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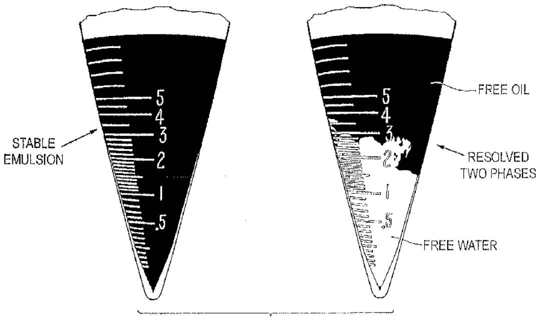
Fig. 2



(57) Abstract: This invention relates to compounds and methods for making and breaking emulsions of water and hydrocarbons with asphaltenes. The solutes of this invention include chaotropes and kosmotropes, which decrease or increase the order of water molecules respectively. Aggregated asphaltenes form a coalescing barrier at the oil-water interface to result in a stable emulsion and keep water droplets from uniting. Conversely, dispersed asphaltenes allow a coalescing interface at the oil-water interface to resolve the emulsion and allow water droplets to unite. Some applications of this invention include crude oil processing, refinery applications and water treatment methods.

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CONTROLLING EMULSION STABILITY DURING FUEL STOCK PROCESSING

Background

Field of the Invention

This invention relates to compounds for making and breaking emulsions in hydrocarbons with asphaltenes.

Discussion of Related Art

The current trend in refining includes utilization of heavier crude oil and alternative hydrocarbon sources, such as bitumen and tar sands. These heavier materials include an increased amount of asphaltenes which makes processing difficult due to among other things, viscosity, fouling, and emulsion issues.

Since it is not always possible to control the crude oil properties or composition for a refinery stream to prevent fouling, there is a need and a desire for additional materials and processes that allow asphaltene control and/or management, particularly regarding emulsions. In some circumstances, it is advantageous to form emulsions and in other circumstances it is advantageous break emulsions.

In response to this need, the petroleum refining industry has developed efforts and resources to develop new ways to solve problems associated with emulsions in asphaltene containing streams. However, such efforts have only partially succeeded in providing practical methods and compositions to control emulsions.

Durrieu et al., U.S. Patent 5,154,857, discloses a water-soluble demulsifying and antifouling agent of a quaternary tetraalkylammonium halide; and at least one polyalkyloxylated alkylenediamine or its sulfate for desalting and dehydrating crude petroleums. Durrieu et al. does not disclose compounds and methods for both forming and breaking emulsions.

Watkins et al., U.S. Patent 4,775,489, discloses a self-breaking foamed oil in water emulsion for stimulation of wells blocked by paraffinic deposits. The composition requires: 1) an organic solvent, 2) an aqueous liquid, 3) an inert gas, and 4) surface active agent.

Huang et al., U.S. Patent 6,262,168, discloses aqueous dispersions of cationic water-soluble polymers with the addition of kosmotropes and chaotropes as viscosity reducers for use in the water treatment industry.

In the field of biology, Knowles et al., U.S. Patent 4,658,022, discloses the use of chaotropes to denature (unfold) proteins. But Knowles fails to teach or suggest using chaotropes with hydrocarbons or asphaltenes.

Although the foregoing disclosures provide advances in the art, there is still a need for a method of both breaking and forming emulsions of hydrocarbon streams with asphaltenes.

Summary

These and other aspects of this invention are met at least in part by methods and compounds for asphaltene control to form and/or break emulsions with kosmotropes and/or chaotropes.

According to one embodiment, this invention relates to a composition of matter including more than one liquid phase, where the composition includes a hydrocarbon phase with asphaltenes and an aqueous phase with a kosmotropic solute and/or a chaotropic solute.

According to another embodiment, this invention also relates to a method of breaking or forming emulsions in hydrocarbon applications including combining a hydrocarbon phase having asphaltenes with an aqueous phase having a kosmotropic solute and/or a chaotropic solute.

According to another embodiment, this invention relates to a method of breaking water-in-oil emulsions in hydrocarbon applications by combining a hydrocarbon stream with a water stream. The hydrocarbon stream includes a water-in-oil emulsion and asphaltenes, and the water stream includes at least one solute modifying properties of at least a portion of the water. The combining forms a continuous water phase and a continuous oil phase. The method further includes separating the continuous water phase from the continuous oil phase.

According to another embodiment, this invention relates to a method of removing and/or reducing at least a portion of asphaltenes from a hydrocarbon stream including combining a hydrocarbon stream with a water stream. The hydrocarbon stream includes asphaltenes, and the water stream includes at least one solute modifying a portion of the water. The combining forms at least one emulsion, at least one aqueous layer, and at least one hydrocarbon layer. Desirably, the emulsion includes a water-in-oil emulsion or a oil-in-water emulsion. The method further includes separating the aqueous layer from the hydrocarbon layer and from the emulsion.

According to another embodiment, this invention relates to a method of accelerating analytical testing of emulsions having hydrocarbons and aqueous solutions by combining a hydrocarbon phase including asphaltenes with an aqueous phase including a kosmotropic solute and/or a chaotropic solute. The method further includes forming or resolving an emulsion to result in one or more layers and measuring one or more characteristics in the one or more layers.

According to another embodiment, this invention relates to a method of forming an emulsion including combining hydrocarbons and water, and aggregating asphaltenes to form a coalescing barrier. Alternately, this invention relates to a method of breaking an emulsion including unaggregating asphaltenes to at least partially remove a coalescing barrier, and coalescing water droplets.

Brief Description of the Figures

The above and other features and aspects of this invention are better understood from the following detailed description taken in view of the drawings wherein:

FIG. 1 shows a table of solute concentration versus water resolved from the emulsion, according to one embodiment;

FIG. 2 shows a first sample of a stable emulsion and a second sample resolved into two layers by a solute, according to one embodiment;

FIG. 3A shows asphaltenes absorbed at the water droplet interface;

FIG. 3B shows reduced asphaltenes at the water droplet interface following treatment with a solute, according to one embodiment;

FIG. 4 shows a table of solute concentration versus water resolved from the emulsion, according to one embodiment;

FIG. 5A shows aggregated asphaltenes without a solute;

FIG. 5B shows aggregated asphaltenes with some solute, according to one embodiment;

FIG. 5C shows aggregated asphaltenes with more solute than FIG. 5B, according to one embodiment;

FIG. 6 shows a graduated centrifuge tube with a separated emulsion, according to one embodiment; and

FIG. 7 shows a flow diagram for crude oil dewatering, according to one embodiment.

Detailed Description

As used herein the term "asphaltene" refers broadly to molecular substances found in crude oil, bitumen, tar sands, coal, intermediate refinery streams and/or the like. Asphaltenes generally refer to polyaromatic carbon materials further including hydrogen, sulfur, nitrogen, and/or metals. Typically, asphaltenes are defined operationally as the n-heptane (C_7H_{16}) insoluble, toluene ($C_6H_5CH_3$) soluble component of a carbonaceous material. Asphaltenes may include at least one polar section and/or portion. Often, individual asphaltenes aggregate into larger and/or more complex structures. Asphaltenes may appear as a suspended solid in a hydrocarbon, but are distinguishable from other suspended matter, such as mineral sediment.

Asphaltene aggregates may stabilize water-in-oil emulsions as they collect at an oil and water interface. Asphaltene aggregates may form a barrier between water droplets and prevent coalescing. By preventing formation of asphaltene aggregates at the oil and water interface, water may then more easily coalesce and improve the separation of water from the oil, according to one embodiment.

As used herein the term "hydrocarbon" refers broadly to substances including primarily and/or substantially carbon and/or hydrogen atoms. Hydrocarbons further can include other atoms, such as nitrogen, oxygen, sulfur, metals and/or the like. Sources of hydrocarbon materials include, without limitation, fossil fuels, crude oil, tar sands, bitumen, coal, peat, biomass, synthetic reactions, and/or any other suitable supply of material. According to one embodiment, the hydrocarbons of this invention exclude molecules formed by amino acids, such as proteins.

As used herein the term "BS&W" refers broadly to basic sediment and water, bottom sediment and water, and/or bottom solids and water as determined by ASTM D1796, ASTM D9570, API 2548, API 2560 and any other suitable test. The text of the above referenced tests is hereby incorporated by reference. BS&W typically includes solids, water and emulsions withdrawn from and/or separated from a hydrocarbon material, such as from a bottom of a crude oil storage tank.

As used herein the term “combining” refers to mixing, intimately mixing, contacting, and/or putting together two or more items, materials, and/or streams.

As used herein the term “aqueous” refers broadly to substances including primarily and/or substantially water (H_2O). Aqueous materials and/or solutions further can include one or more additional substances, such as in solution and/or in suspension. Water includes an at least somewhat polar nature, such as can affect the adsorption of asphaltenes to the oil-water interface. Water also includes hydrogen bonding and/or other weak molecular forces, for example.

As used herein the terms “emulsion” and “dispersion” refer broadly to a mixture of two immiscible substances, where one substance is distributed and/or mixed in a second substance. Exemplary emulsions include water-in-crude oil, water-in-hydrocarbons, hydrocarbons-in-water and/or the like. Emulsions also include water-in-oil, oil-in-water and/or combinations thereof, such as oil-in-water-in-oil or water-in-oil-in-water. Sometimes the later may be referred to as complex and/or compound emulsions.

As used herein the term “stable emulsion” refers broadly to an emulsion that does not significantly resolve into two or more layers in less than about thirty days, such as at about 1 G force and ambient (room) temperature conditions.

As used herein the term “unstable emulsion” refers broadly to an emulsion that significantly resolves into two or more layers within about 24 hours, such as at about 1 G force and ambient (room) temperature conditions.

As used herein the term “phase” refers broadly to a physically distinctive form of a substance. Phases can be continuous, discontinuous and/or noncontinuous.

As used herein the term “layer” refers broadly to a discrete usually horizontal expanse of material and/or a stratum.

As used herein the term "coalescing barrier" broadly refers to a barrier, wall, obstruction, and/or impediment of the asphaltenes, aggregated asphaltenes, inorganic solids, metals, and/or metal complexes. The coalescing barrier typically, but not necessarily, forms around and/or encircles a water droplet, to prevent, block and/or reduce coalescing and/or uniting with other water droplets. Essentially, the asphaltenes impede and/or inhibit water droplets coming together as part of the separation process. A portion of the coalescing barrier may optionally include inorganic solids.

As used herein the term "coalescing interface" broadly refers to the intersection of a phase and/or a layer where water droplets can unite without crossing an asphaltene barrier and/or other similar obstruction.

As used herein the term "solution" refers broadly to a mixture of miscible substances, where one substance dissolves in a second substance.

As used herein the term "solvent" refers broadly to a substance in a solution that dissolves a solute. Typically, but not necessarily, the solvent is present in the solution in an amount greater than other substances.

As used herein the term "solute" refers broadly to a substance in a solution dissolved by the solvent. Solutes may include solids, liquids, and/or gases. Desirably, the solutes of this invention comprise a relatively simple molecule and may exclude polymer materials, for example. The solutes may desirably consist of a single compound and/or alternately, comprise multiple compounds, for example.

As used herein the terms "kosmotropic" or "kosmotropes" refer broadly to substances that, without being bound by theory are thought to contribute to the stability and structure of water-water interactions. Kosmotropes typically cause water molecules to favorably interact, which also stabilizes intermolecular interactions in macromolecules, such as asphaltenes. Kosmotropes can be ionic and/or nonionic. Desirably, kosmotropes increase the order of the water molecules.

Typically, but not necessarily, kosmotropes tend to be small and/or have a high charge density. Exemplary ionic kosmotropes include sulfate, phosphate, magnesium(2+), lithium(1+), and/or any other suitable substance. Based on free energy of hydration (ΔG_{hydr}) of the salts, an increasing negative

ΔG_{hydr}, results in a more kosmotropic the salt, for example. Other suitable kosmotropes may include a sulfate, phosphate, hydrogenphosphate salt, ammonium sulfate, sodium sulfate, citrates, oxalates, and/or any other order increasing substance. The counterion may include Group IA metal ions, Group IIA metal ions, ammonium ions, and/or other suitable ions.

Typically, but not necessarily, nonionic kosmotropes have no net charge, but are readily soluble and become readily hydrated.

As used herein the terms "chaotropic" or "chaotrope" refer broadly to substances that without being bound by theory are thought to disrupt the three dimensional structure of water. Chaotropes typically interfere with stabilizing intra-molecular interactions mediated by non-covalent forces, such as hydrogen bonds, Van der Waals forces, and/or hydrophobic effects. Exemplary chaotropes include urea, guanidinium chloride, lithium perchlorate and/or any other suitable substance. Desirably, chaotropes decrease the order of the water molecules. In some embodiments, water soluble chlorides are excluded from possible chaotropes.

Some inorganic, organic and/or mixed salts can have chaotropic properties, by shielding charges and preventing the stabilization of salt bridges, for example. Typically, hydrogen bonding may be stronger in nonpolar media, so salts, which increase the dipole moment of the solvent, can also destabilize hydrogen bonding. Alternately, large ions or ions with a low charge density act as chaotropes, such as bromide, iodide, potassium(1+), cesium(1+), and/or any other suitable substance. Additional suitable chaotropes may include thiocyanates, perchlorates, chlorates, nitrates, bromides, iodides, anionic surfactants and anionic hydrotropic salts, alkyl and substituted alkyl sulfonates, dialkylsulfosuccinates, diarylsulfosuccinates, benzenesulfonates, benzenedisulfonates, naphthalensulfonates, naphthalenedisulfonates and/or any other order disrupting substance.

As used herein the terms "Hofmeister salts" or "Hofmeister series" refer broadly to a classification of ions in order of their ability to change water structure. The pairing of anion and cations can be selected for tuning the water and where each ion alters the properties of the water to different degrees.

Typically, but not necessarily, anions have a larger effect than cations. Exemplary ions in relative order and/or rank are listed below.

Anions: $SO_4 > HPO_4 >$ acetate $> Cl > NO_3$
Cations: $Mg > Li > Na > K > NH_4$

Without being bound by theory, it is believed a mechanism of the Hofmeister salts include changes in the water structure and/or properties, such as interactions between ions, asphaltenes and/or water molecules. Some salts of the series, when dissolved in water, increase solvent surface tension and change the solubility of asphaltenes at the oil and water interface, resulting in the precipitation and/or "salting out" of the asphaltenes from the oil at the oil/water interface, for example, by strengthening the hydrophilic interaction. Desirably, the solutes and/or salts of this invention tune the properties of the water, such as to have the asphaltenes preferentially interact (aggregate or disperse) with other hydrocarbons or the water molecules.

Desirably, other salts in the Hofmeister series, when dissolved in water, increase the solubility of nonpolar molecules resulting in solubilizing and/or "salting in" of the asphaltenes into the oil; for example, by weakening the hydrophilic effect. These salts may also interact directly with asphaltenes. Exemplary Ions that have a strong "salting in" effect may include I^- and SCN^-, and may affect grouping or aggregating of asphaltenes, secondary structures and/or tertiary structures.

There are many applications for the present invention including, but not limited to, hydrocarbon processing, crude oil extraction, oilfield services, bitumen removal, tar sands mining, coal systems, refinery operations, dewatering units, desalter units, crude units, coker units, hydrocracker units, deasphalting units, fuel oil emulsions, hydrocarbon transportation, oil spill clean up, wastewater treatment and/or any other suitable use.

According to one embodiment, the kosmotropic and/or chaotropic solutes can be added to the wash water in a desalter unit, where the solutes desirably more quickly resolve the oil water emulsion, such as to prevent water carryover to the hydrocarbon layer and/or improve dewatering of the crude oil.

Alternately, the solutes of this invention also may more quickly resolve the emulsion to prevent excursions of oil carry under to the water layer and/or reduce the oil loading in the water stream from the desalter unit.

According to another embodiment, the solutes of this invention concentrate at least a portion of the asphaltenes from the crude oil in an interface and/or a rag layer, such as between a hydrocarbon layer and a water layer. Desirably, the rag layer forms an emulsion of oil, water, solute and asphaltenes, such as can be withdrawn from the desalter on a continuous and/or intermittent manner.

According to one embodiment, the kosmotropic and/or chaotropic solutes of this invention can also be added to a coking process. Typically, some water is added with the coker unit feedstocks, such as vacuum residue. Including the solutes with the added water prior to entering a coking furnace may reduce furnace fouling by keeping asphaltenes in the emulsion, for example. Alternately, this invention may be practiced by adding the solutes to any other suitable asphaltene-containing stream.

According to one embodiment, a solute in the form of a dry salt mixes with a water-in-oil emulsion or an oil-in-water emulsion to resolve the emulsion, for example. Other suitable forms of solute including pellets, powders, crystals, pastes, slurries, concentrates, and the like are possible.

Orimulsion® is a registered trademark by Intevep for emulsions to lower viscosity during transportation and burning of heavy oil and/or bitumen. Intevep is the Research and Development Affiliate of Petroleos de Venezuela SA, also known as PDVSA. According to one embodiment, the chaotropic solute of this invention can be added to the water to further stabilize the emulsion during transport in a pipeline and/or an ocean tanker, for example. Then upon reaching a suitable destination, a kosmotropic solute of this invention can be added to break the emulsion and reduce the water that is sent to the fuel burner, for example. A significant amount of heat and/or thermal energy typically is used to vaporize and/or heat up the water in the Orimulsion® to the temperatures for full and efficient combustion of the bitumen. Removing water from the emulsion before combustion allows more efficient use of the fuel.

According to one embodiment, the kosmotropic and/or chaotropic solutes of this invention are used to enhance oil recovery, such as in the oilfield, refinery slop oil systems and/or any other suitable application. Alternately, the solutes can be used in any situation, where water and/or moisture are present with a hydrocarbon during transportation, such as by pipeline, rail car, barge, ship, tanker, truck, and the like. One useful application is treatment to remove hydrocarbons from the ballast water before discharge from a ship. Desirably, the solutes also can be used for assisting in clean up of hydrocarbon spills and/or releases.

According to one embodiment, the kosmotropic and/or chaotropic solutes of this invention can be used to assist in dewatering of crude oil, such as by drawing water from a bottom of a storage tank before refinery processing.

According to one embodiment, the kosmotropic and/or chaotropic solutes of this invention assist lab methods, such as by more quickly resolving emulsions than without the solute, which desirably allows for more rapid and accurate results. Alternately, the solutes stabilize the emulsion and allows for more rapid and accurate results.

According to one embodiment, the method of using the kosmotropic and/or chaotropic solutes of this invention include the tuning of pH (neutral, acidic and/or caustic) of an emulsion, dispersion, water and/or solution. For example, the solute may be acidic, such as in preventing the formation of naphthenate salts. Alternately, a basic solute may react with metals in the crude oil, for example.

According to one embodiment, this invention includes a composition of matter comprising more than one liquid phase, where the composition includes a hydrocarbon phase comprising asphaltenes and an aqueous phase comprising a kosmotropic solute and/or a chaotropic solute. The solutes may include Hofmeister salts, non-ionic molecules and/or ionic salts, as discussed above. The more than one liquid phase can be continuous or discontinuous, for example.

Desirably, the solute modifies properties of at least a portion of water in the aqueous phase, such as changing the hydrogen bonding, increasing polarity, decreasing polarity, increasing conductivity, decreasing conductivity, increasing surface tension, decreasing surface tension, increasing order of the water molecules, decreasing order of the water molecules, increasing water-asphaltene stability at an oil-water interface, decreasing water-asphaltene stability at an oil-water interface, and/or any other suitable property of the water. The solutes of this invention may include any suitable compound. Desirably, the solute does not comprise a surfactant and/or a detergent. Alternately, the solute may include a surfactant and/or a detergent. Desirably, the solutes may comprise components compatible with downstream refinery processing, such as to minimize corrosion, fouling, and/or catalyst poisoning, for example.

The amount of solute in the water may be present in any suitable amount. Suitable amounts of solute may include between about 0.1 % by weight of an amount to form a saturated solution and an amount to form a saturated or a supersaturated solution, desirably, between about 1.0 % by weight of an amount to form a saturated solution and about 90 % by weight of an amount to form a saturated solution, and more desirably between about 1.0 % by weight of an amount to form a saturated solution and about 70 % by weight of an amount to form a saturated solution.

The composition of matter may include a coalescing barrier of the asphaltenes and/or aggregated asphaltenes. The coalescing barrier typically, but not necessarily, forms around and/or encircles a water droplet, to prevent and/or reduce coalescing and/or uniting with other water droplets. Essentially, the asphaltenes impede and/or inhibit water droplets coming together as part of the separation process.

Alternately, the composition of matter may include a coalescing interface, such as generally without or a mitigated amount of asphaltenes and/or aggregated asphaltenes around a water droplet, to allow and/or not reduce coalescing and/or uniting with other water droplets. Essentially, the asphaltenes disperse in the hydrocarbon to not impede and/or not inhibit water droplets coming together as part of the separation process.

According to one embodiment, this invention includes a method of breaking or forming emulsions in hydrocarbon applications. Breaking and/or resolving emulsions includes separating at least a substantial portion of the emulsion into two or more discrete continuous phases and more desirably into two or more discrete layers. Forming and/or making emulsions include generating at least one phase and more desirably a discrete layer of a mixture of water and/or oil from a source of water and/or oil. The method includes combining a hydrocarbon phase having asphaltenes with an aqueous phase having a kosmotropic solute and/or a chaotropic solute.

Desirably, but not necessarily, the hydrocarbon phase and the aqueous phase form a water-in-oil emulsion, an oil-in-water emulsion, at least one hydrocarbon layer along with at least one aqueous layer, and/or any other suitable resulting system. A water-in-oil emulsion may include an amount of water dispersed in a continuous phase and/or a layer of oil. An oil-in-water emulsion may include an amount of oil dispersed in a continuous phase and/or a layer of water.

According to one embodiment, the method further includes resolving an emulsion with a kosmotropic solute to form a continuous hydrocarbon layer and a continuous aqueous layer. Alternately, the method further includes stabilizing an emulsion with a chaotropic solute to form one or more liquid phases including a discontinuous oil phase, a continuous oil phase, a discontinuous aqueous phase, a continuous aqueous phase, and/or any other suitable resulting system.

According to one embodiment, the method further includes forming an emulsion with a crude oil and a wash water, wherein at least a portion of the crude oil forms the hydrocarbon phase and at least a portion of the wash water forms the aqueous phase. Desirably, but not necessarily, the forming an emulsion occurs in a desalter unit, such as in and/or after a mixing valve, a static mixer and/or any other mixing equipment, for example. The method may further include applying an electrostatic field to aid in breaking the emulsion, such as by coalescing the water droplets from the oil. The desalter electrodes may include one or more levels and/or heights for operating within a vessel. The solutes of this invention may improve desalter operation, such as by allowing a higher voltage and a lower amperage through the electrodes.

According to one embodiment, the method further includes forming and/or removing a coalescing barrier of the asphaltenes. Forming and/or making the coalescing barrier may include aggregating and/or increasing an amount of asphaltenes at the hydrocarbon and water interface. Removing and/or reducing the coalescing barrier may include deaggregating and/or decreasing an amount of asphaltenes at the hydrocarbon and water interface.

The coalescing barrier may be part of a stable emulsion system, for example. Alternately, when the coalescing barrier is removed, the water droplets unite to resolve the emulsion and may form separate phases and/or layers, for example.

According to one embodiment, this invention includes a method of breaking water-in-oil emulsions in hydrocarbon applications including combining a hydrocarbon stream having a water-in-oil emulsion and asphaltenes with a water stream having at least one solute modifying properties of at least a portion of the water. Desirably, the combining forms a continuous water phase and a continuous oil phase. The method further includes separating the continuous water phase from the continuous oil phase.

The combining and the separating may occur in a tank, vessel, basin, separator and/or desalter unit and further include applying an electrostatic field to aid in breaking the emulsion, for example. Alternately, the combining and the separating further include removing metals from the hydrocarbon phase, such as nickel and/or vanadium. The removed metal may be in the form of a porphyn and/or other complexing molecules.

The solute may include kosmotropic solutes, chaotropic solutes and/or Hofmeister salts. According to one embodiment, the solute includes ammonium sulfate (emulsion breaking), guanidine HCl (emulsion stabilizing), ammonium chloride (emulsion breaking), and/or sodium citrate (emulsion breaking). Other suitable salts are possible. Desirably, the solute with the water forms a coalescing interface at the edge of the water and the hydrocarbon, such as the asphaltenes disperse in the hydrocarbon away from the coalescing interface. Alternately, the solute with the water causes the formation of a coalescing barrier at the edge of the water and the hydrocarbon, such as the asphaltenes aggregate from the hydrocarbon and concentrate as the coalescing barrier.

According to one embodiment, this invention includes a method of removing at least a portion of asphaltenes from a hydrocarbon stream. The method may include combining a hydrocarbon stream comprising asphaltenes with a water stream comprising at least one solute modifying a portion of the water, so the combining forms at least one emulsion, at least one aqueous layer and/or at least one hydrocarbon layer. Desirably, the emulsion comprises a water-in-oil emulsion and/or an oil-in-water emulsion. The method further includes separating the aqueous layer from the hydrocarbon layer and from the emulsion. The method may further include separating the hydrocarbon layer from the aqueous layer. The method may include separating two, three and/or more discrete layers, such as a hydrocarbon layer, a rag layer, and a water layer. The method may occur in a desalter unit. The method may further include adding at least one emulsion breaking salt to the emulsion, wherein the emulsion breaking salt includes kosmotropic solutes and/or chaotropic solutes. The adding at least one emulsion breaking salt may occur outside a desalter unit, such as in a wastewater treatment unit.

According to one embodiment, this invention includes a method of accelerating analytical testing of emulsions, hydrocarbons, and/or aqueous solutions. The method includes combining a hydrocarbon phase having asphaltenes with an aqueous phase having a kosmotropic solute and/or a chaotropic solute. The method further includes forming or resolving an emulsion to result in one or more layers, and measuring one or more characteristics in the one or more layers. Desirably, the characteristic includes a volume fraction, a mass fraction, a molar fraction, a composition, a density, a specific gravity, an optical property, a boiling point, a freezing point, and/or any other suitable measurable attribute.

According to one embodiment, this invention includes a method of forming an emulsion comprising combining hydrocarbons and water, and aggregating asphaltenes to form a coalescing barrier and/or impede a coalescing interface. Desirably, the aggregating comprises adding at least one solute selected from the group consisting of kosmotropes, chaotropes and combinations thereof.

According to one embodiment, this invention includes a method of breaking an emulsion comprising unaggregating and/or dispersing asphaltenes to at least partially remove a coalescing barrier and/or form a coalescing interface; and coalescing water droplets. Desirably, the unaggregating comprises adding at least one solute selected from the group consisting of kosmotropes, chaotropes and combinations thereof.

Examples

Example 1

A sample of a relatively heavy crude oil was mixed with water resulting in a stable emulsion that did not separate even after weeks. This result was consistent with the interaction of water with the asphaltenes in the crude oil to form a stable emulsion. The same type of crude oil was mixed with aqueous ammonium sulfate at 25 % saturation by weight, 50 % saturation by weight, 75 % saturation by weight and 100 % saturation by weight. As shown in FIG. 1, the percent of water resolved increased from 0 % by weight to 55 % by weight within 15 minutes. This is a surprising and unexpected result since the addition of a salt rapidly resolved the stable emulsion. This example showed the salts of this invention break and/or resolve stable emulsions.

Example 2

Two mixtures of equal parts of water and crude oil were prepared, as shown in FIG. 2. The first mixture resulted in a stable emulsion having the water and oil in a single opaque phase. The second mixture included ammonium sulfate, a Hofmeister salt. The second mixture resulted in a clear water layer on top of a black oil layer, demonstrating the ammonium sulfate improved the oil-water separation.

Example 3

A sample of a desalter water-in-oil emulsion was withdrawn from an operating unit. FIG. 3A shows asphaltenes absorbed at the water droplet interface and was stable indefinitely under typical desalter operating conditions. FIG. 3B shows the same emulsion following treatment with a kosmotropic solute of this invention. The emulsion was broken and the asphaltenes on the oil-water interface reduced. The solute was ammonium sulfate in a saturated solution.

Example 4

A sample of a different crude oil was mixed with water and no significant emulsion formed (90 % by weight water remained resolved in a separate layer). Guanidine HCl was added at 25 % saturation by weight, 50 % saturation by weight, 75 % saturation by weight and 100 % saturation by weight.

As shown in FIG. 4, the percent water resolved decreased from 90 % by weight to 50 % by weight. This example showed the solutes of this invention can form emulsions, where normally no emulsion would form.

Surprisingly and unexpectedly, the same solutes of this invention also include the ability to both form and break emulsions depending upon concentration, as shown in FIG. 4. As shown in FIG. 5A without Guanidine HCl, there were few asphaltenes at the water drop interface. As shown in FIG. 5B with some Guanidine HCl, asphaltenes absorbed at the water drop interface. While FIG. 5C with an increased amount of Guanidine HCl showed a reduced amount of asphaltenes at the water drop interface.

Example 5

A stable emulsion of crude oil and water was combined with sodium citrate breaking the emulsion. FIG. 6 shows a graduated tube containing a water layer on the bottom and an oil layer on the top.

Example 6

Certain crude oils do not readily dewater. As shown in FIG. 7, the crude oil can be placed in a storage tank and a water phase withdrawn from the bottom of the storage tank. The water phase can then be combined with a solute to form a saturated solution and returned to the inlet of storage tank. The added solute assists in the dewatering of the crude oil by breaking the emulsion. Net or excess water from the crude oil can be removed from the system.

Example 7

Typically, laboratory desalting tests of crude oils are limited to those crude oils which do not form extensive emulsions when mixed with water. A sample of a stable emulsion forming crude oil was unsuccessfully analyzed in the laboratory due to the stable emulsion that formed when laboratory wash water was combined with the crude oil. Surprisingly and unexpectedly the addition of a kosmotropic salt of this invention to the laboratory wash water resulted in a clean separation of the oil from the water and allowed for laboratory testing of mixtures of the oil and the water without altering the composition of the oil.

While in the foregoing specification this invention has been described in relation to certain preferred embodiments, and many details are set forth for purpose of illustration, it will be apparent to those skilled in the art that this invention is susceptible to additional embodiments and that certain of the details described in this specification and in the claims can be varied considerably without departing from the basic principles of this invention.

WHAT IS CLAIMED IS:

1. A composition of matter comprising more than one liquid phase, the composition comprising:

a hydrocarbon phase comprising asphaltenes; and

an aqueous phase comprising a solute, wherein the solute is selected from the group consisting of kosmotropic solutes, chaotropic solutes and combinations thereof.

2. The composition of claim 1, wherein the solute is selected from the group consisting of non-ionic molecules, ionic salts, Hofmeister salts, and combinations thereof.

3. The composition of claim 1, further comprising a coalescing barrier of the asphaltenes.

4. The composition of claim 1, further comprising a coalescing interface.

5. The composition of claim 1, wherein the solute modifies properties of at least a portion of water in the aqueous phase.

6. The composition of claim 1, wherein the solute does not comprise a surfactant or a detergent.

7. The composition of claim 1, wherein an amount of solute comprises between about 0.1 % by weight of an amount to form a saturated solution and an amount to form a saturated or a supersaturated solution.

8. The composition of claim 1, wherein the solute comprises kosmotropic solutes.

9. The composition of claim 1, wherein the solute comprises chaotropic solutes.

10. A method of breaking or forming emulsions in hydrocarbon applications, the method comprising:

combining a hydrocarbon phase comprising asphaltenes with an aqueous phase comprising a solute, wherein the solute is selected from the group consisting of kosmotropic solutes, chaotropic solutes, and combinations thereof.

11. The method of claim 10, wherein the hydrocarbon phase and the aqueous phase is selected from the group consisting of a water-in-oil emulsion, a oil-in-water emulsion, at least one hydrocarbon layer along with at least one aqueous layer, and combinations thereof.

12. The method of claim 10, further comprising resolving an emulsion with a kosmotropic solute to form a continuous hydrocarbon layer and a continuous aqueous layer.

13. The method of claim 10, further comprising stabilizing an emulsion with a chaotropic solute to form one or more liquid phases, wherein the one or more liquid phases is selected from the group consisting of a discontinuous oil phase, a continuous oil phase, a discontinuous aqueous phase, a continuous aqueous phase and combinations thereof.

14. The method of claim 10, wherein an amount of solute comprises between about 0.1 % by weight of an amount to form a saturated solution and an amount to form a saturated or a supersaturated solution.

15. The method of claim 10, further comprising forming an emulsion with a crude oil and a wash water, wherein at least a portion of the crude oil forms the hydrocarbon phase and at least a portion of the wash water forms the aqueous phase.

16. The method of claim 10, further comprising forming a coalescing barrier of the asphaltenes.

17. The method of claim 10, further comprising removing a coalescing barrier of the asphaltenes.

18. A method of breaking water-in-oil emulsions in hydrocarbon applications, the method comprising:

combining a hydrocarbon stream with a water stream, the hydrocarbon stream comprising a water-in-oil emulsion and asphaltenes, the water stream comprising at least one solute modifying properties of at least a portion of the water, wherein the combining forms a continuous water phase and a continuous oil phase; and

separating the continuous water phase from the continuous oil phase.

19. The method of claim 18, wherein the solute is selected from the group consisting of kosmotropic solutes, chaotropic solutes, Hofmeister salts and combinations thereof.

20. The method of claim 18, wherein the solute comprises kosmotropic solutes.

21. The method of claim 18, wherein the combining and the separating occur in a desalting unit and further comprises applying an electrostatic field to aid in breaking the emulsion.

22. The method of claim 18, wherein the solute causes a coalescing interface without asphaltenes.

23. The method of claim 18, wherein the solute is selected from the group consisting of ammonium sulfate, sodium citrate and combinations thereof.

24. The method of claim 18, wherein the combining and the separating further comprise removing metals from the hydrocarbon phase.

25. A method of removing at least a portion of asphaltenes from a hydrocarbon stream, the method comprising:

combining a hydrocarbon stream with a water stream, the hydrocarbon stream comprising asphaltenes, the water stream comprising at least one solute modifying a portion of the water, wherein the combining forms at least one emulsion, at least one aqueous layer, and at least one hydrocarbon layer, the emulsion comprises a water-in-oil emulsion or a oil-in-water emulsion;

separating the aqueous layer from the hydrocarbon layer and from the emulsion; and

separating the hydrocarbon layer from the aqueous layer and from the emulsion.

26. The method of claim 25, wherein the separating occurs in a desalter unit.

27. The method of claim 25, wherein the solute comprises chaotropic solutes.

28. The method of claim 25, further comprising:

adding at least one emulsion breaking salt to the emulsion, wherein the emulsion breaking salt is selected from the group consisting of kosmotropic solutes, chaotropic solutes and combinations thereof.

29. The method of claim 28, wherein the emulsion breaking salt comprises kosmotropic solutes.

30. The method of claim 28, wherein the adding at least one emulsion breaking salt occurs outside a desalter unit.

31. A method of accelerating analytical testing of emulsions, hydrocarbons, and aqueous solutions, the method comprising:

combining a hydrocarbon phase comprising asphaltenes with an aqueous phase comprising a solute, wherein the solute is selected from the group consisting of kosmotropic solutes, chaotropic solutes and combinations thereof;

forming or resolving an emulsion to result in one or more layers; and

measuring one or more characteristics in the one or more layers.

32. A method of forming an emulsion comprising:

combining hydrocarbons and water; and

aggregating asphaltenes to form a coalescing barrier.

33. The method of claim 32, wherein the aggregating comprises adding at least one solute, wherein the at least one solute is selected from the group consisting of kosmotropes, chaotropes and combinations thereof.

34. The method of claim 32, wherein the aggregating comprises adding chaotropes.

35. The method of claim 32, wherein the aggregating comprises adding guanidine HCl.

36. A method of breaking an emulsion comprising;

unaggregating asphaltenes to at least partially remove a coalescing barrier; and

coalescing water droplets.

37. The method of claim 36, wherein the unaggregating comprises adding at least one solute, wherein the at least one solute is selected from the group consisting of kosmotropes, chaotropes and combinations thereof.

38. The method of claim 36, wherein the unaggregating comprises adding kosmotropes.

39. The method of claim 36, wherein the unaggregating comprises adding sodium citrate.

Fig. 1

% OF AMMONIUM SULFATE SATURATION IN WATER	% WATER RESOLVED AFTER 15 MINUTES
0	0
25	20
50	25
75	45
100	55

Fig. 2

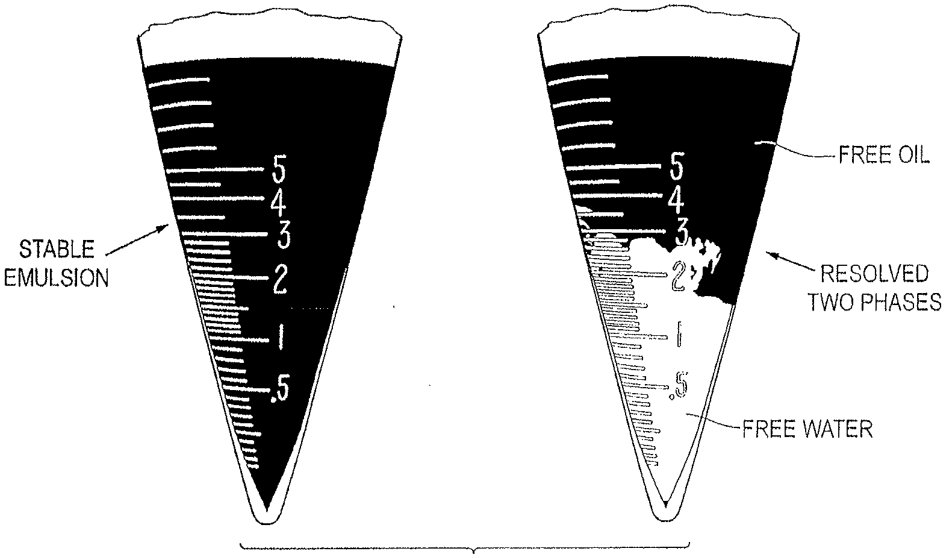

STABLE
EMULSION
5
4
3
2
1
.5
FREE OIL
RESOLVED
TWO PHASES
FREE WATER

Fig. 3A

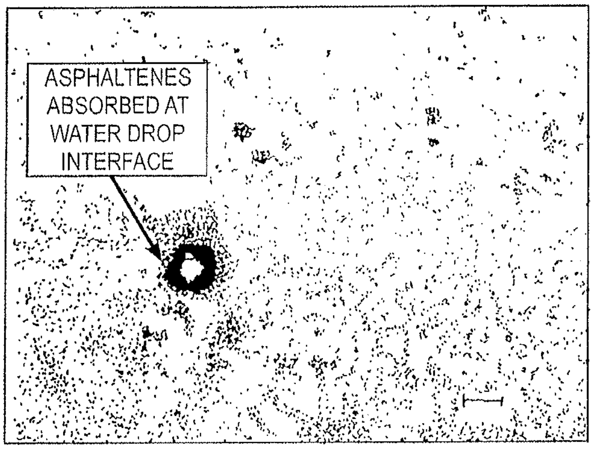

ASPHALTENES ABSORBED AT WATER DROP INTERFACE

Fig. 3B

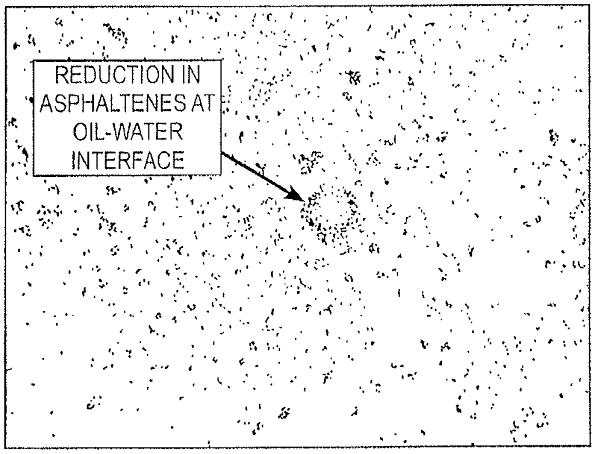

REDUCTION IN ASPHALTENES AT OIL-WATER INTERFACE

Fig. 4

% OF GUANIDINE HCL SATURATION IN WATER	% WATER RESOLVED AT THE INDICATED TIME		
	5 MIN	2 HR	2 DAYS
0	75	90	90
25	60	50	60
50	70	60	70
75	60	60	70
100	50	60	80

Fig. 5A

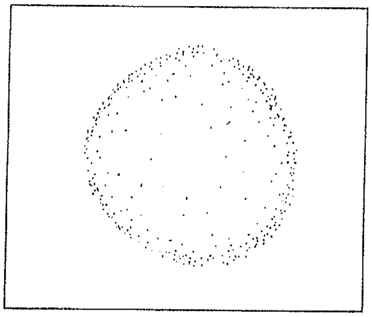


Fig. 5B

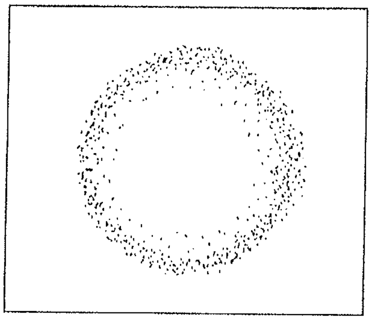


Fig. 5C

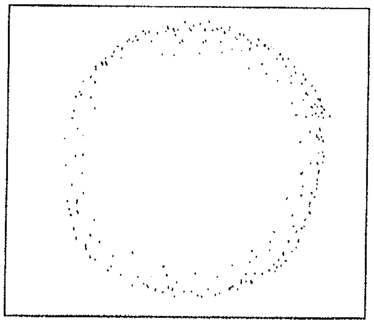


Fig. 6

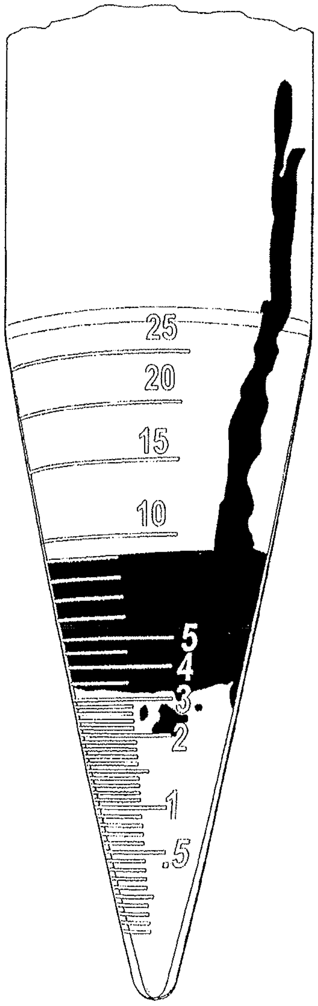
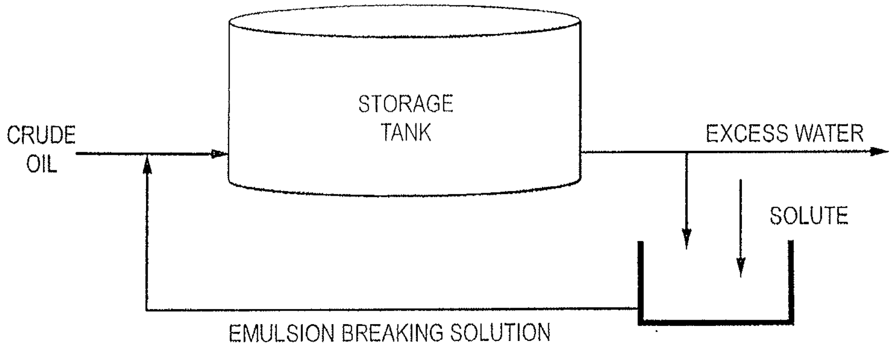


Fig. 7


STORAGE TANK
CRUDE OIL
EXCESS WATER
SOLUTE
EMULSION BREAKING SOLUTION