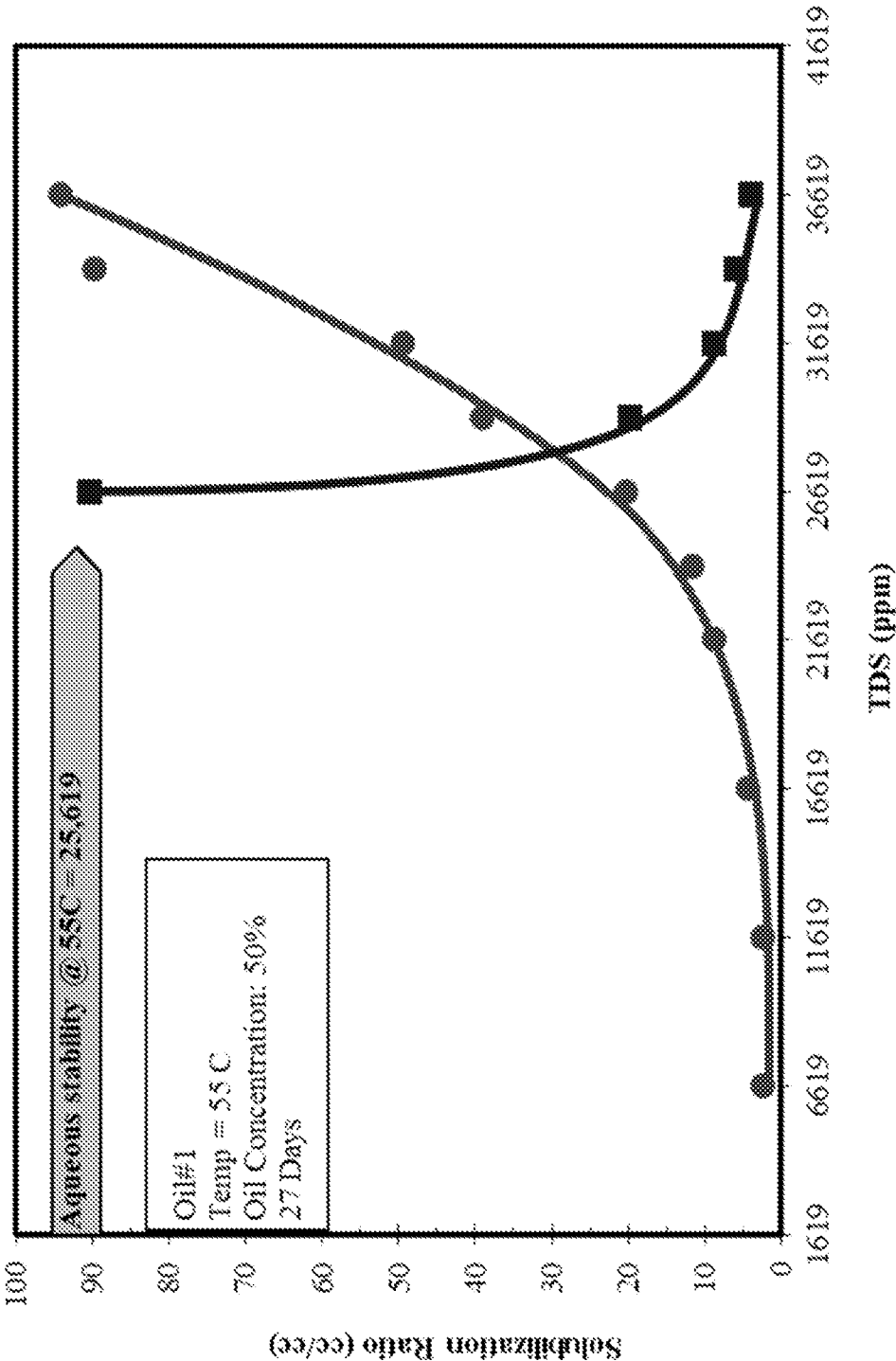


Figure 12

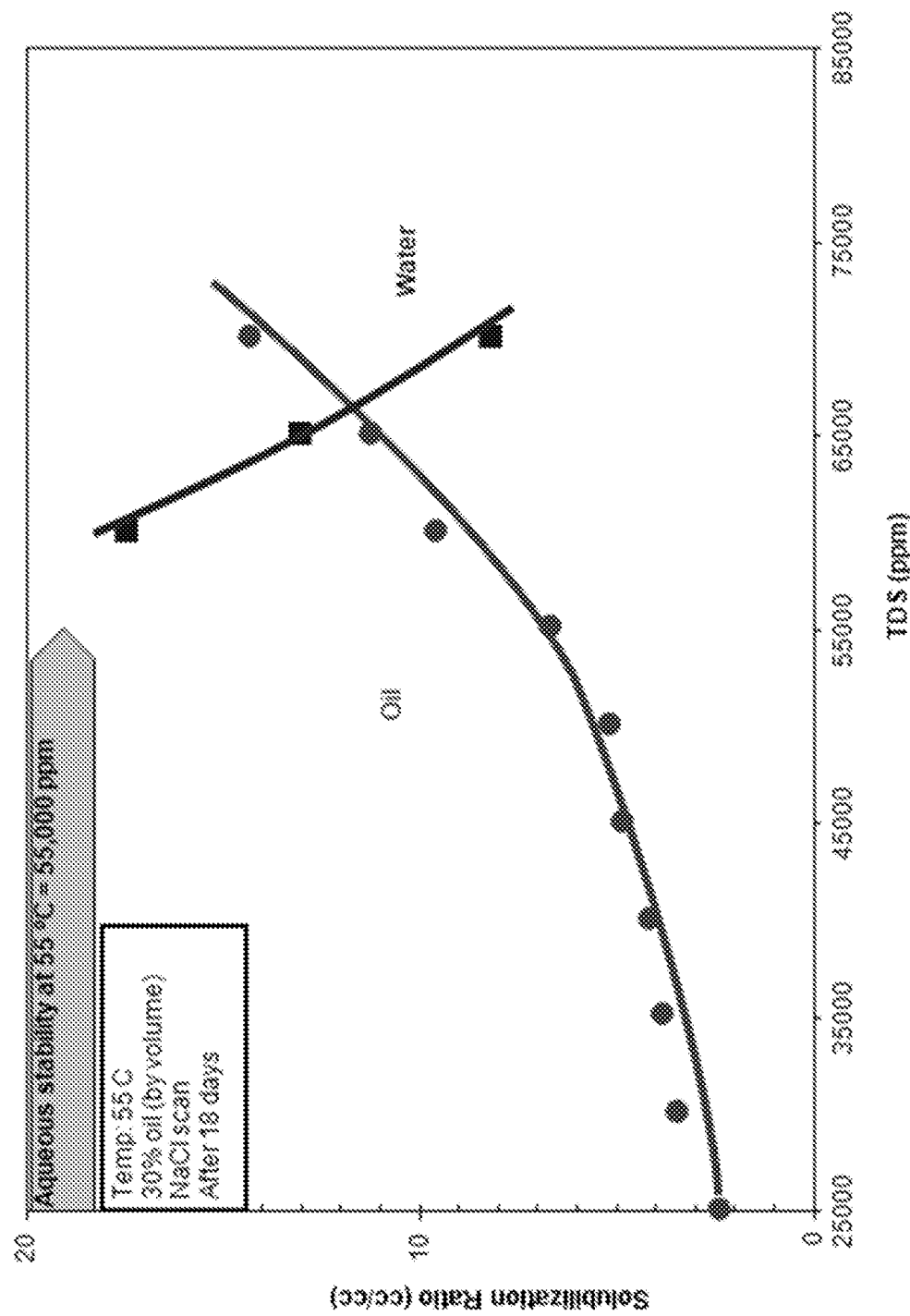


Figure 13

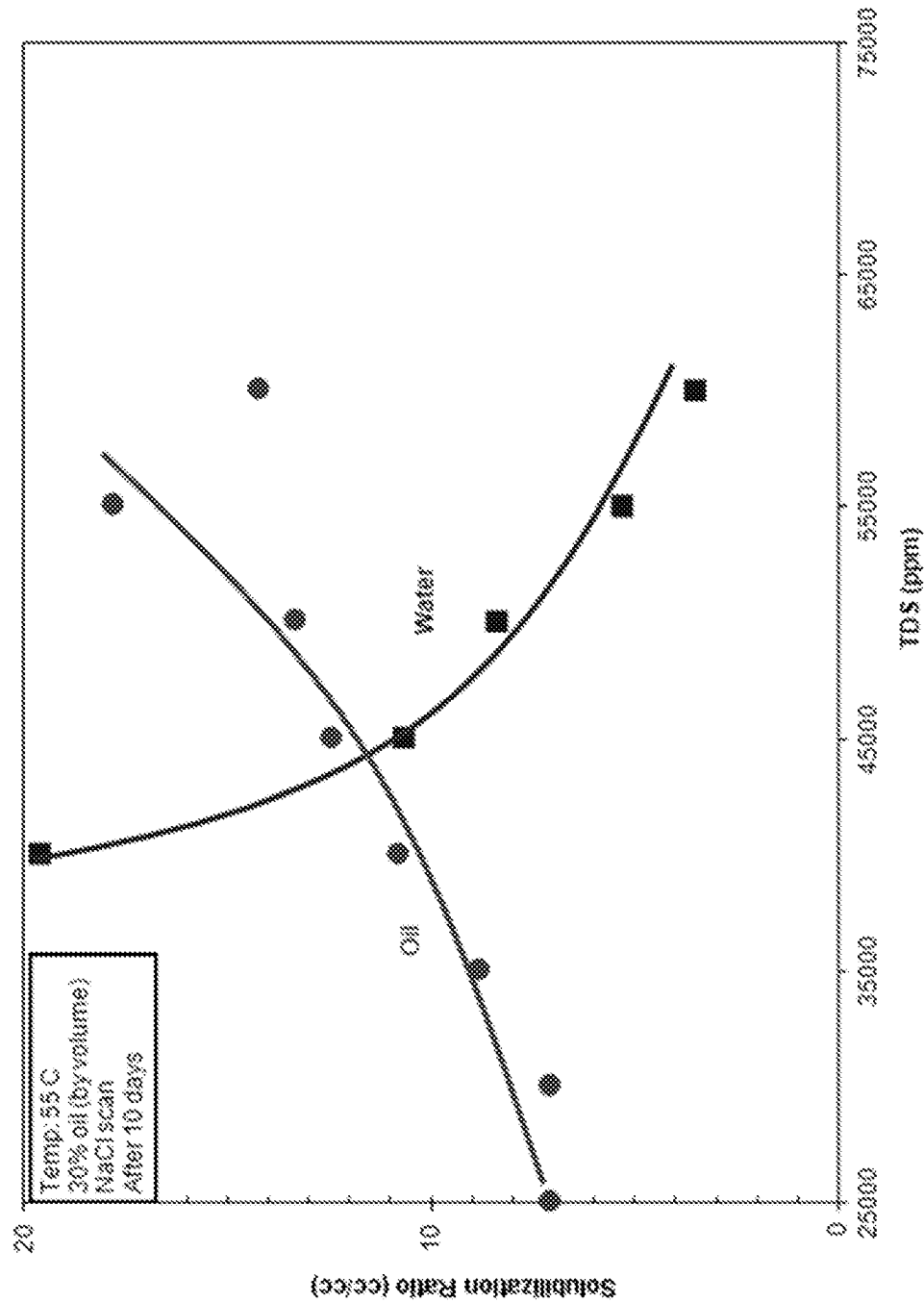


Figure 14



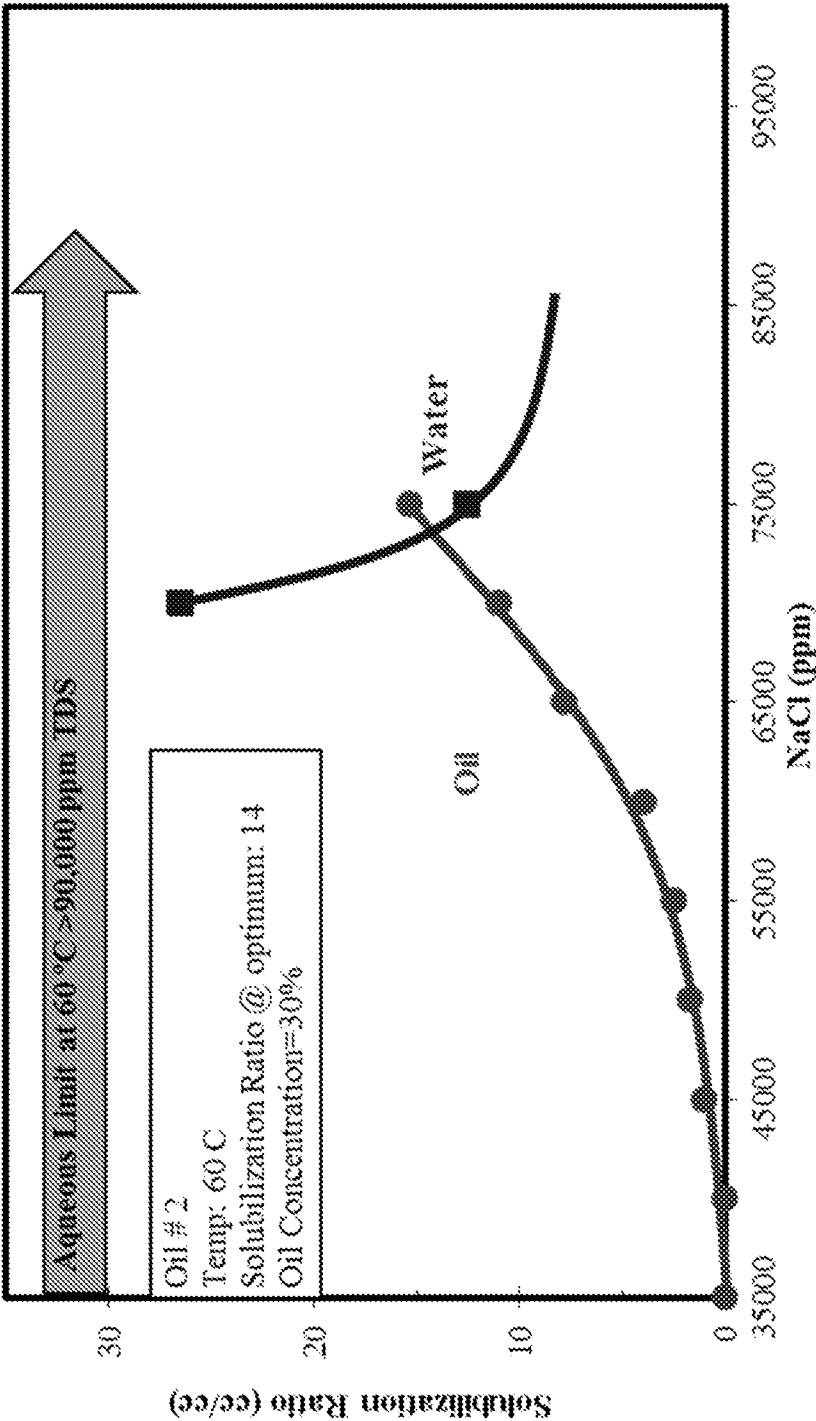


Figure 15

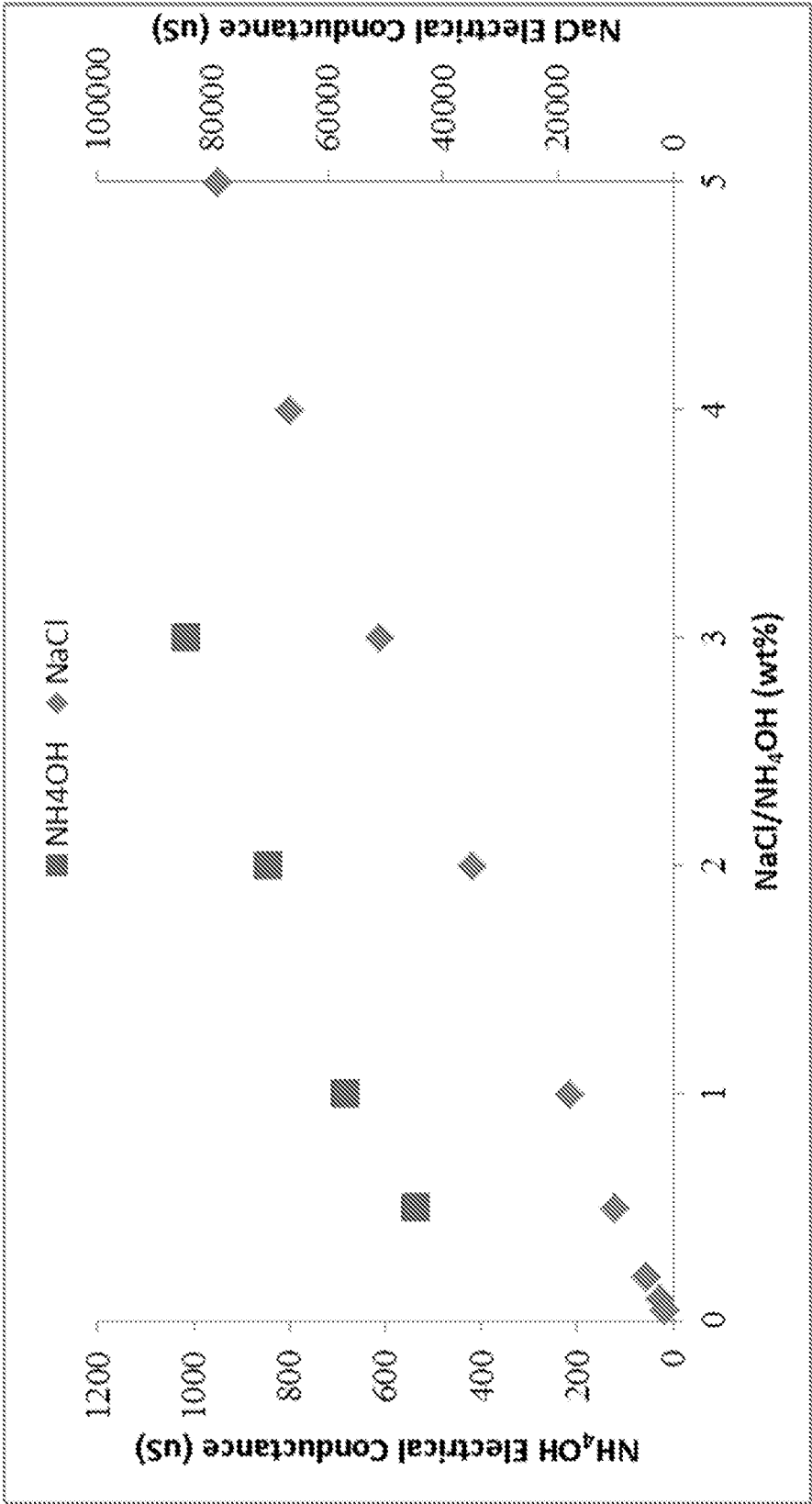


Figure 16

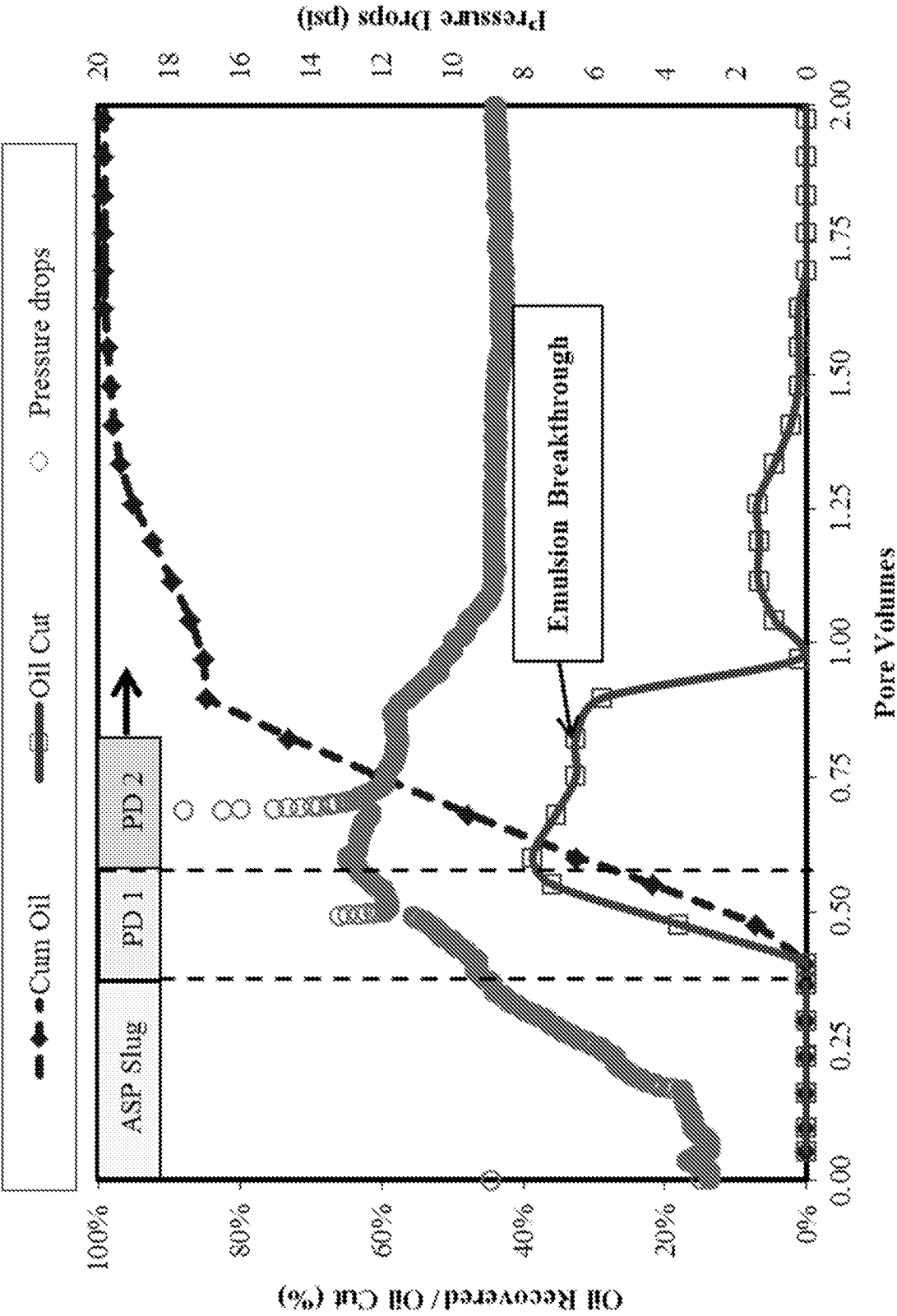


Figure 17

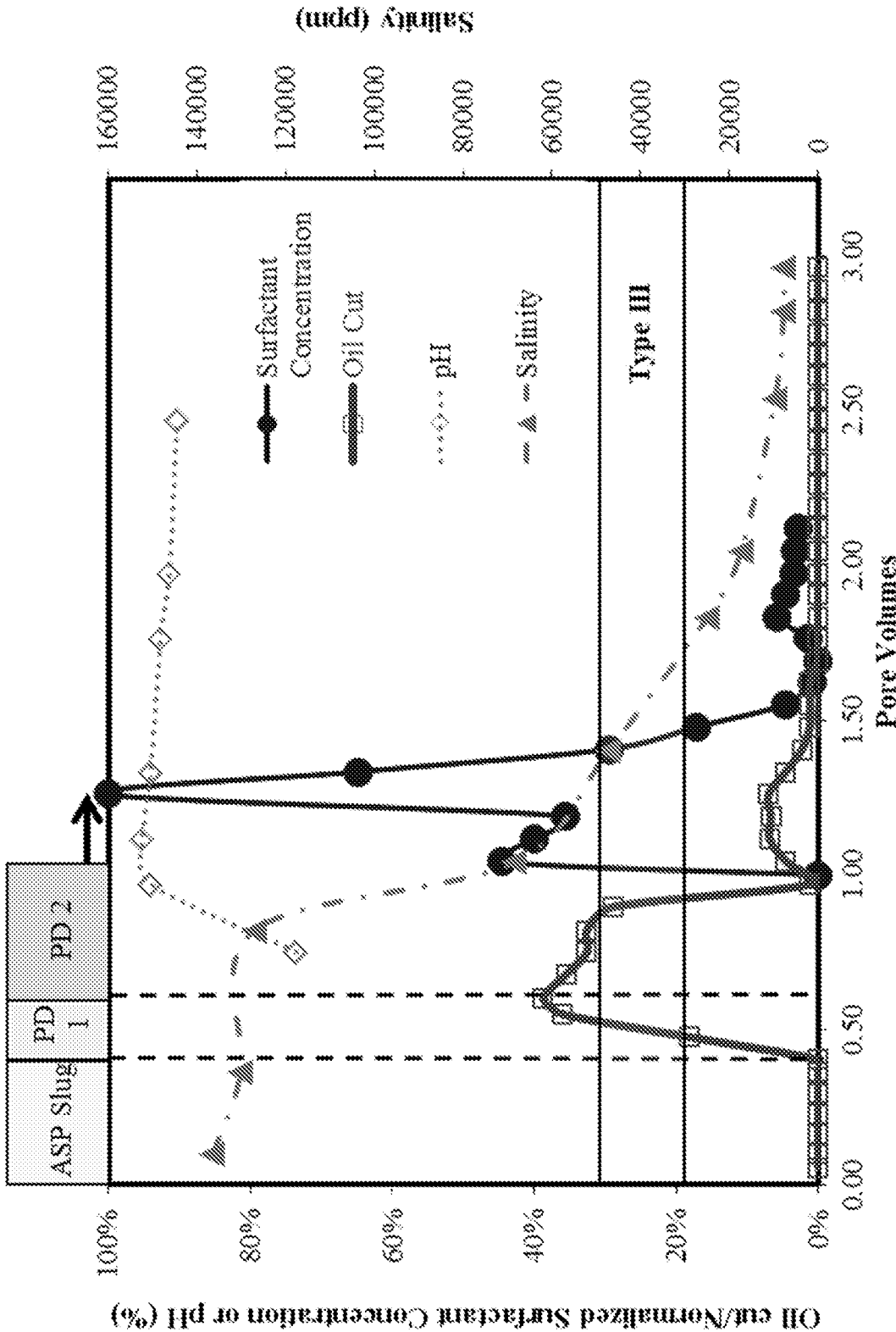


Figure 18

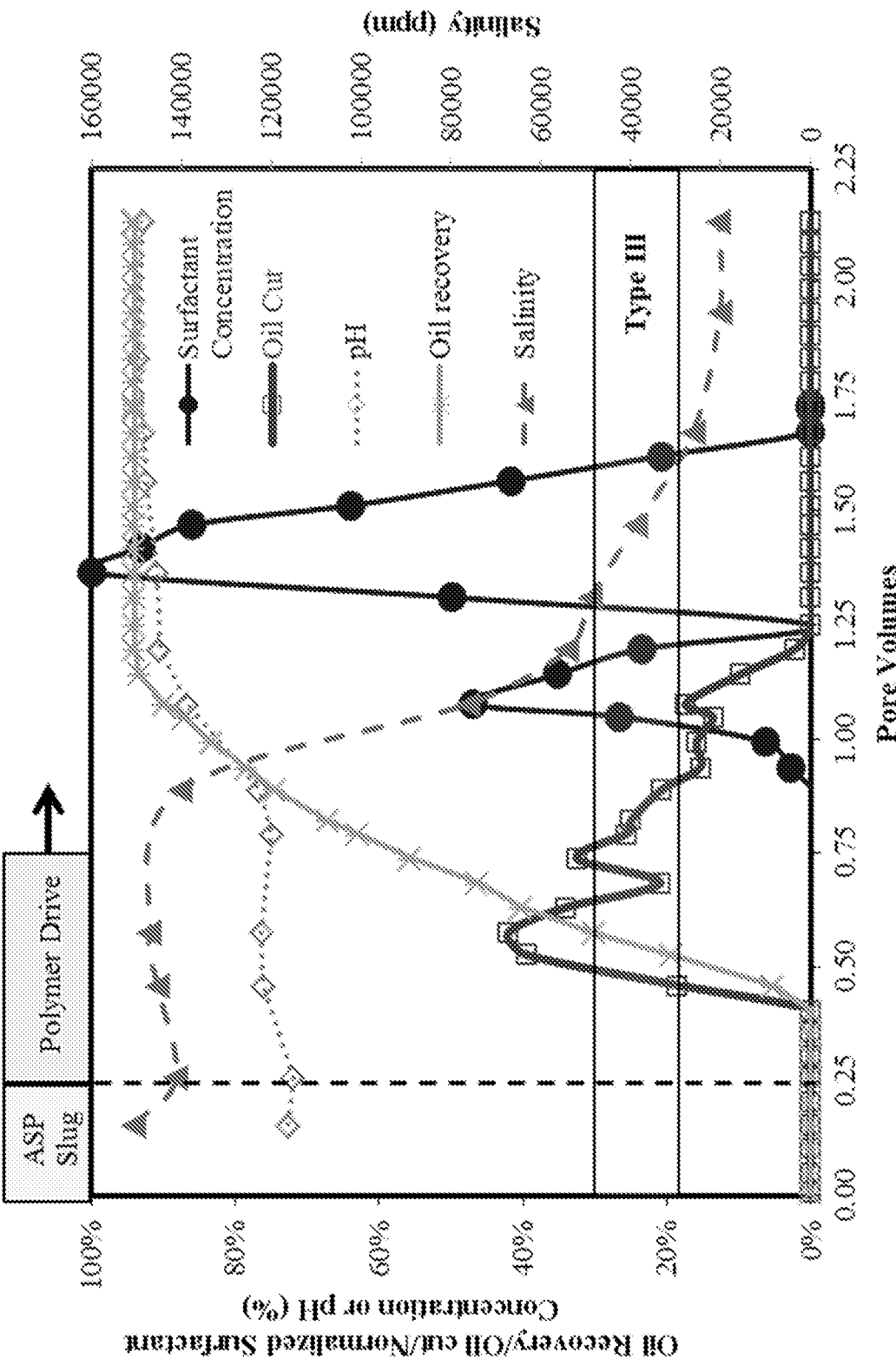


Figure 19

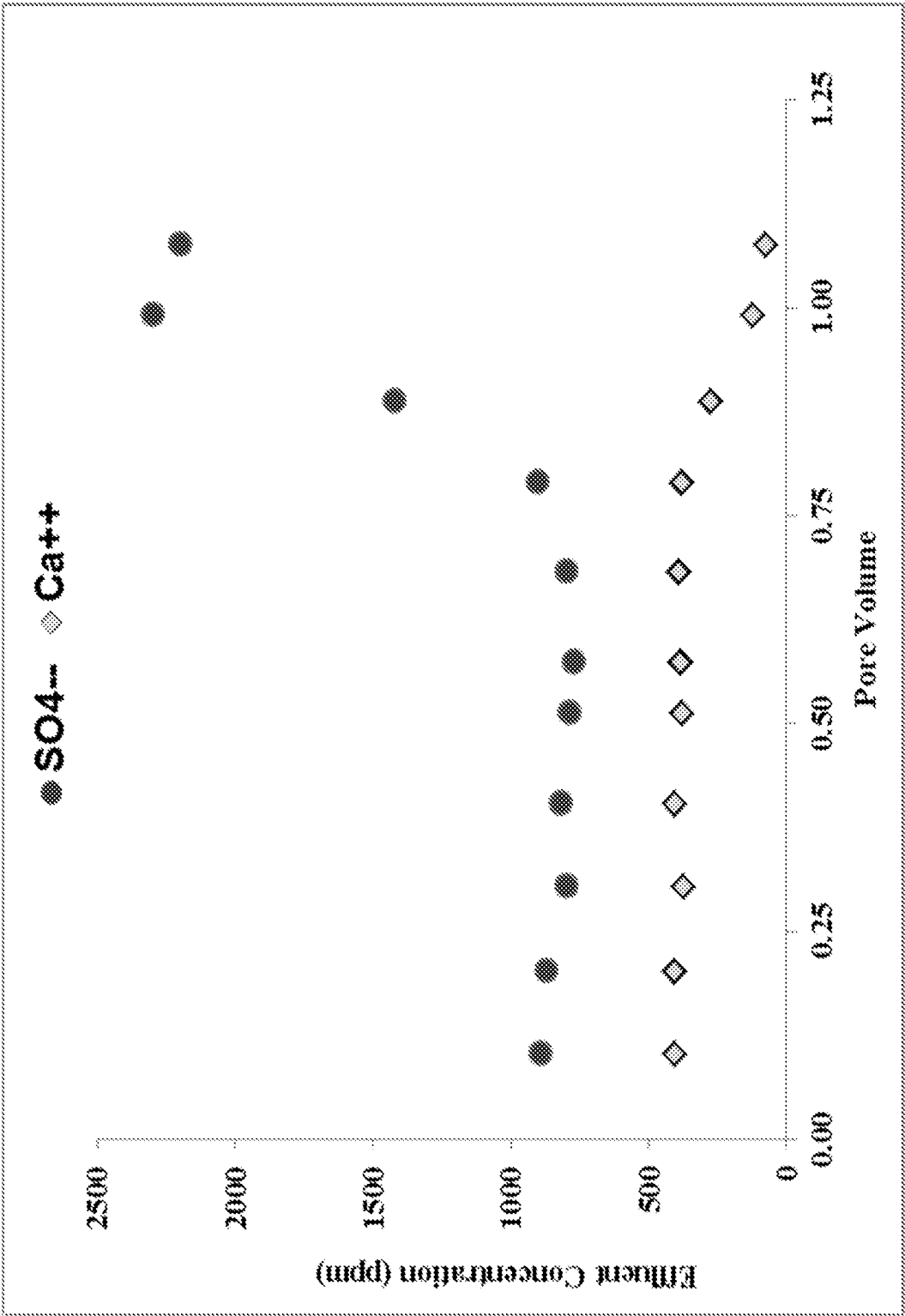


Figure 20

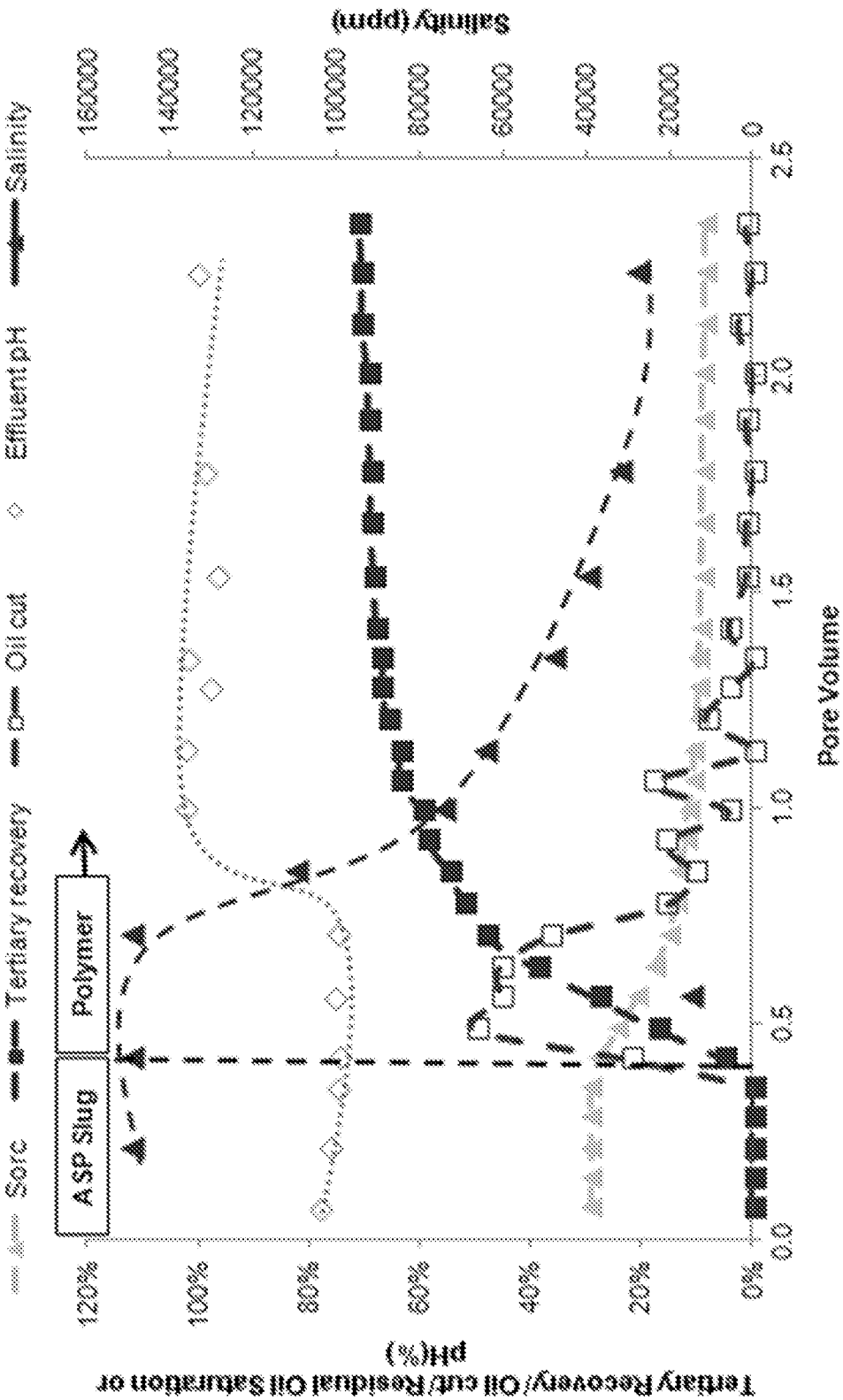


Figure 21

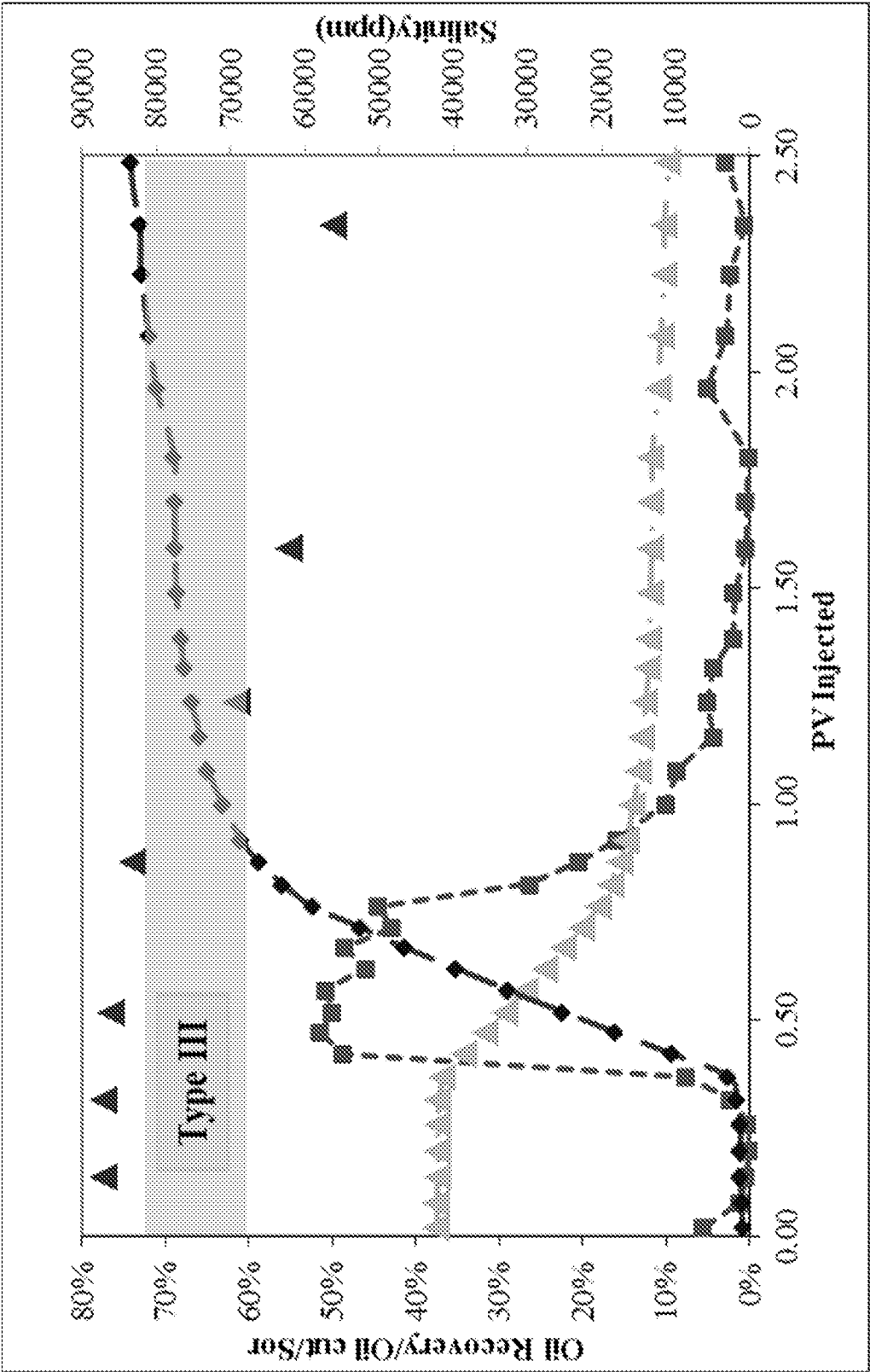


Figure 22



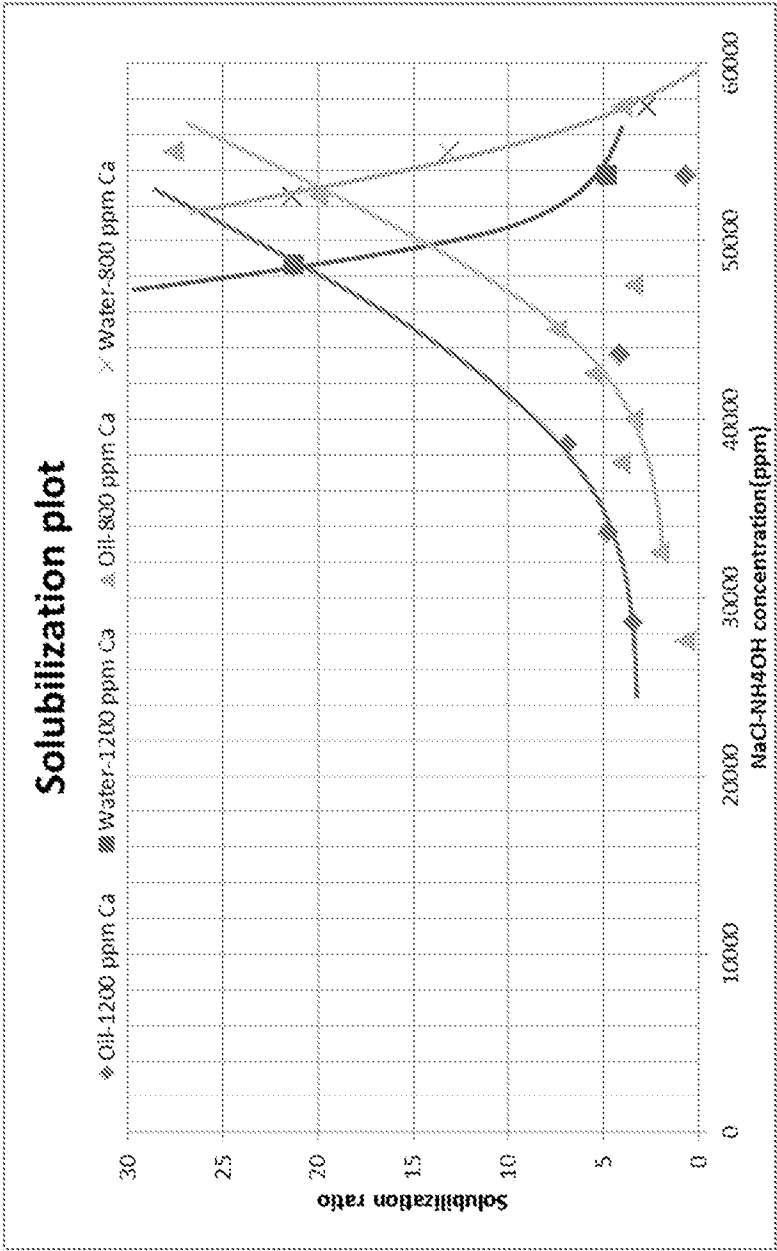


Figure 23

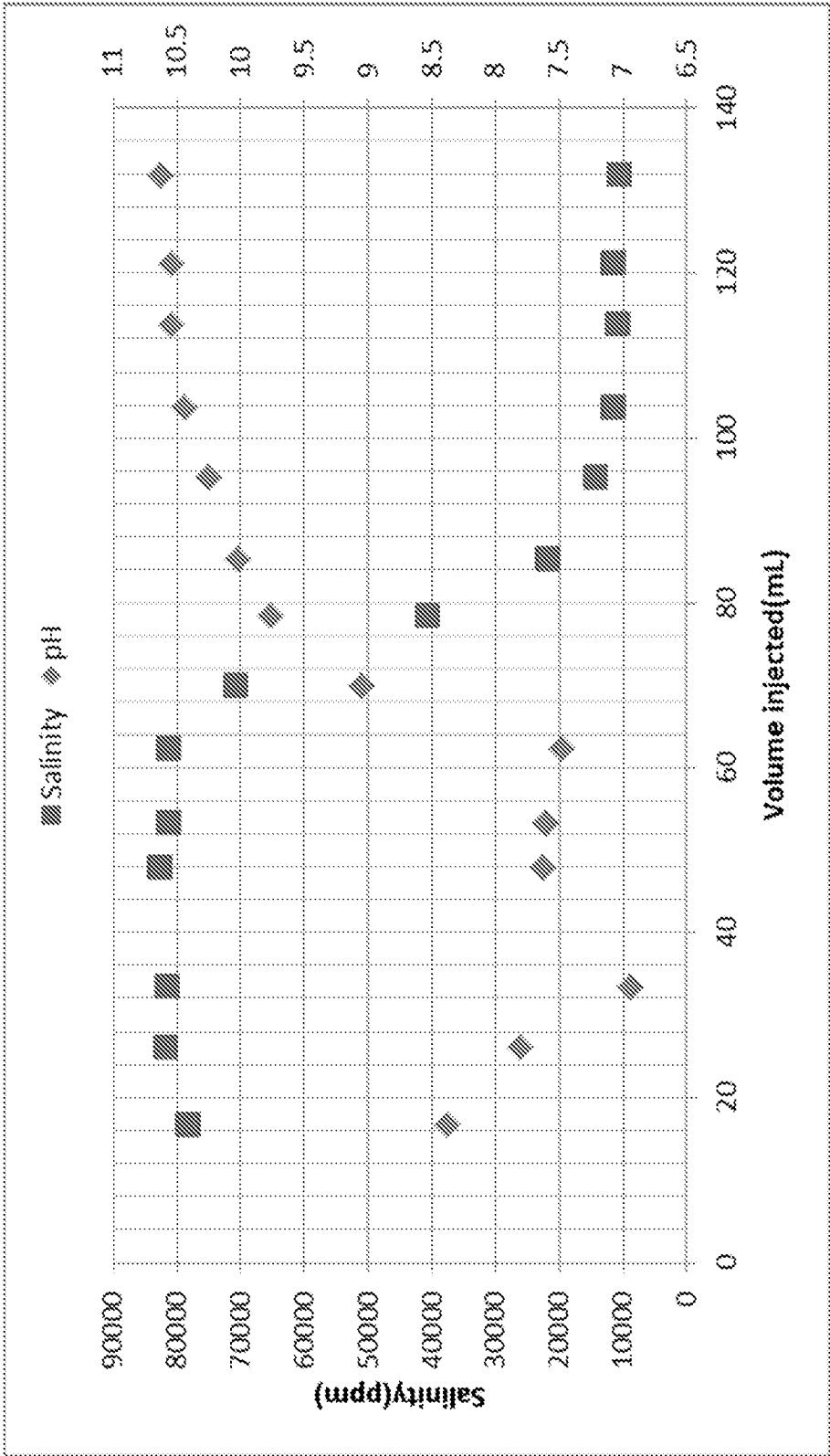


Figure 24

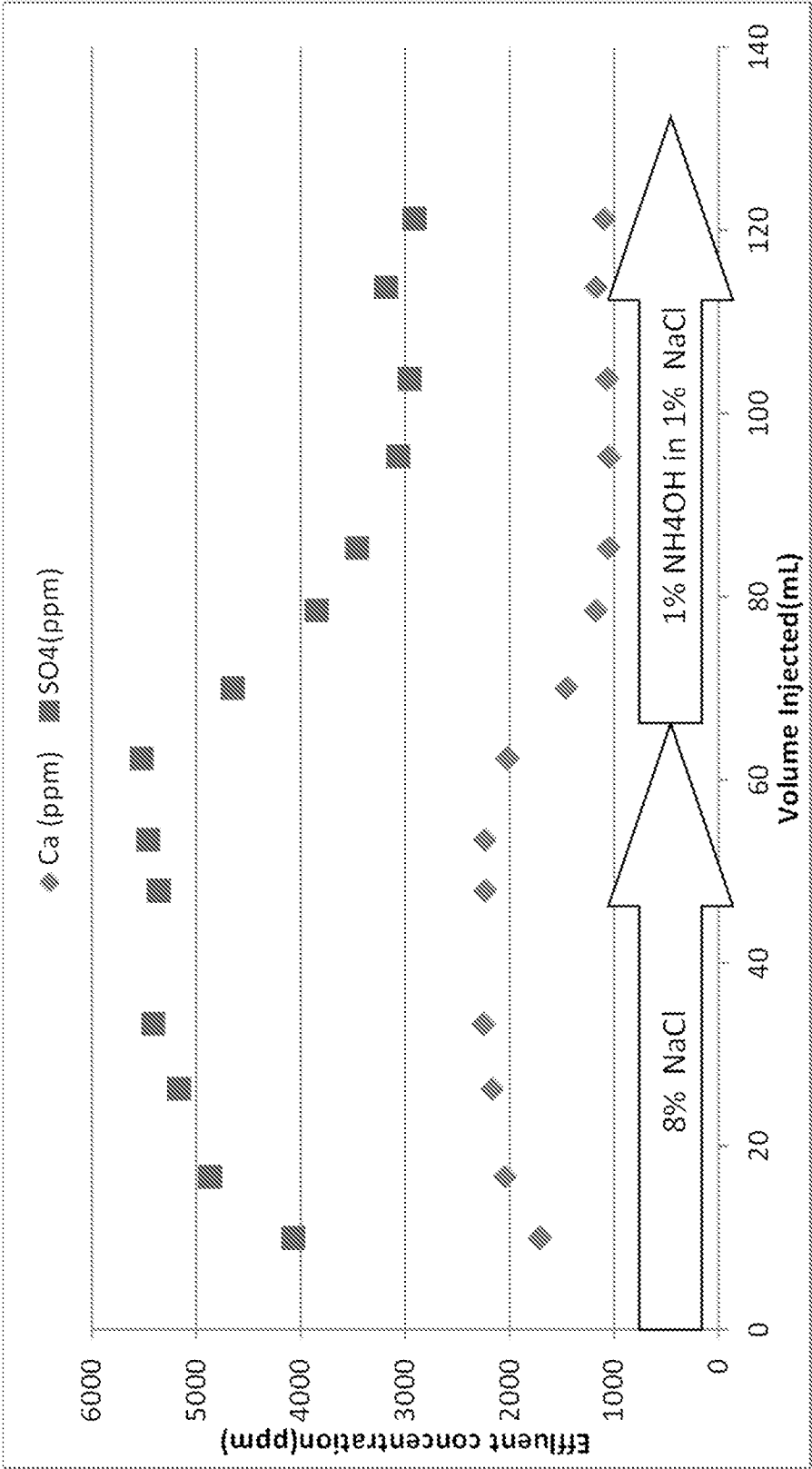


Figure 25

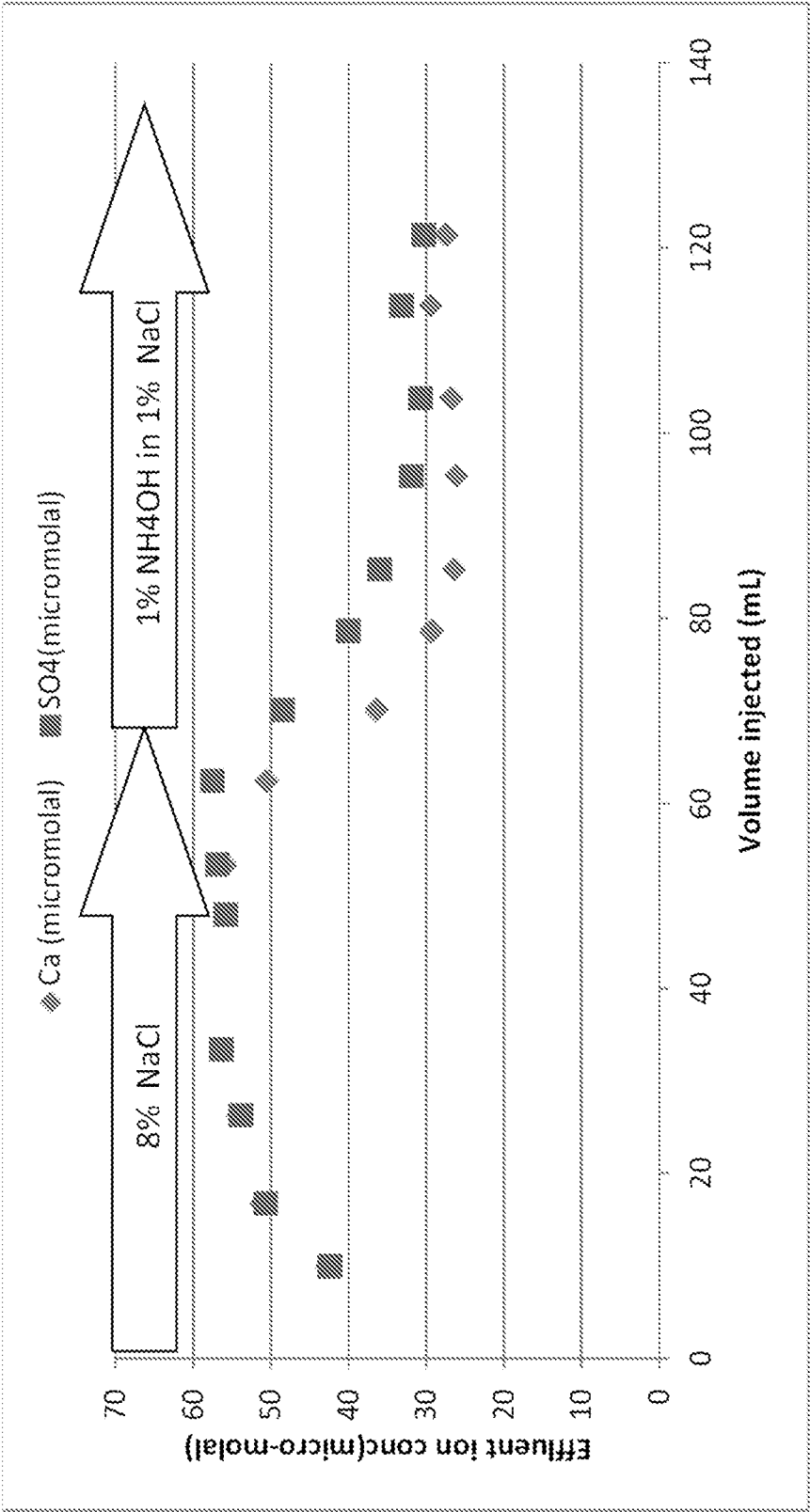


Figure 26

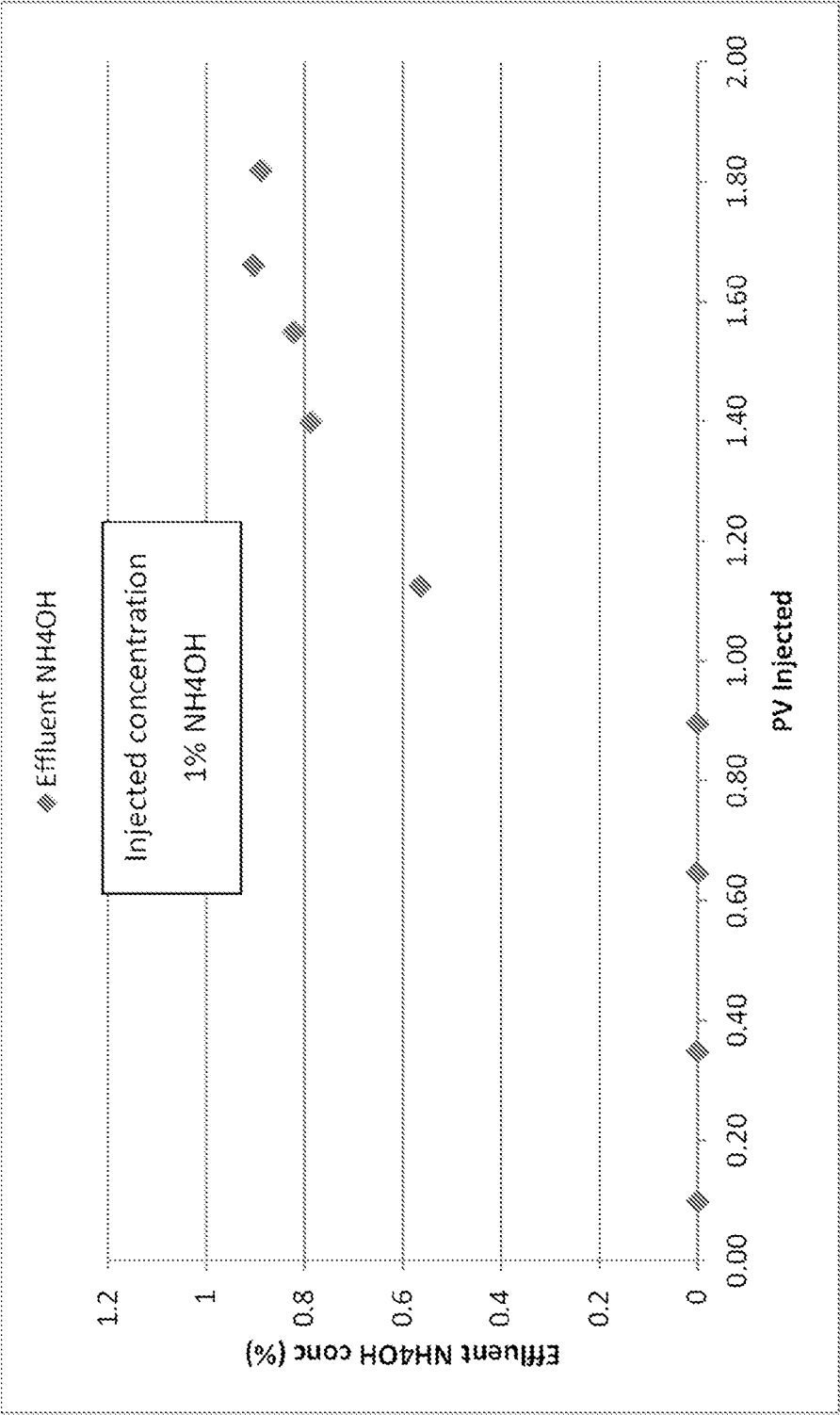


Figure 27

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Figure 28

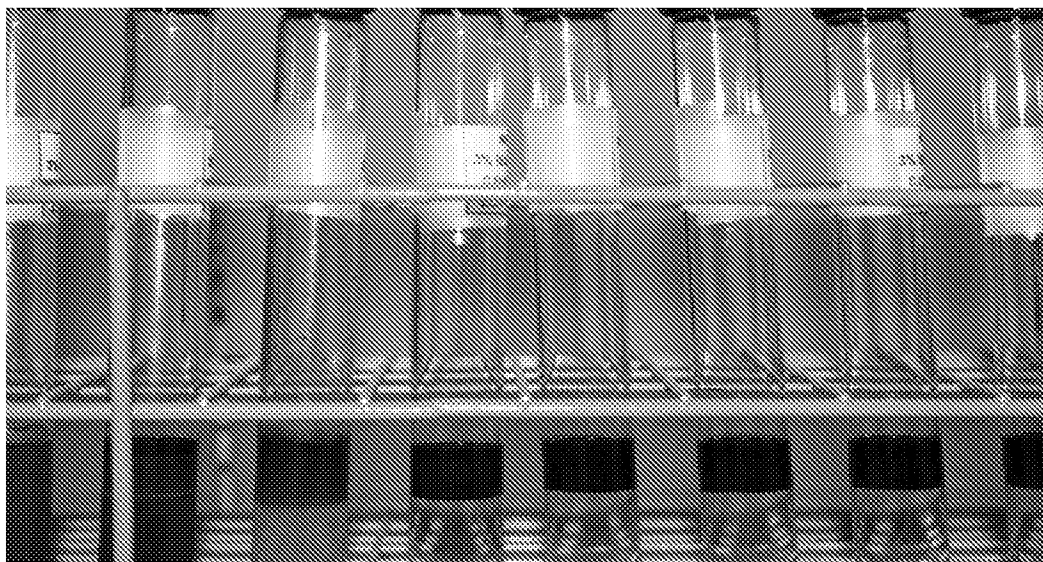


Figure 29

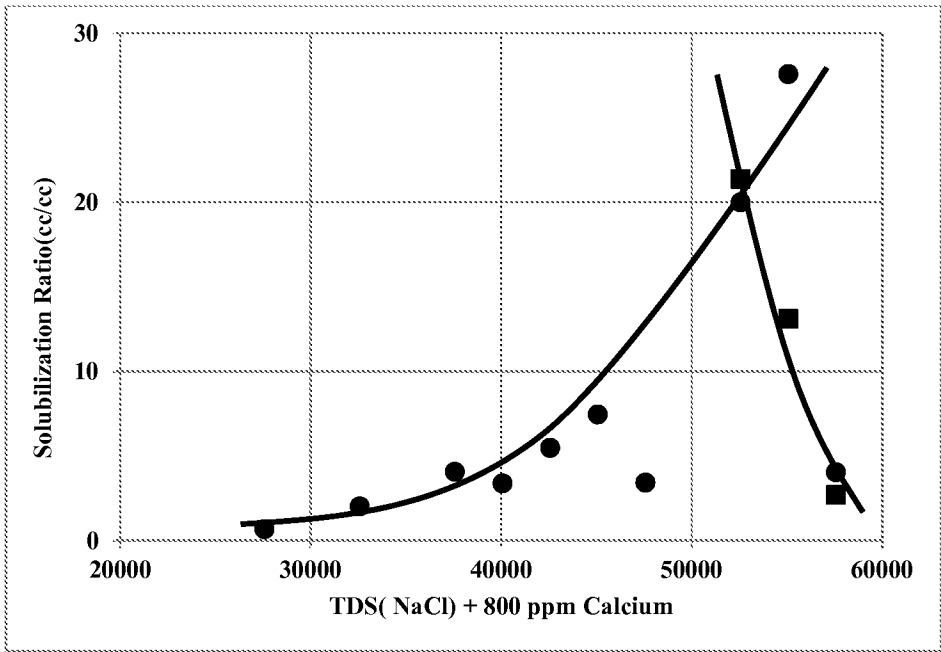


Figure 30

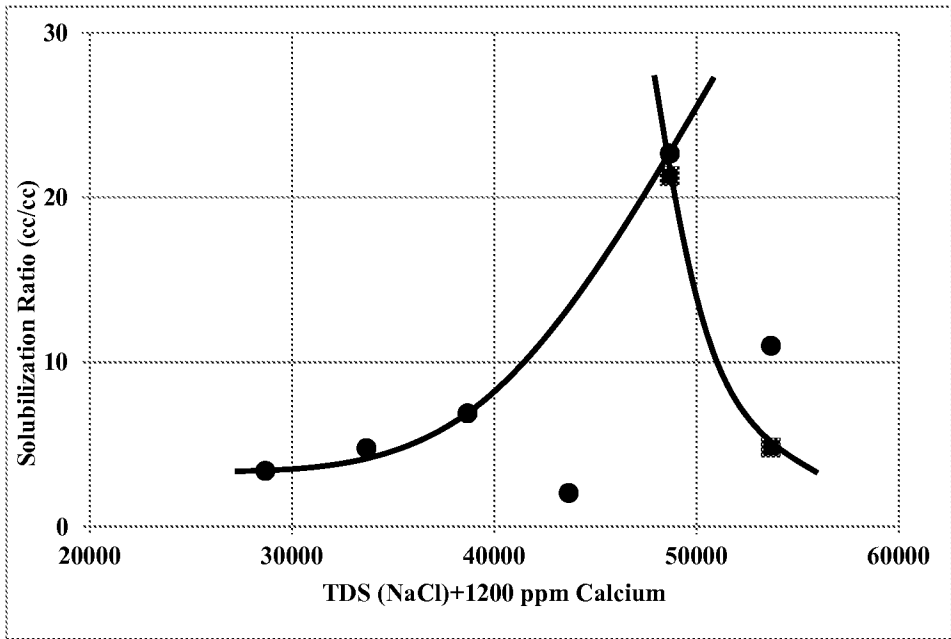


Figure 31

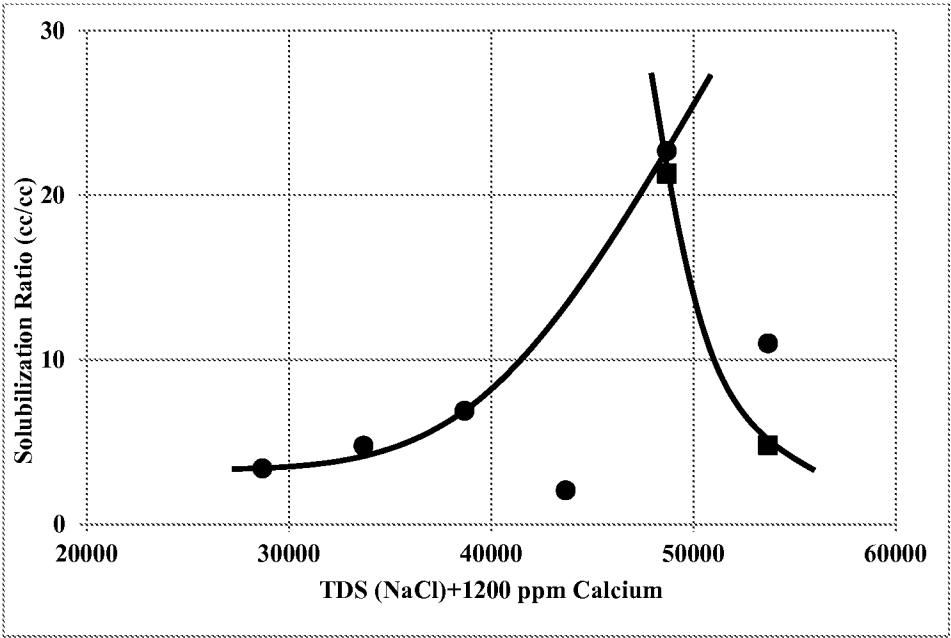


Figure 32

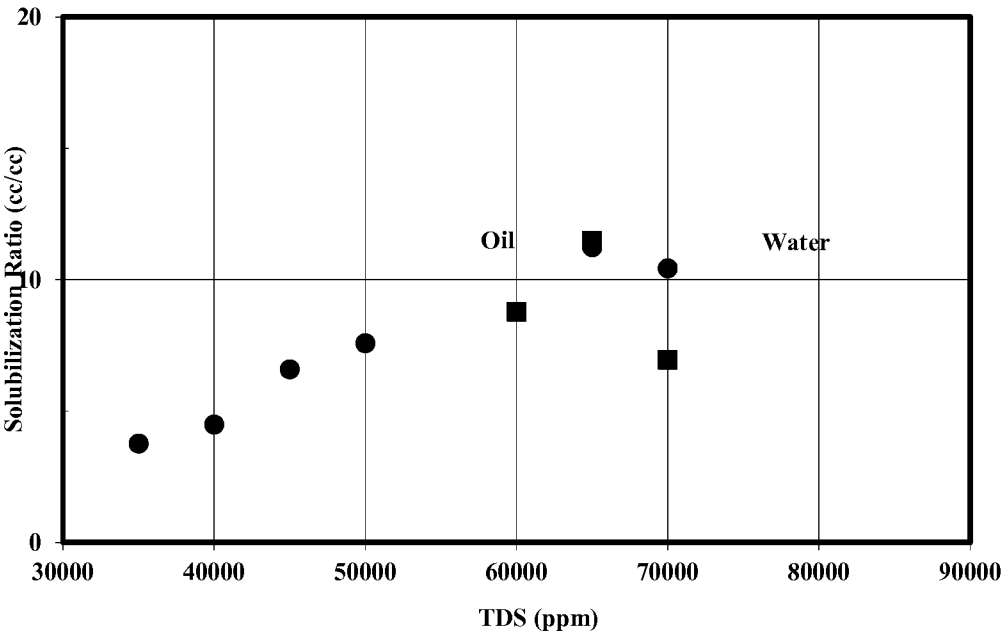


Figure 33



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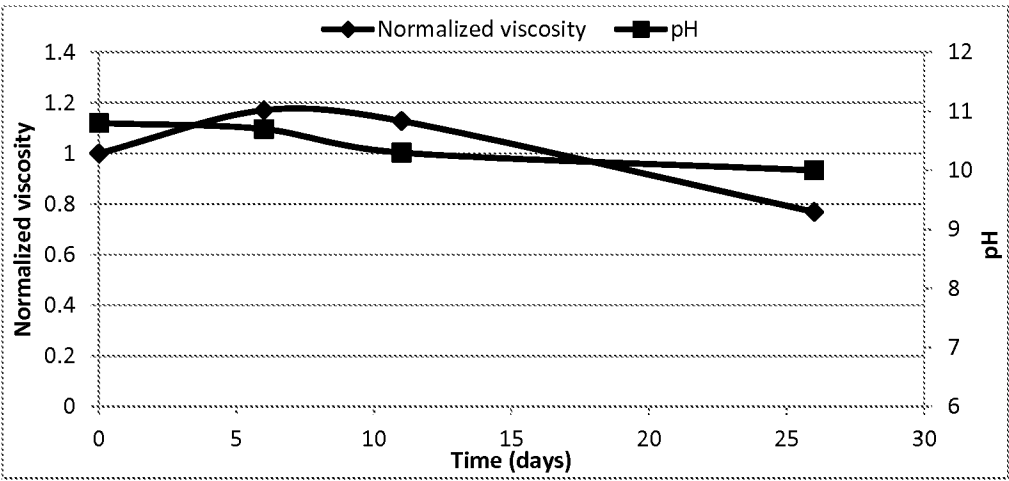


Figure 34

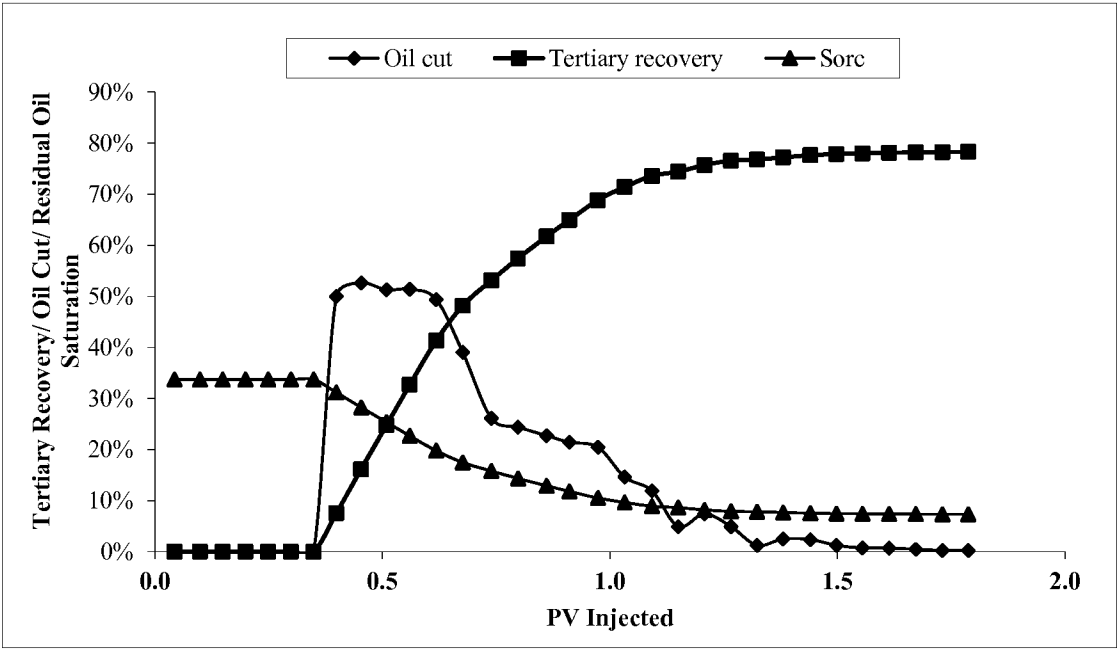


Figure 35

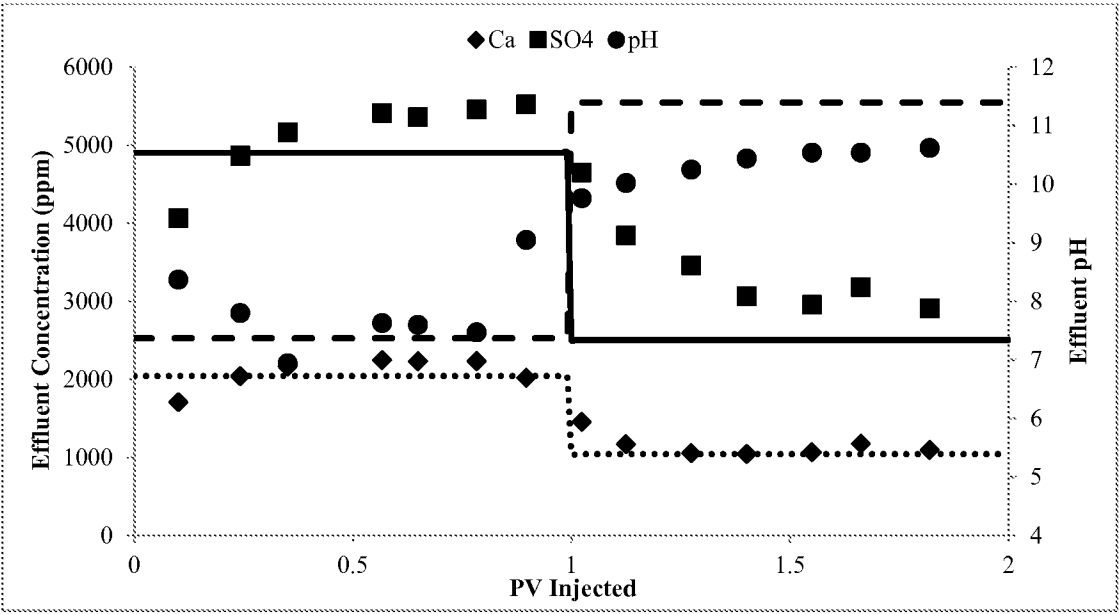


Figure 36

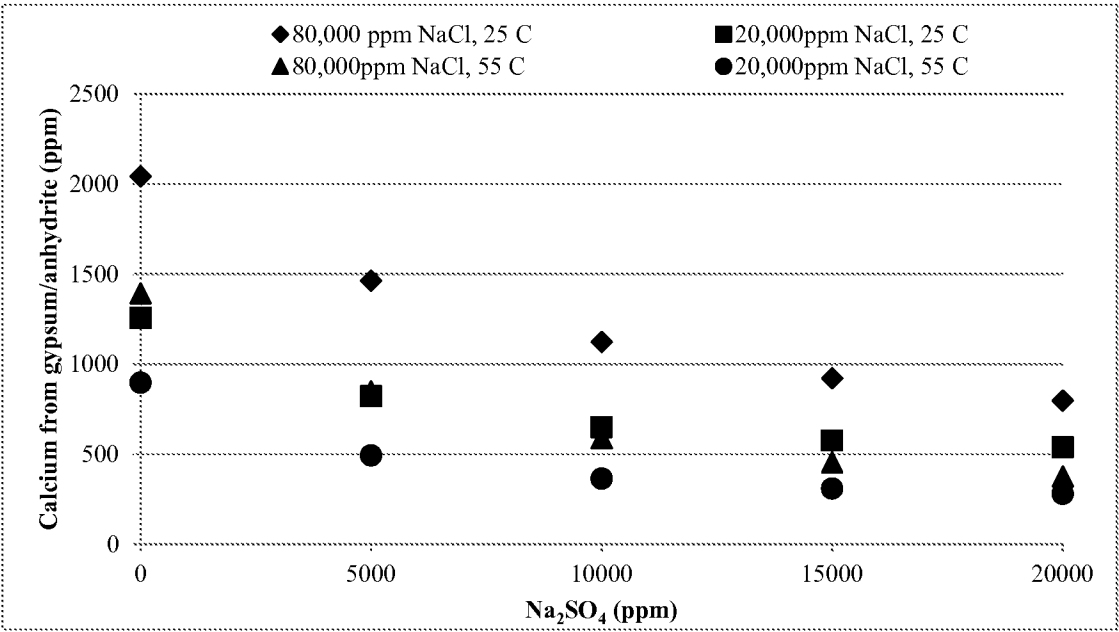


Figure 37

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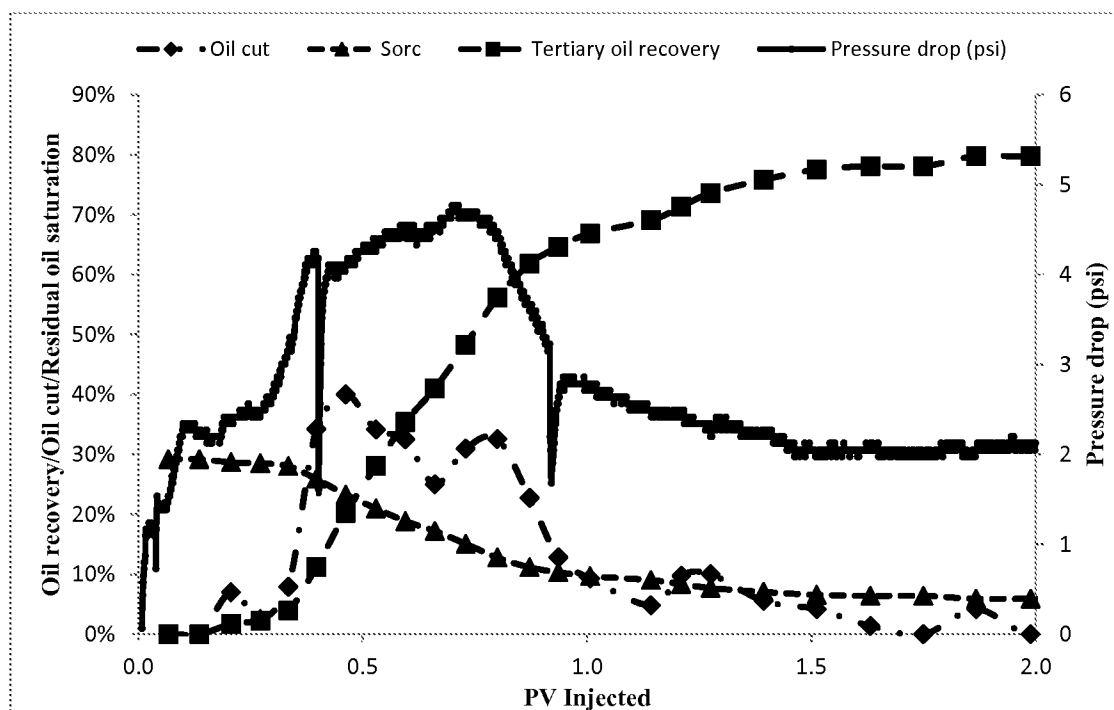


Figure 38

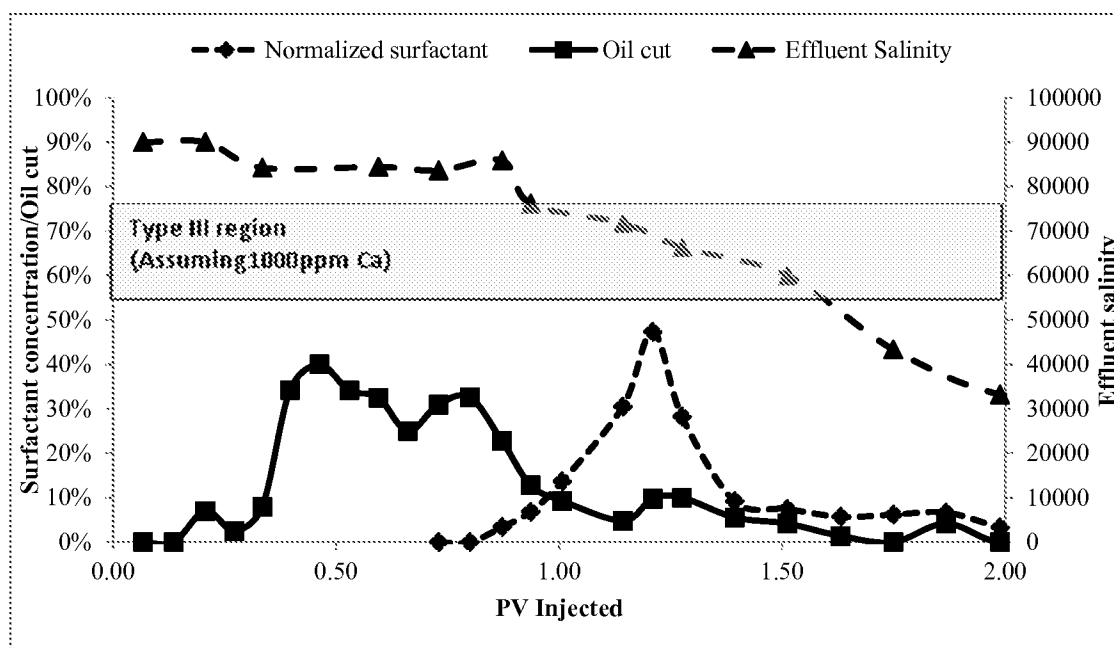


Figure 39

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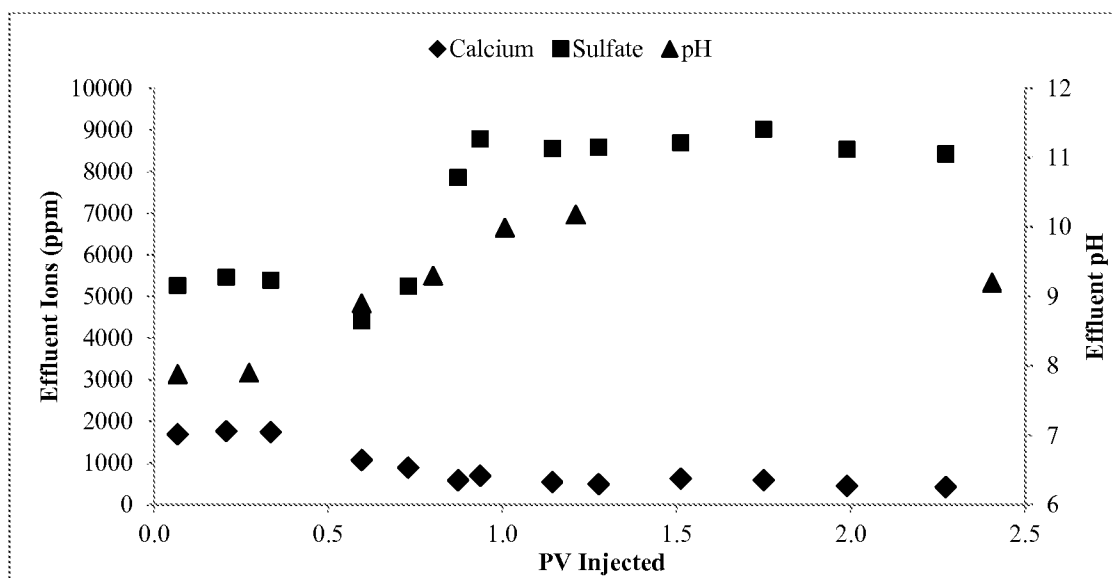


Figure 40

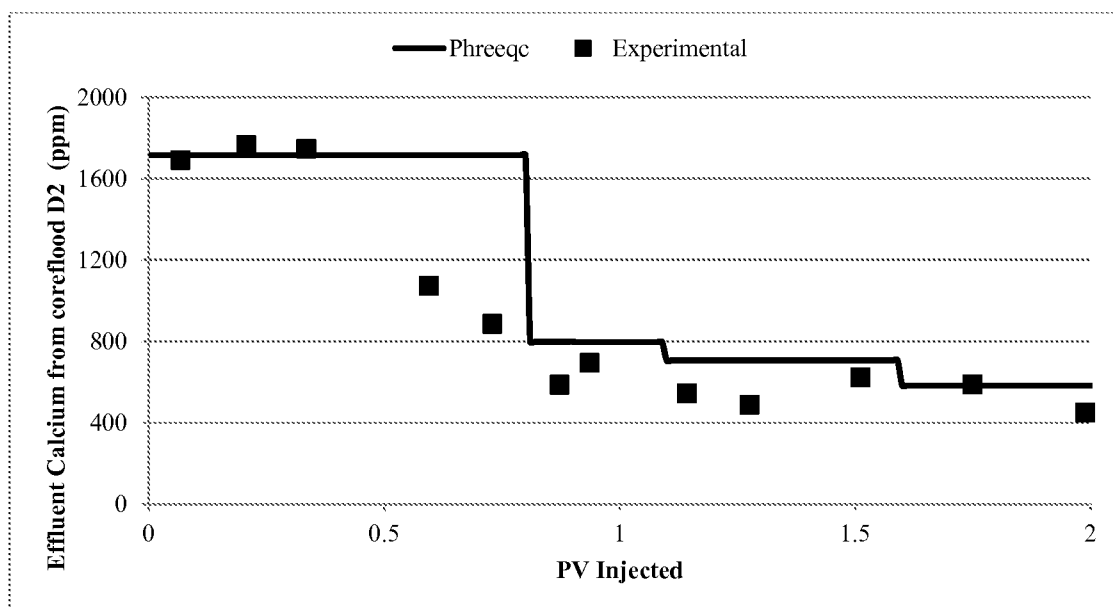


Figure 41

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/19695

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - E21B 43/22; C09K 8/035; C09K 8/60 (2015.01)

CPC - C09K 8/584; C09K 8/05

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): E21B 43/22; C09K 8/035; C09K 8/60 (2015.01)

CPC: C09K 8/584; C09K 8/05

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
USPC: 166/308.3; 166/270.1; 507/239

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatBase, Google Scholar, PubWEST

hydrocarbon, petroleum, oil, formation, well, recovery, enhanced, improved, tertiary, oil recovery, aqueous ammonia, amine, alkylamine, gypsum, solubilize, surfactant, co-solvent

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 7,559,372 B2 (COBB) 14 July 2009 (14.07.2009) col 2, ln 34 to col 3, ln 5; col 3, ln 16-25; col 4, ln 39-44	1-6, 40-48
Y	US 3,508,612 A (REISBERG et al.) 28 April 1970 (28.04.1970) col 2, ln 34-55; col 4, ln 71 to col 5, ln 3	1-6, 40-48
Y	US 7,938,183 B2 (HART et al.) 10 May 2011 (10.05.2011) abstract; col 9, ln 24-37; col 10, Table 2	5, 47

☐ Further documents are listed in the continuation of Box C.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

24 April 2015 (24.04.2015)

Date of mailing of the international search report

29 MAY 2015

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents  
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/19695

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 7-39 and 49-75  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.