

ABSTRACT**EMULSION STABILIZING AGENTS FOR DRILLING AND COMPLETION FLUIDS**

The present invention provides a stabilized emulsion composition comprising: an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound. The present invention also provides methods involving the use of the stabilized emulsion composition and methods of preparing the stabilized emulsion composition.

WE CLAIM

1. A stabilized emulsion composition comprising: an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound.
2. A stabilized emulsion composition according to claim 1, wherein the first ionic compound, the second ionic compound, or both comprise an ionic surfactant.
3. A stabilized emulsion composition according to claim 1 or 2, wherein the first ionic compound, the second ionic compound, or both comprise an ionic polyelectrolyte.
4. A stabilized emulsion composition according to claim 2 or claim 3 when dependent on claim 2, wherein the ionic surfactant comprises an anionic surfactant.
5. A stabilized emulsion composition according to claim 4, wherein the anionic surfactant comprises at least one compound selected from the group consisting of: an alkyl carboxylate, an alkylether carboxylate, a N-acylaminoacid, a N-acylglutamate, a N-acylpolypeptide, an alkylbenzenesulfonate, a paraffinic sulfonate, an α -olefinsulfonate, a lignosulfate, a derivative of a sulfosuccinate, a polynaphthylmethylsulfonate, an alkyl sulfate, an alkylethersulfate, a monoalkylphosphate, a polyalkylphosphate, a fatty acid, an alkali salt of an acid, an alkali salt of a fatty acid, an alkaline salt of an acid, a sodium salt of an acid, a sodium salt of a fatty acid, an alkyl ethoxylate, a soap, a combination thereof, and a derivative thereof.
6. A stabilized emulsion composition according to claim 2 or any claim dependent on claim 2, wherein the ionic surfactant comprises a cationic surfactant.
7. A stabilized emulsion composition according to claim 6, wherein the cationic surfactant comprises at least one compound selected from the group consisting of: an alkyl amine, an alkyl amine salt, a quaternary ammonium salt, an ethoxylated quaternary ammonium salt, an amine

oxide, an alkyltrimethyl amine, a triethyl amine, an alkyldimethylbenzylamine, a derivative thereof, and a combination thereof.

8. A stablized emulsion composition according to claim 3 or any claim dependent on claim 3, wherein the ionic polyelectrolyte comprises an anionic polyelectrolyte.

9. A stablized emulsion composition according to claim 8, wherein the anionic polyelectrolyte comprises at least one compound selected from the group consisting of: a polymer or copolymer comprising a carboxylate group, a sulfonate group, a phosphate group, a phosphonate group, an acrylate monomer, a methacrylate monomer, a styrene carboxylate, a vinyl sulfonate, a 2-acrylamine-2-methyl-propyl sulfonate, a 3-acrylamide-3-methyl butanoate, a salt of malic acid, a polyacrylic acid, a partially-hydrogenated polyacrylamide, a carboxy methyl cellulose, a cellulose modified with an anionic functional group, a polysaccharide modified with an anionic functional group, a galactomannan modified with an anionic functional group, a derivative thereof, and a combination thereof.

10. A stablized emulsion composition according to claim 3 or any claim dependent on claim 3, wherein the ionic polyelectrolyte comprises a cationic polyelectrolyte.

11. A stablized emulsion composition according to claim 10, wherein the cationic polyelectrolyte comprises at least one compound selected from the group consisting of: a polyethylene imine, a polyamide amine, a polyamine, a vinyl benzyl trimethyl ammonium chloride, a dimethyldiallyl ammonium chloride, a 3-acrylamido-3-methyl butyl trimethyl ammonium chloride, a polyvinylpyrrolidone, chitosan modified with a cationic functional group, a gelatin modified with a cationic functional group, a galactomannan modified with a cationic functional group, a cellulose modified with a cationic functional group, a derivative thereof, and a combination thereof.

12. A stablized emulsion composition according to any preceding claim, wherein the oleaginous fluid comprises at least one fluid selected from the group consisting of: a diesel oil, a crude oil, a paraffin oil, a mineral oil, a low toxicity mineral oil, an olefin, an ester, an amide, an amine, a polyolefin, a polydiorganosiloxane, a siloxane, an organosiloxane, an ether, an acetal, a dialkylcarbonate, a hydrocarbon, a derivative thereof, and a combination thereof.

13. A stablized emulsion composition according to any preceding claim, wherein the fluid that is at least partially immiscible with the oleaginous fluid comprises at least one fluid selected from the group consisting of: glycerin, a glycol, a polyglycol amine, a polyol, fresh water, sea water, salt water, a brine, a derivative thereof, and a combination thereof.

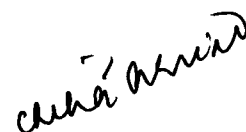
14. A method comprising: providing a stabilized emulsion composition according to any one of claims 1 to 13; and placing the stabilized emulsion composition in a subterranean formation as part of a subterranean application.

15. A method comprising: providing a stabilized emulsion composition according to any one of claims 1 to 13; and drilling a well bore in a subterranean formation using the stabilized emulsion composition.

16. A method of preparing a stabilized emulsion composition, the method comprising: providing an oleaginous fluid; providing a fluid that is at least partially immiscible with the oleaginous fluid; providing an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises: a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound; and combining the oleaginous fluid, the fluid that is at least partially immiscible with the oleaginous fluid, and the emulsion stabilizing agent to form a stabilized emulsion composition.

17. A method according to claim 16, further comprising placing the stabilized emulsion composition in a subterranean formation as part of a drilling operation.

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BACKGROUND

[0001] The present invention relates to emulsions and methods of using such emulsions. More particularly, the present invention relates to emulsion stabilizing agents and their uses in subterranean applications.

[0002] Emulsions usually comprise two immiscible phases. The two immiscible phases may include a continuous (or external) phase and a discontinuous (or internal) phase. The discontinuous phase may comprise the secondary fluid that usually exists in droplets in the continuous phase. Two varieties of emulsions are oil-in-water and water-in-oil. Oil-in-water emulsions usually include a fluid at least partially immiscible in an oleaginous fluid (usually an aqueous-based fluid) as the continuous phase and an oleaginous fluid as the discontinuous phase. Water-in-oil emulsions are the opposite, having the oleaginous fluid as the continuous phase and a fluid at least partially immiscible in the oleaginous fluid (usually an aqueous-based fluid) as the discontinuous phase. Water-in-oil emulsions may be also referred to as invert emulsions.

[0003] Such emulsions have been used in various oil and gas applications. For instance, emulsions may be used in the oil and gas industry for subterranean treatment applications, including drilling, production, and completion operations. Invert emulsions may be used because oleaginous-based treatment fluids (also known as muds) may have desirable performance characteristics when compared with water-based muds in some situations. *e.g.*, when there is an abundance of water reactive materials in a well bore. These performance characteristics may include, *e.g.*, better lubrication of the drilling strings and downhole tools, thinner filter cake formation, and better hole stability.

[0004] A water-in-oil type emulsion, that does not have an emulsifying agent capable of stabilizing the fluid that is at least partially immiscible in the oleaginous fluid typically will undergo natural degradation processes, such as droplet coalescence and Ostwald ripening, until the two phases which are at least partially immiscible separate and the emulsion no longer exists. Having an unstable invert emulsion may be problematic because if the emulsion destabilizes, it may not have consistent, reliable properties. This problem may be exacerbated by the physical forces that the emulsion may undergo when being used in subterranean applications, such as thermal, mechanical, and chemical stresses. Emulsion stabilizing agents, sometimes referred to as emulsifiers, may be useful in emulsions as

stabilizers, especially when used in subterranean applications. The term “emulsion stabilizing agent” or emulsifier as used herein may refer to any compound capable of lowering the interfacial tension between an oleaginous fluid and a fluid at least partially immiscible in the oleaginous fluid.

[0005] Some traditional emulsion stabilizing agents are surfactant-based. Surfactant-based emulsion stabilizing agents usually comprise a hydrophobic part that interacts with the oil phase and a hydrophilic part that interacts with the non-oleaginous phase. These interactions generally decrease the surface tension of the interface between the water droplet and the oil, which may slow the natural tendency of the two immiscible phases to separate.

SUMMARY

[0006] The present invention relates to emulsions and methods of using such emulsions. More particularly, the present invention relates to emulsion stabilizing agents and their uses in subterranean applications.

[0007] According to a first aspect of the present invention, there is provided a stabilized emulsion composition comprising: an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound.

[0008] In an embodiment, the first ionic compound, the second ionic compound, or both comprise an ionic surfactant.

[0009] In an embodiment, the first ionic compound, the second ionic compound, or both comprise an ionic polyelectrolyte.

[0010] In an embodiment, one of the first ionic compound and the second ionic compound comprises an ionic surfactant and the other of the first ionic compound and the second ionic compound comprises an ionic polyelectrolyte.

[0011] In an embodiment, the ionic surfactant comprises an anionic surfactant.

[0012] In an embodiment, the anionic surfactant comprises at least one compound selected from the group consisting of: an alkyl carboxylate, an alkylether carboxylate, a N-acylaminoacid, a N-acylglutamate, a N-acylpolypeptide, an alkylbenzenesulfonate, a paraffinic sulfonate, an α -olefinsulfonate, a lignosulfate, a derivative

of a sulfosuccinate, a polynaphthylmethylsulfonate, an alkyl sulfate, an alkylethersulfate, a monoalkylphosphate, a polyalkylphosphate, a fatty acid, an alkali salt of an acid, an alkali salt of a fatty acid, an alkaline salt of an acid, a sodium salt of an acid, a sodium salt of a fatty acid, an alkyl ethoxylate, a soap, a combination thereof, and a derivative thereof.

[0013] In an embodiment, the ionic surfactant comprises a cationic surfactant.

[0014] In an embodiment, the cationic surfactant comprises at least one compound selected from the group consisting of: an alkyl amine, an alkyl amine salt, a quaternary ammonium salt, an ethoxylated quaternary ammonium salt, an amine oxide, an alkyltrimethyl amine, a triethyl amine, an alkyldimethylbenzylamine, a derivative thereof, and a combination thereof.

[0015] In an embodiment, the ionic polyelectrolyte comprises an anionic polyelectrolyte.

[0016] In an embodiment, the anionic polyelectrolyte comprises at least one compound selected from the group consisting of: a polymer or copolymer comprising a carboxylate group, a sulfonate group, a phosphate group, a phosphonate group, an acrylate monomer, a methacrylate monomer, a styrene carboxylate, a vinyl sulfonate, a 2-acrylamine-2-methyl-propyl sulfonate, a 3-acrylamide-3-methyl butanoate, a salt of malic acid, a polyacrylic acid, a partially-hydrogenated polyacrylamide, a carboxy methyl cellulose, a cellulose modified with an anionic functional group, a polysaccharide modified with an anionic functional group, a galactomannan modified with an anionic functional group, a derivative thereof, and a combination thereof.

[0017] In an embodiment, the ionic polyelectrolyte comprises a cationic polyelectrolyte.

[0018] In an embodiment, the cationic polyelectrolyte comprises at least one compound selected from the group consisting of: a polyethylene imine, a polyamide amine, a polyamine, a vinyl benzyl trimethyl ammonium chloride, a dimethyldiallyl ammonium chloride, a 3-acrylamido-3-methyl butyl trimethyl ammonium chloride, a polyvinylpyrrolidone, chitosan modified with a cationic functional group, a gelatin modified with a cationic functional group, a galactomannan modified with a cationic functional group, a cellulose modified with a cationic functional group, a derivative thereof, and a combination thereof.

[0019] In an embodiment, the oleaginous fluid comprises at least one fluid selected from the group consisting of: a diesel oil, a crude oil, a paraffin oil, a mineral oil, a low toxicity mineral oil, an olefin, an ester, an amide, an amine, a polyolefin, a

polydiorganosiloxane, a siloxane, an organosiloxane, an ether, an acetal, a dialkylcarbonate, a hydrocarbon, a derivative thereof, and a combination thereof.

[0020] In an embodiment, the fluid that is at least partially immiscible with the oleaginous fluid comprises at least one fluid selected from the group consisting of: glycerin, a glycol, a polyglycol amine, a polyol, fresh water, sea water, salt water, a brine, a derivative thereof, and a combination thereof.

[0021] According to another aspect of the present invention, there is provided a method comprising: providing a stabilized emulsion composition formed by combining components that comprise: an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound, and placing the stabilized emulsion composition in a subterranean formation as part of a subterranean application. The stabilized emulsion composition may comprise one or more of the embodiments described above.

[0022] According to another aspect of the present invention, there is provided a method comprising: providing a stabilized emulsion composition comprising: an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound, and drilling a well bore in a subterranean formation using the stabilized emulsion composition. The stabilized emulsion composition may comprise one or more of the embodiments described above.

[0023] Yet another aspect of the present invention comprises a method of preparing a stabilized emulsion composition comprising: providing an oleaginous fluid; providing a fluid that is at least partially immiscible with the oleaginous fluid; providing an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises: a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic

compound; and combining the oleaginous fluid, the fluid that is at least partially immiscible with the oleaginous fluid, and the emulsion stabilizing agent to form a stabilized emulsion composition. The stabilized emulsion composition may comprise one or more of the embodiments described above.

[0024] The features and advantages of the present invention will be apparent to those skilled in the art. While numerous changes may be made by those skilled in the art, such changes are within the scope of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0025] The present invention relates to emulsions and methods of using such emulsions. More particularly, the present invention relates to emulsion stabilizing agents and their use in subterranean applications.

[0026] While there are many advantages to the present invention, only some are disclosed herein. The emulsion stabilizing agents provided by the present invention may be advantageous because it is believed that the electrostatic interactions of the molecules may serve to anchor the surfactants to the interface between the two phases present in the emulsion or invert emulsion, potentially resulting in an increased surfactant or polyelectrolyte concentration at the interface. This may result in an improved stability of the emulsion and allow a relatively low amount of the emulsion stabilizing agent to be used to achieve a stable emulsion.

[0027] The present invention provides emulsion stabilizing agents that comprise a pair of charged surfactant or polyelectrolyte compounds of opposite charge. The emulsion stabilizing agents of the present invention may be used beneficially to stabilize emulsion compositions. Such emulsion compositions that comprise the emulsion stabilizing agents of the present invention may be referred to herein as the “stabilized emulsion compositions” of the present invention. These stabilized emulsion compositions are formed by combining components that comprise an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent of the present invention. After mixing, these components may or may not be separately identifiable, depending on the sophistication of the technique used. The stabilized emulsion compositions may be suitable for use in a variety of subterranean applications wherein oil-in-water or a water-in-oil emulsions are suitable. These may include subterranean applications comprising stimulation operations such as fracturing and sand control treatments such as installing a gravel pack. These may also include drilling and

completion operations. Other subterranean applications also may be suitable. One of ordinary skill in the art, with the benefit of this disclosure, will recognize other suitable uses for these emulsion compositions.

[0028] The oleaginous fluid utilized in the stabilized emulsion compositions may comprise any traditional oil-based fluids suitable for use in emulsions. The oleaginous fluid may be from a natural or synthetic source. Examples of suitable oleaginous fluids include diesel oils, crude oils, paraffin oils, mineral oils, low toxicity mineral oils, olefins, esters, amides, amines, synthetic oils (such as polyolefins, polydiorganosiloxanes, siloxanes, organosiloxanes and combinations thereof), ethers, acetals, dialkylcarbonates, hydrocarbons and combinations thereof. Examples of suitable oleaginous fluids include those commercially available from Halliburton Energy Services, Inc., in Houston, Tex., U.S.A., under the tradenames “ACCOLADE™,” an internal olefin and ester blend invert emulsion base fluid, “PETROFREE®,” an ester based invert emulsion base fluid, “PETROFREE® LV” an ester based invert emulsion base fluid, and “PETROFREE® S.F.,” an internal olefin based invert emulsion base fluid. Factors that may determine what oleaginous fluid will be used in a particular application, include but are not limited to, cost and performance characteristics of the oleaginous fluid. An additional factor that may be considered is the polarity of the oleaginous fluid. For example, diesel oils are generally more polar than paraffin oils. Other factors that may be considered are environmental compatibility and regional drilling practices. For example, in North Sea applications, an ester or internal olefin (IO) may be preferred. In the Gulf of Mexico, applications may prefer to utilize “ACCOLADE™” or a low toxicity mineral oil. One skilled in the art with the benefit of this disclosure will be able to choose a suitable oleaginous fluid for a particular application in view of these considerations. In certain exemplary embodiments of the present invention, the oleaginous fluid may be crude oil.

[0029] The emulsion compositions of the present invention also comprise a fluid that is at least partially immiscible in the oleaginous fluid. This partially immiscible fluid may be a non-oleaginous fluid that is mutually insoluble with the chosen oleaginous fluid. Suitable examples of partially immiscible fluids include aqueous-based fluids, glycerin, glycols, polyglycol amines, polyols, derivatives thereof that are partially immiscible in the oleaginous fluid, and combinations thereof. The term “derivative” is defined herein to include any compound that is made from one of the listed compounds, for example, by replacing one atom in the base compound with another atom or group of atoms. Aqueous-based fluids may include, but are not limited to, fresh water, sea water, salt water, and brines (*e.g.*, saturated salt waters).

Any brine may be used with the emulsions of the present invention that does not interfere with the emulsion stabilizing agents. One of ordinary skill in the art will appreciate that detrimental interactions may occur between some components of some brines and charged surfactants or polyelectrolyte pairs. Suitable brines may include heavy brines. Heavy brines, for the purposes of this application, include brines that may be used to weight up a fluid, such as a treatment fluid, instead of using traditional weighting agents. Brines may comprise H₂O soluble salts. In certain exemplary embodiments, suitable H₂O soluble salts may comprise sodium chloride, calcium chloride, calcium bromide, zinc bromide, potassium carbonate, sodium formate, potassium formate, sodium acetate, potassium acetate, calcium acetate, ammonium acetate, ammonium chloride, ammonium bromide, sodium nitrate, potassium nitrate, ammonium nitrate, calcium nitrate, sodium carbonate, potassium carbonate, and combinations thereof. In other exemplary embodiments, the H₂O soluble salt may be any salt which reduces the water phase activity of the emulsion. Factors that determine what partially immiscible fluid will be used in a particular application may include cost, availability, and which oleaginous fluid has been chosen. Another factor that may be considered is the application of the emulsion. For example, if the application needs an emulsion with a heavy weight, a zinc bromide or calcium chloride brine may be chosen. One skilled in the art with the benefit of this disclosure in view of the considerations will be able to choose a particularly suitable partially immiscible fluid for a particular application.

[0030] As noted above, the stabilized emulsion compositions of the present invention also comprise an emulsion stabilizing agent of the present invention. The emulsion stabilizing agents comprise at least a pair of compounds that may generally comprise two surfactant molecules, polyelectrolyte molecules, or any combination thereof that have opposite charges, which may or may not be of the same magnitude. In general, the members of the pair will be either cationic or anionic. The charge on one or both of the compounds may result from one or more ionic functional groups. As used herein, the term “ionic” or “ionic functional group” may refer to any compound capable of carrying at least a partial positive or negative charge, whether inherent in the chemical structure or formed due to the presence of any other components in a mixture. Such compounds may include ionic groups or compounds, polar groups or compounds, amphoteric groups or compounds, or any other type of material capable of carrying or developing a charge. In some embodiments, the anionic member of the pair may be at least partially soluble in the oleaginous phase while the cationic member may be at least partially soluble in the fluid that is at least partially immiscible in the oleaginous fluid. In other

embodiments, the cationic member of the pair may be at least partially soluble in the oleaginous phase while the anionic member may be at least partially soluble in the fluid that is at least partially immiscible in the oleaginous fluid. While not wishing to be limited by theory, it is believed that the electrostatic interactions may occur at the interface between the oleaginous phase and the fluid that is at least partially immiscible in the oleaginous fluid. While each member of the emulsion stabilizing agent pair may be soluble in one of the phases, the combined component formed by the electrostatic interactions may be at least partially insoluble in both phases. The resulting emulsion stabilizing agent pair may remain at the interface between the phases, resulting in an improved stability of the emulsion.

[0031] In an embodiment, a member of the emulsion stabilizing agent pair may be a surfactant that may carry an anionic or cationic charge. In an embodiment, a surfactant useful with the emulsion stabilizing agent disclosed herein may comprise at least one ionic functional group. Exemplary functional groups may include carboxylates, sulfonates, sulfates, amines, imines, phosphates, and phosphonates. Exemplary cationic surfactants may include, but are not limited to, alkyl amines, alkyl amine salts, quaternary ammonium salt, ethoxylated quaternary ammonium salts, amine oxides, alkyltrimethyl amine, triethyl amine, alkyldimethylbenzylamine. Exemplary anionic surfactants may include, but are not limited to, alkyl carboxylates, alkylether carboxylates, N-acylaminoacids, N-acylglutamates, N-acylpolypeptides, alkylbenzenesulfonates, paraffinic sulfonates, α -olefinsulfonates, lignosulfates, derivatives of sulfosuccinates, polynaphthylmethylysulfonates, alkyl sulfates, alkylethersulfates, monoalkylphosphates, polyalkylphosphates, fatty acids, alkali salts of acids, alkali salts of fatty acids, alkaline salts of acids, sodium salts of acids, sodium salts of fatty acid, alkyl ethoxylate, and soaps. One of ordinary skill in the art would be able to determine the phase to which the ionic surfactant should be added, which may be based on the composition of each phase in the emulsion, the solubility of the component in each phase, the operating conditions (*e.g.*, temperature), and any additives present in either phase (*e.g.*, salts). For example, anionic surfactants may react with any calcium present in the fluid that is at least partially immiscible in the oleaginous fluid to form compounds that may not be effective stabilizers. As such, one of ordinary skill in the art may avoid the use of anionic surfactants in the fluid that is at least partially immiscible in the oleaginous fluid when calcium ions are present.

[0032] In an embodiment, a member of the emulsion stabilizing agent pair may be a polyelectrolyte that may carry an anionic or cationic charge. As used herein, a

polyelectrolyte may be a polymer whose repeating units comprise an electrolyte group. These groups may dissociate in solutions comprising an aqueous fluid, allowing the polymers to carry a formal charge to some degree. For example, a polymer may be prepared that contains an anionic monomer to impart an anionic character to the molecule. Exemplary anionic polyelectrolytes include, but are not limited to, polymers or copolymers derived from anionic monomers containing carboxylates, sulfonates, phosphates, phosphonates, acrylate monomers, methacrylate, 2-acrylamine-2-methyl-propyl sulfonate, 3-acrylamide-3-methyl butanoate, styrene carboxylate, vinyl sulfonate, salts of malic acid, polyacrylic acid (PAA), partially-hydrogenated polyacrylamide (PHPA), carboxy methyl cellulose, derivatives of cellulose, polysaccharides (*e.g.*, xanthan, arabic gum), and galactomannans modified with anionic functional groups. Non-ionic monomers may be included in these compounds, *e.g.*, as in a copolymer between an anionic monomer and a neutral monomer. Exemplary cationic polyelectrolytes include, but are not limited to, polymers or copolymers comprising cationic groups such as imines, amines, and copolymers with neutral monomers. Specific examples may include, but are not limited to, polyethylene imine, polyamide amine, polyamines, vinyl benzyl trimethyl ammonium chloride, dimethyldiallyl ammonium chloride, 3-acrylamido-3-methyl butyl trimethyl ammonium chloride, and polyvinylpyrrolidone. For example, polymers comprising chitosanes, gelatins, galactomannans and cellulose may be modified with cationic monomers to form cationic polyelectrolytes. The polyelectrolytes useful with the emulsion stabilizing agents disclosed herein may be prepared by any method known to one of ordinary skill in the art.

[0033] In an embodiment, the emulsion stabilizing agent may be added to the stabilized emulsion composition in any amount capable of stabilizing the emulsion to a desired degree. The emulsion stabilizing agent pair may be added on a charge balanced basis. For example, if the anionic member of the emulsion stabilizing agent pair carried a formal charge equal to twice that of the cationic member of the emulsion stabilizing agent pair, then the anionic member of the emulsion stabilizing agent pair may be added in an amount equal to half of the total amount of the cationic member of the emulsion stabilizing agent pair on a mole basis. In other embodiments, the members of the emulsion stabilizing agent pair may be added in a ratio not related to the charge on the emulsion stabilizing agent pair members. For example, if it is expected that one member of the pair may interact with other components of the stabilized emulsion, then more or less of that member of the pair may be added to compensate for the interaction. In an embodiment, the emulsion stabilizing agent may be added to a stabilized

emulsion composition in an amount ranging from about 0.1 pounds per barrel (lb/bbl) to about 12 lb/bbl (about 0.29 kg/metre³ to about 34 kg/metre³) of the stabilized emulsion composition. In another embodiment, the emulsion stabilizing agent may be added to a stabilized emulsion composition in an amount ranging from about 0.25 lb/bbl to about 4 lb/bbl (about 0.71 kg/metre³ to about 11 kg/metre³) of the stabilized emulsion composition.

[0034] The stabilized emulsion compositions of the present invention may optionally contain a variety of additives. Examples of additives useful in the stabilized emulsions may include, but are not limited to, solids, weighting agents, inert solids, fluid loss control agents, emulsifiers, salts, dispersion aids, corrosion inhibitors, emulsion thinners, emulsion thickeners, viscosifiers, and any combination thereof.

[0035] In some embodiments, a weighting agent may be used to increase the density of the stabilized emulsion. The weighting agents, which serve to increase the density of the stabilized emulsions, may be any solids known to those skilled in the art as useful for such purpose that do not adversely interact with the emulsion stabilizing agent composition. Examples of weighting agents may include, but are not limited to, barite, calcite, ilmenite, mullite, gallena, manganese oxides, iron oxides, mixtures of these and the like. For example, a ground barium sulfate additive having the tradename BAROID[®] available from Halliburton Energy Services, Inc. in Houston, Tex., U.S.A. may be used as a weighting agent. The weighting material may typically be added in order to alter the density of the stabilized emulsion. The density of the fluid may be less than about 20 (about 2400 kg/metre³), or less than about 15 (about 1800 kg/metre³), or alternatively less than about 10 pounds per gallon (about 1200 kg/metre³). One of ordinary skill in the art would be able to determine the amount of weighting agent to add to produce a stabilized emulsion with a desired density.

[0036] In an embodiment, the stabilized emulsion may comprise fluid-loss control additives, emulsifiers, or both. Fluid loss control agents such as modified lignite, polymers, oxidized asphalt and gilsonite may also be added to the stabilized emulsion. Usually such fluid loss control agents may be employed in an amount which is at least about 0.1, at least about 1, or at least about 5 percent by weight of the total fluid. For example, an additive having the trade name ADAPTA[™] available from Halliburton Energy Services, Inc. in Houston, Tex., U.S.A. may be used as a fluid loss control additive. Alkali may also be used, preferably lime (calcium hydroxide or calcium oxide), to bind or react with acidic gases (*e.g.* CO₂ and H₂S) encountered during drilling in the formation so long as the alkali does not interfere with the emulsion stabilizing agents disclosed herein. The quantity of free lime in a drilling fluid may

range from about 1 to about 10 lbs/bbl (about 2.9 kg/metre³ to about 29 kg/metre³), or more preferably about 1 to about 4 lbs/bbl (about 2.9 kg/metre³ to about 11 kg/metre³), although lower ranges such as less than about 2 lbs/bbl (about 5.7 kg/metre³) are preferred for certain esters that tend to hydrolyze in the presence of alkaline compounds as will be known to those skilled in the art. Other suitable agents as an alternative to lime may also be used to adjust and/or stabilize the emulsions with respect to acids.

[0037] Various supplemental surfactants and wetting agents conventionally used in emulsions may optionally be incorporated in the stabilized emulsions. Such surfactants may be, for example, fatty acids, soaps of fatty acids, amido amines, polyamides, polyamines, imidazoline derivatives, oxidized crude tall oil, organic phosphate esters, alkyl aromatic sulfates and sulfonates, as well as, mixtures of the above. Generally, such surfactants may be employed in an amount which does not interfere with the use of the stabilized emulsions. For example, the surfactants or wetting agents may be used in an amount that does not interfere with the ability of an a stabilized emulsion to act as a drilling fluid or drill in fluid and remove cuttings from the well bore.

[0038] Further, the stabilized emulsion may have added to it or mixed with the stabilized emulsion, other fluids or materials. Such materials may include for example additives to reduce or control temperature rheology or to provide thinning, such as, for example, additives having the tradenames COLDTROL[®], RHEMOD[™] L, ATC[®], and OMC 2[™]; additives for providing temporary increased viscosity for shipping (transport to the well site) and for use in sweeps, such as, for example an additive having the tradename TEMPERUS[™] (modified fatty acid); additives for bridging porous rock, such as, for example additives having the tradename BARACARB[®] 50; additives for high temperature high pressure filtration control (HTHP FILTRATE) and emulsion stability, such as, for example, additives having the tradename FACTANT[™] (highly concentrated tall oil derivative); and supplemental additives for emulsification, such as, for example additives having the tradenames EZ MUL[™] NT or LE SUPERMUL[™] (polyaminated fatty acids). Blends of thinners such as the OMC 2[™], COLDTROL[®], and ATC[®] may also be effective in stabilized emulsions of the invention. All of the aforementioned trademarked products are available from Halliburton Energy Services, Inc. in Houston, Tex., U.S.A.

[0039] Viscosifying agents may optionally be employed in the stabilized emulsions of the present invention. Usually, viscosifying agents such as oil and water soluble polymers, polyamide resins, polycarboxylic acids and fatty acid soaps may be employed. The

amount of viscosifying agent used in the composition will necessarily vary depending upon the end use of the composition. Usually such viscosifying agents are employed in an amount which is at least about 0.1, at least about 2, or at least about 5 percent by weight of the total fluid. For example, TAU-MOD™ or BARAZAN® D PLUS, both available from Halliburton Energy Services, Inc. in Houston, Tex., U.S.A., may be used as a viscosifying agent.

[0040] Still further, dispersion aids, corrosion inhibitors and/or defoamers may be used. These and other suitable auxiliaries and additives are used in amounts known to those skilled in the art depending on the conditions of the particular well bore and subterranean formation.

[0041] Generally, the stabilized emulsions of the present invention may be formed using any technique known in the art. For example, the components may be mixed together in any order under agitation condition. A representative method of preparing the stabilized emulsion may comprises mixing an appropriate quantity of the fluid that is at least partially insoluble in the oleaginous fluid and an appropriate quantity of the emulsion stabilizing agent and any optional additives during continuous, mild agitation. An oleaginous fluid may then be added while mixing until a stabilized emulsion is formed. If weighting agents, such as those described above, are to be added, then the weighting agents are typically added after the stabilized emulsion is formed. Alternatively, the stabilized emulsions of the present invention may be prepared by simply adding the emulsion stabilizing agent to an existing stock of drilling fluid. The effectiveness of this treatment may depend on the constituents of the fluid.

[0042] An example of a method of the present invention is a method of treating a subterranean formation comprising the steps of providing a treatment fluid comprising a stabilized emulsion comprising an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent; and treating the subterranean formation. In certain exemplary embodiments of the present invention, a method of treating a subterranean formation includes a well completion operation or a drilling operation. In other exemplary embodiments of the present invention, a method of treating a subterranean formation includes a stimulation operation. Examples of stimulation operations of the present invention include fracturing operations and acid stimulation operations, like matrix acidizing and a fracturing acidizing processes. In other exemplary embodiments of the present invention, a method of treating a subterranean formation includes a sand control operation such as installing a gravel pack.

[0043] Another example of a method of the present invention is a method of drilling a well bore in a subterranean formation using a stabilized emulsion drilling fluid comprising an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent.

[0044] An exemplary method of the present invention is a method of emulsifying crude oil comprising the steps of providing crude oil, a fluid that is at least partially immiscible with the crude oil and an emulsion stabilizing agent; and mixing the crude oil, the fluid that is at least partially immiscible with the crude oil and the emulsion stabilizing agent so as to form a stabilized crude oil emulsion.

[0045] To facilitate a better understanding of the present invention, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the scope of the invention.

EXAMPLES

[0046] In order to demonstrate the stabilization of an emulsion with the emulsion stabilizing agents disclosed herein, several samples of stabilized emulsions were prepared and allowed to age different time periods. In this example, 1.5 lb/bbl of polyelectrolyte (EZ-MUD[®] GOLD, available from Halliburton Energy Services of Houston, Texas) and 6 lb/bbl of a filtration control agent (N-DRIL[®] HT PLUS, available from Halliburton Energy Services of Houston, Texas) were mixed with 3% KCl salt water using a multi-mixer for 5 minutes followed with 1.0 lb/bbl of hydrophobic surfactants (Octadecylamine with a technical grade of 90%) for another 5 minutes. An amount of diesel comprising 20% of the overall fluid volume was added and mixed for another 30 minutes. The resulting mixture was hot-rolled for 16 hours at 230°F (110°C) to form a sample labeled “Sample 1.” A second batch of the fluid was prepared according to the same procedure and labeled “Sample 2.” The second batch of fluid was viscosified with a viscosifier (BARAZAN[®] D PLUS, available from Halliburton Energy Services, of Houston, Texas) and hot-rolled for 16 hours. The fluid appearance showed little to no phase separation after 24 hours and 72 hours. The rheological properties of the 8.0 lb/gal fluids are shown Table 1.

Table 1. Formulation and Properties of Diesel in an Aqueous Fluid

Description	Units	Sample 1	Sample 2
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Table 1. Formulation and Properties of Diesel in an Aqueous Fluid			
Description	Units	Sample 1	Sample 2
Density	lb/gal (kg/metre ³)	8.0 (960)	8.0 (960)
Water	bbl (metre ³)	0.789 (0.094)	0.789 (0.094)
BARAZAN [®] D PLUS	lb (kg)	0	0.5 (0.2)
N-DRIL [™] HT PLUS	lb	6 (2.7)	6 (2.7)
Emulsifier Blend	lb	2.5 (1.1)	2.5 (1.1)
Diesel	bbl	0.199 (0.0316)	0.199 (0.0316)
Rheological Properties			
Hot-rolled at 120°F (49°C)	hr	0	16
Remixed on a Multi-mixer	min	3	3
Plastic viscosity	cP (gram/cm.second)	29 (0.29)	37 (0.37)
Yield Point	lb/100ft ² (kPa)	71 (34)	53 (25)
10 Sec gel	lb/100ft ² (kPa)	11 (5.3)	5 (2.4)
10 Min gel	lb/100ft ² (kPa)	14 (6.7)	4 (1.9)
Fann 35 Readings @120°F (49°C)			
600 rpm		129	127
300 rpm		100	90
200 rpm		86	71
100 rpm		66	46
6 rpm		18	6
3 rpm		13	4

[0047] A fluid sample prepared according to the procedure described above was prepared and allowed to age for approximately six weeks. A visual inspection of the fluid confirmed that little to no phase separation had occurred. This result demonstrates that the emulsion is capable of remaining stable for extended periods of time using the emulsion stabilizing agents disclosed herein. Further, the stable emulsion offered the opportunity to adjust the viscosity of the fluid with BARAZAN[®] D PLUS without adversely affecting the stability of the emulsion.

[0048] Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the

teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered or modified and all such variations are considered within the scope of the present invention. While compositions and methods are described in terms of “comprising,” “containing,” or “including” various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, “from about a to about b,” or, equivalently, “from approximately a to b,” or, equivalently, “from approximately a-b”) disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Moreover, the indefinite articles “a” or “an”, as used in the claims, are defined herein to mean one or more than one of the element that it introduces. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. If there is any conflict in the usages of a word or term in this specification and one or more patent or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.