

SURFACTANTS FOR USE IN AGRICULTURAL FORMULATIONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Patent Application No. 18/795,176, filed August 5, 2024, which claims priority to U.S. Provisional Patent Application Serial No. 63/531,188, filed August 7, 2023, the entire disclosures of which are incorporated by reference in their entireties.

FIELD

[0002] The present disclosure pertains to surfactants for use in agricultural products. Such surfactants may include siloxane derivatives of amino acids wherein the siloxane derivatives have surface-active properties.

BACKGROUND

[0003] Surfactants (molecules with surface-active properties) are widely used in commercial agricultural formulations. These formulations may include a variety of active agricultural agents, such as pesticides, plant growth regulators, fungicides, herbicides, and/or insecticides. Many such active agricultural agents display limited water solubility or may be prone to crystallization. Precipitation of the active agricultural agent can result in a loss of efficiency. Should the active agent be concentrated in the precipitates, it may be unevenly distributed when sprayed on a field. Thus, surfactants may be included in formulations to improve solubility, wetting, and spreadability of the active agent.

[0004] The surfactants may be uncharged, zwitterionic, cationic, or anionic. Although in principle any surfactant class (e.g., cationic, anionic, nonionic, amphoteric) is suitable, it is possible that a formulation may include a combination of two or more surfactants from two or more surfactant classes.

[0005] Often, surfactants are amphiphilic molecules with a relatively water-insoluble hydrophobic "tail" group and a relatively water-soluble hydrophilic "head" group. These compounds may adsorb at an interface, such as an interface between two liquids, a liquid and a gas, or a liquid and a solid. In systems comprising relatively polar and relatively non-polar components the hydrophobic tail

preferentially interacts with the relatively non-polar component(s) while the hydrophilic head preferentially interacts with the relatively polar component(s). In the case of an interface between water and oil, the hydrophilic head group preferentially extends into the water, while the hydrophobic tail preferentially extends into the oil. When added to a water-gas interface, the hydrophilic head group preferentially extends into the water, while the hydrophobic tail preferentially extends into the gas. The presence of the surfactant disrupts at least some of the intermolecular interaction between the water molecules, replacing at least some of the interactions between water molecules with generally weaker interactions between at least some of the water molecules and the surfactant. This results in lowered surface tension and can also serve to stabilize the interface.

[0006] At sufficiently high concentrations, surfactants may form aggregates which serve to limit the exposure of the hydrophobic tail to the polar solvent. One such aggregate is a micelle. In a typical micelle the molecules are arranged in a sphere with the hydrophobic tails of the surfactant(s) preferentially located inside the sphere and the hydrophilic heads of the surfactant(s) preferentially located on the outside of the micelle where the heads preferentially interact with the more polar solvent. The effect that a given compound has on surface tension and the concentration at which it forms micelles may serve as defining characteristics for a surfactant.

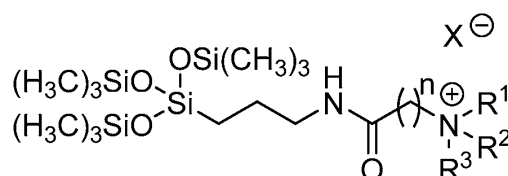
SUMMARY

[0007] The present disclosure provides formulations of agricultural products, such as pesticides, plant growth regulators, fungicides, herbicides, and insecticides. These products may be formulated to include one or more surfactants from one or more surfactant classes disclosed herein. The surfactants may be used as emulsifiers, wetting agents, dispersants, and/or agents to improve spreadability. Sometimes, surfactants may be used as adjuvants and agents to control spin drift, or otherwise impact other properties of the formulated products.

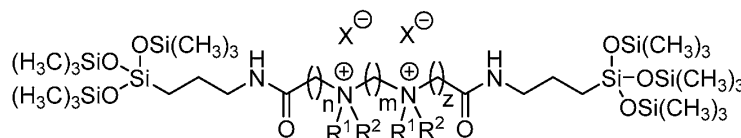
[0008] The present disclosure provides surfactants for agricultural products in the form of siloxane derivatives of amino acids that have surface-active properties. The amino acids may be naturally occurring or synthetic amino acids, or they may be obtained via ring-opening reactions of molecules such as lactams, for example

caprolactam. The amino acids may be functionalized with different types of siloxane groups to form compounds with surface-active properties. Characteristically, these compounds may have low critical micelle concentrations (CMC) and/or the ability to reduce the surface tension of a liquid.

[0009] The present disclosure provides a formulation for a pesticide or plant growth regulator, comprising one or more surfactant molecules bearing the structure(s) of Formula I or II,



Formula I



Formula II

wherein R^1 and R^2 may be the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R^3 may be selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_{12} linker attached to an additional surfactant molecule having a structure represented by Formula I, wherein the additional surfactant molecule of Formula I is the same or different from the surfactant molecule of Formula I;

n and z may be selected independently from any integer from 1 to 12;

m may be any integer from 1 to 12; and

X may be selected from the group consisting of chloride, bromide, and iodide;

a pesticide or plant growth regulator; and
optionally a water-insoluble solvent.

[0010] For clarity, as disclosed herein, and with respect to any of the formulations provided herein, the molecule of Formula II may represent a construct of the following structure:

Formula I – Linker – Formula I,

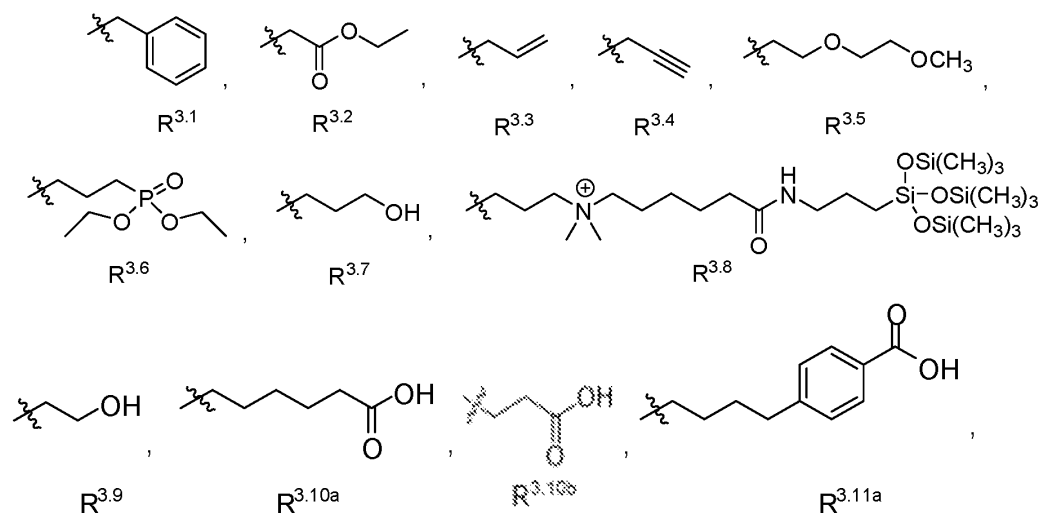
wherein one molecule of Formula I may be the same as, or different from, the other molecule of Formula I. In this exemplary construct, the Linker is R^3 in Formula I, a C_1 - C_{12} linker.

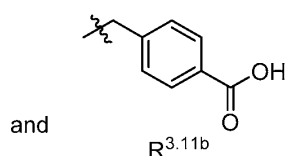
[0011] Further surfactant molecules provided by the present disclosure are those compounds of Formula I or II, wherein R^1 and R^2 are methyl.

[0012] Other surfactant molecules provided by the present disclosure are compounds of Formula I or II, wherein n and/or z are 5.

[0013] Specifically, R^3 may be selected from the group consisting of C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_2 - C_{12} ester, C_1 - C_{10} hydroxyl, benzyl, C_2 - C_{12} alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_5 alkyl benzoic acid, and a three-carbon linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same as the first molecule of Formula I.

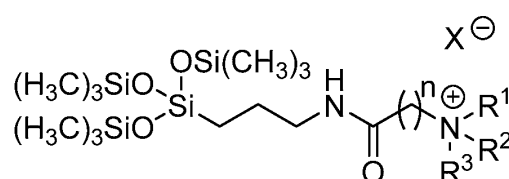
[0014] More specifically, R^3 may be selected from the group consisting of the formulas below:



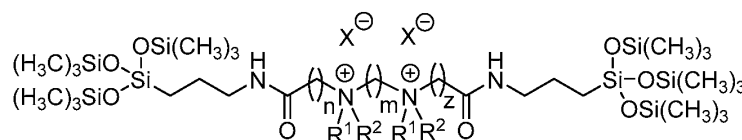


[0015] There is further disclosed, the use as a surfactant of a compound of Formula I or II as described herein in a pesticide or plant growth regulator formulation as described herein.

[0016] The present disclosure further provides a formulation for a fungicide, comprising one or more surfactant molecules bearing the structure(s) of Formula I or II,



Formula I



Formula II

wherein R^1 and R^2 may be the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R^3 may be selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_{12} linker attached to an additional surfactant molecule having a structure represented by Formula I, wherein the additional surfactant molecule of Formula I is the same or different from the surfactant molecule of Formula I;

n and z may be selected independently from any integer from 1 to 12;

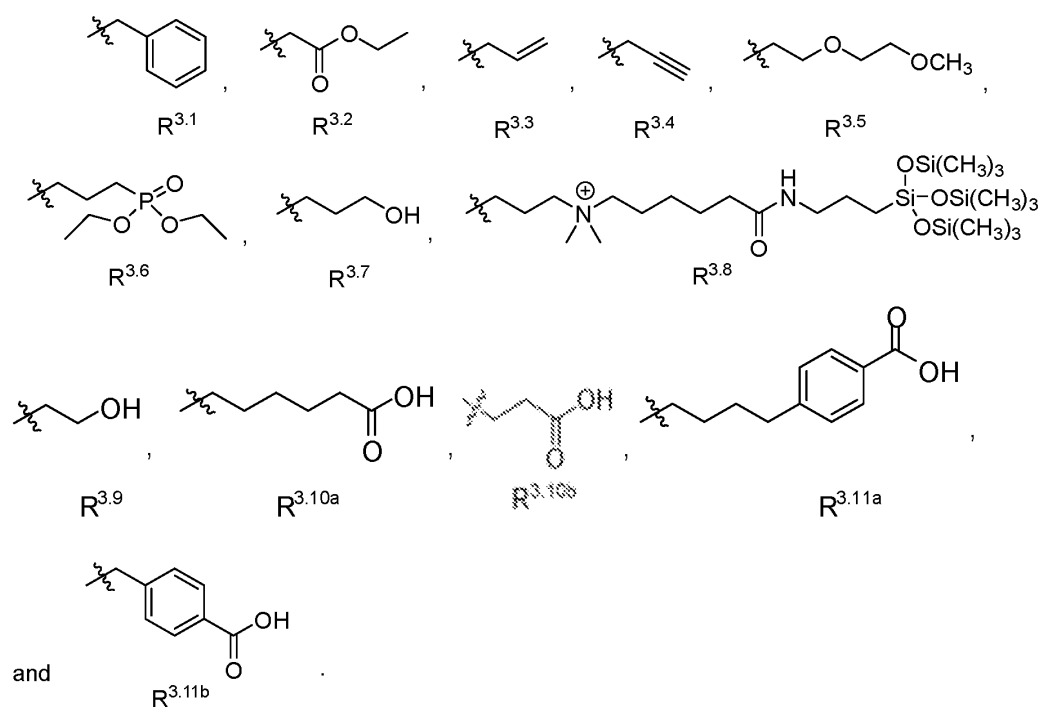
m may be any integer from 1 to 12; and

X may be selected from the group consisting of chloride, bromide, and iodide,

a fungicide, optionally a co-surfactant, and/or an optional carrier agent, such as a solvent or solid carrier.

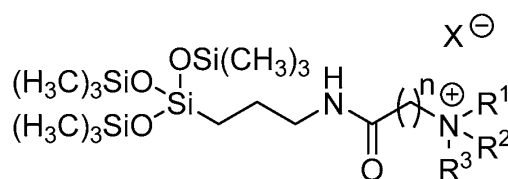
[0017] Specifically, R^3 may be selected from the group consisting of C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_2 - C_{12} ester, C_1 - C_{10} hydroxyl, benzyl, C_2 - C_{12} alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_5 alkyl benzoic acid, and a three-carbon linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same as the first molecule of Formula I.

[0018] More specifically, R^3 may be selected from the group consisting of the formulas below:

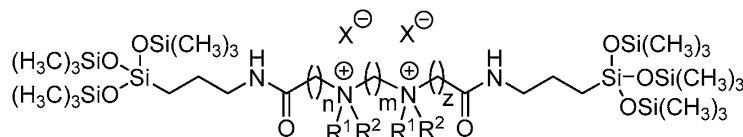


[0019] There is further disclosed, the use as a surfactant of a compound of Formula I or II as described herein in a fungicide formulation.

[0020] The present disclosure further provides a formulation for an insecticide, comprising one or more surfactant molecules bearing the structure(s) of Formula I or II,



Formula I



Formula II

wherein R^1 and R^2 may be the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R^3 may be selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_{12} linker attached to an additional surfactant molecule having a structure represented by Formula I, wherein the additional surfactant molecule of Formula I is the same or different from the surfactant molecule of Formula I;

n and z may be selected independently from any integer from 1 to 12;

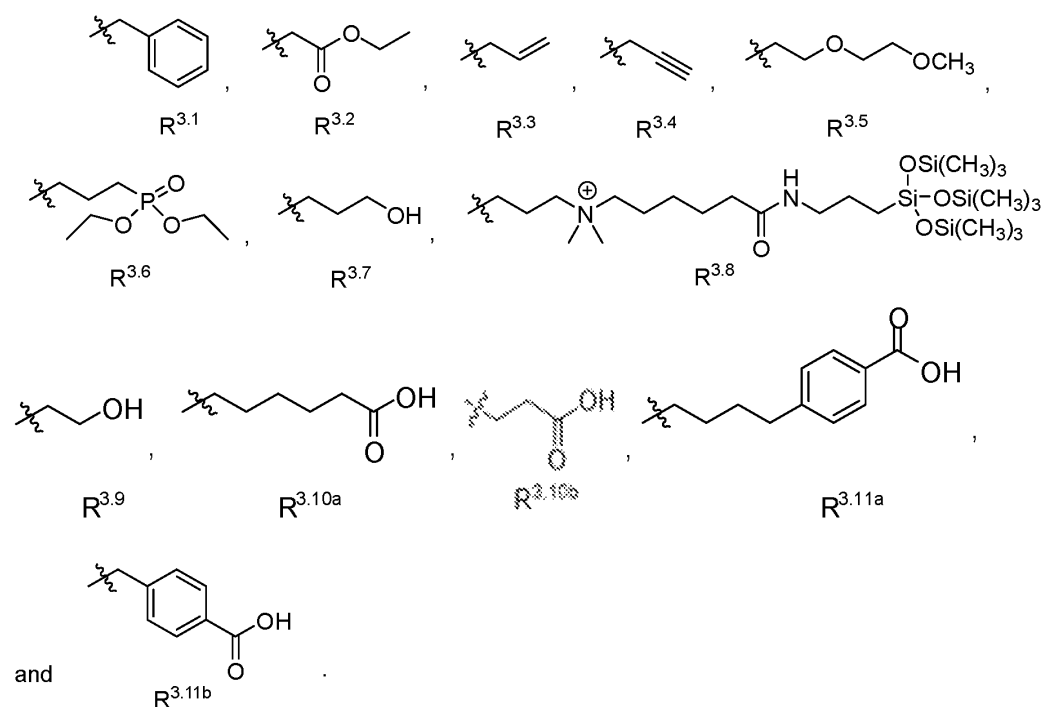
m may be any integer from 1 to 12; and

X may be selected from the group consisting of chloride, bromide, and iodide;

an insecticide, an optional antifoaming agent, an optional antifreezing agent, and/or water.

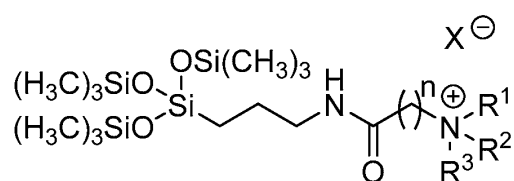
[0021] Specifically, R^3 may be selected from the group consisting of C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_2 - C_{12} ester, C_1 - C_{10} hydroxyl, benzyl, C_2 - C_{12} alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_5 alkyl benzoic acid, and a three-carbon linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same as the first molecule of Formula I.

[0022] More specifically, R^3 may be selected from the group consisting of the formulas below:

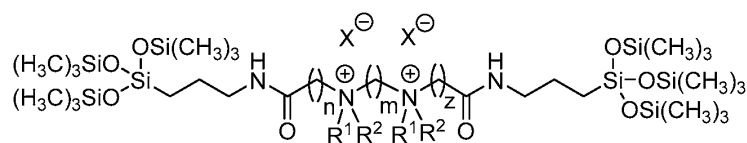


[0023] There is further disclosed, the use as a surfactant of a compound of Formula I or II as described herein in an insecticide formulation.

[0024] The present disclosure further provides a formulation for a herbicide, comprising one or more surfactant molecules bearing the structure(s) of Formula I or II,



Formula I



Formula II

wherein R^1 and R^2 may be the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R^3 may be selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_{12} linker attached to an additional surfactant molecule having a structure represented by Formula I, wherein the additional surfactant molecule of Formula I is the same or different from the surfactant molecule of Formula I;

n and z may be selected independently from any integer from 1 to 12;

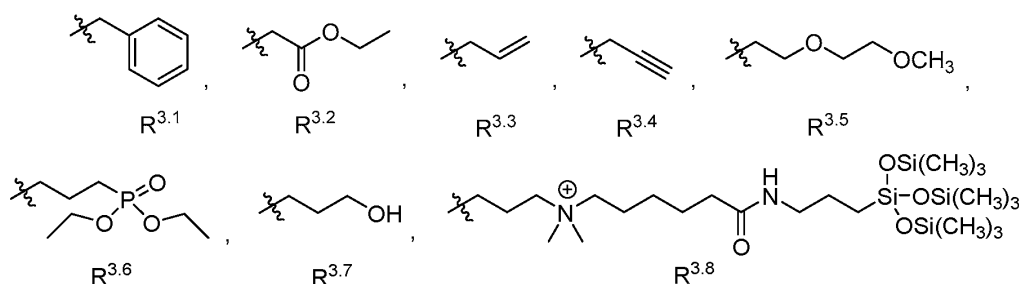
m may be any integer from 1 to 12; and

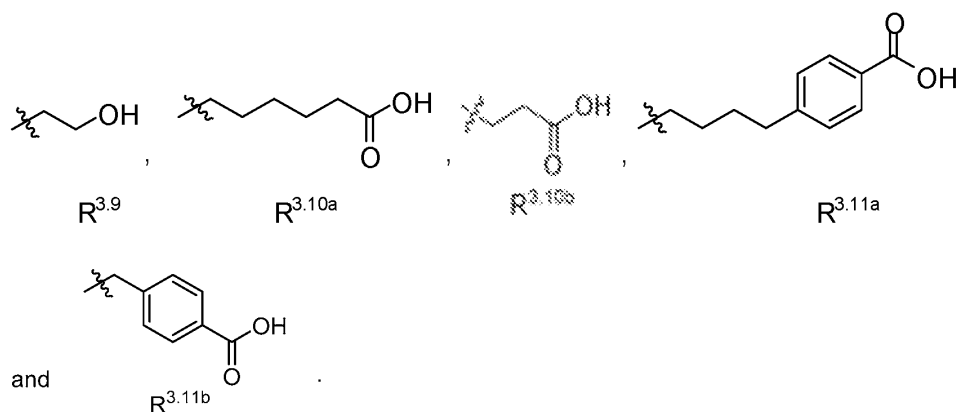
X may be selected from the group consisting of chloride, bromide, and iodide;

and a herbicide, an optional antifoaming agent, an optional antifreezing agent, and/or water.

[0025] Specifically, R^3 may be selected from the group consisting of C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_2 - C_{12} ester, C_1 - C_{10} hydroxyl, benzyl, C_2 - C_{12} alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_5 alkyl benzoic acid, and a three-carbon linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same as the first molecule of Formula I.

[0026] More specifically, R^3 may be selected from the group consisting of the formulas below:





[0027] There is further disclosed, the use as a surfactant of a compound of Formula I or II as described herein in a herbicide formulation.

[0028] The above mentioned and other features of the disclosure, and the manner of attaining them, will become more apparent and will be better understood by reference to the following description of embodiments taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] Fig. 1 shows a plot of surface tension versus concentration for Surfactant 1 as described in Example 2b.

[0030] Fig. 2 shows a plot of surface tension versus concentration for Surfactant 2 as described in Example 3b.

[0031] Fig. 3 shows a plot of surface tension versus concentration for Surfactant 3 as described in Example 4b.

[0032] Fig. 4 shows a plot of surface tension versus concentration for Surfactant 4 as described in Example 5b.

[0033] Fig. 5 shows a plot of surface tension versus concentration for Surfactant 5 as described in Example 6b.

[0034] Fig. 6 shows a plot of surface tension versus concentration for Surfactant 6 as described in Example 7b.

[0035] Fig. 7 shows a plot of surface tension versus concentration for Surfactant 7 as described in Example 8b.

[0036] Fig. 8 shows a plot of surface tension versus concentration for Surfactant 8 as described in Example 9b.

[0037] Fig. 9 shows a plot of surface tension versus concentration for Surfactant 9 as described in Example 11b.

[0038] Fig. 10 shows a plot of surface tension versus concentration for Surfactant 10 as described in Example 10b.

[0039] Fig. 11 shows a plot of surface tension versus concentration for Surfactant as described in Comparative Example A2.

DETAILED DESCRIPTION

[0040] As used herein, the phrase “within any range using these endpoints” literally means that any range may be selected from any two of the values listed prior to such phrase regardless of whether the values are in the lower part of the listing or in the higher part of the listing. For example, a pair of values may be selected from two lower values, two higher values, or a lower value and a higher value.

[0041] As used herein, the word “alkyl” means any saturated carbon chain, which may be a straight or branched chain, and may be substituted at any point along the carbon chain. The carbon chain may have 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 carbons.

[0042] As used herein, the phrase “surface-active” means that the associated compound is able to lower the surface tension of the medium in which it is at least partially dissolved, and/or the interfacial tension with other phases, and, accordingly, may be at least partially adsorbed at the liquid/vapor and/or other interfaces. The term “surfactant” may be applied to such a compound.

[0043] With respect to the terminology of inexactitude, the terms “about” and “approximately” may be used, interchangeably, to refer to a measurement that includes the stated measurement and that also includes any measurements that are reasonably close to the stated measurement. Measurements that are reasonably close to the stated measurement deviate from the stated measurement by a reasonably small amount as understood and readily ascertained by individuals having ordinary skill in the relevant arts. Such deviations may be attributable to measurement error or minor adjustments made to optimize performance, for example. In the event it is determined that individuals having ordinary skill in the relevant arts would not readily ascertain values for such reasonably small differences, the terms “about” and “approximately” can be understood to mean plus

or minus 15% of the stated value, for example, plus or minus 15%, plus or minus 12%, plus or minus 10%, plus or minus 9%, plus or minus 8%, plus or minus 8%, plus or minus 7%, plus or minus 6%, plus or minus 5%, plus or minus 4%, plus or minus 3%, plus or minus 2%, or even plus or minus 1% and so on.

[0044] The present disclosure provides formulations of agricultural products, such as pesticides, plant growth regulators, fungicides, insecticides, and herbicides.

I. Pesticide and Plant Growth Regulator Formulations

[0045] Active agricultural agents such as pesticides have conventionally been provided to the end-user in different concentrated forms to be diluted in water or other suitable medium to a dilute ready-to-use formulation by the end-user. Such concentrated forms include solid formulations, e.g. powders, and liquid formulations. In many applications, liquid formulations are preferred as problems of dusting of toxic powders and slow dissolution in the diluent may be avoided.

[0046] The liquid concentrated formulations include so-called emulsion concentrates and soluble liquid concentrates. An emulsion concentrate comprises a pesticide, a water-insoluble solvent, and an emulsifier, and when added to the water, it spontaneously, or after mixing, forms an oil-in-water emulsion, the agricultural active primarily being present in the emulsion droplets. This type of concentrated formulation is especially suitable for agricultural actives that are water insoluble/have low water solubility, and where the recommended concentration in the ready-to-use formulation exceeds the solubility of the agricultural active.

[0047] The present disclosure provides a pesticide or plant growth regulator formulation with a high concentration of the agriculturally active agent, suitable for long term storage and delivery to the end user, who eventually will treat plants by contacting the plant with an agricultural formulation prepared from the concentrated pesticidal formulation described herein.

[0048] The pesticide formulations of the present disclosure may include an agriculturally active agent (a pesticide or a plant growth regulator), one or more surfactant molecules of the structure(s) of Formula I or II, one or more additional surfactants or co-surfactants chosen from one or more surfactant classes, and a water-insoluble solvent.

[0049] The present disclosure provides the use as a surfactant of a compound of Formula I or II in a pesticide or plant growth regulator formulation. The compounds of Formula I or II and the pesticide or plant growth regulator formulation are as described herein.

1. *Pesticide*

[0050] The term “pesticide,” or synonymously, “pesticidal formulation,” as used herein, is well known in the art and is described at least by the Environmental Protection Agency (EPA), in the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), in the Insecticides and Environmental Pesticide Control Subchapter (7 U.S.C. § 136(u)), in the Code of Federal Regulations (CFR) relating to the “Protection of Environment,” and in the Regulations of the EPA in 40 CFR § 152.3. A pesticide is typically recognized in the art as a substance that is used for preventing, destroying, repelling, regulating, and/or mitigating any pest. A pest is an organism that is deleterious to man or the environment but does not include any internal parasite of living man or other living animal or any fungus, bacterium, virus, or other microorganism on or in living man or other living animals. Said differently, the terminology “pest” does not typically include any organism that infects or sickens humans or animals. In addition, the terminology “pesticide,” as used herein, does not typically include any human or animal drugs or pharmaceuticals, any article that is a “new animal drug” as defined in the art, any liquid sterilant applied to a device used in the human body, and/or any products intended for use against fungi, bacteria, viruses, or other microorganisms in or on living man or living animal. Moreover, the pesticide of this disclosure does not typically include drugs or pharmaceuticals used to control diseases of humans or animals (such as livestock and pets).

[0051] As used herein, the term “plant growth regulator” refers to a compound, which through physiological action will accelerate or retard the rate of growth or rate of maturation or otherwise alter the behavior of ornamental or crop plants or the products thereof.

[0052] Pesticides and plant growth regulators especially contemplated for use in the present invention are organic compounds, such as synthetic organic compounds. Suitable pesticides and plant growth regulators include triazoles, strobilurins, alkylenebis(dithiocarbamate) compounds, benzimidazoles, phenoxy

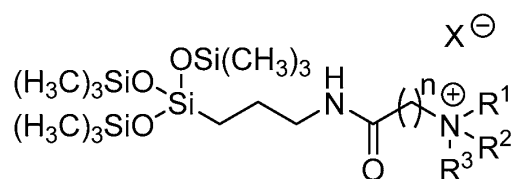
carboxylic acids, benzoic acids, ureas, sulfonylureas, triazines, pyridine carboxylic acids, neonicotinides, amidines, organophosphates, and pyrethroids. The pesticide may have a water solubility of 1g/L or less.

[0053] In a concentrated formulation of the present disclosure, the pesticide or plant growth regulator is present, typically in an amount of about 1 wt.% or greater, 5 wt.% or greater, about 10 wt.% or greater, about 15 wt.% or greater, about 20 wt.% or greater, or in an amount of about 25 wt.% or lower, about 30 wt.% or lower, about 35 wt.% or lower, about 40 wt.% or lower, about 50% or lower, or within any range of 1 wt.% to 50 wt.%, or 5 wt.% to 40 wt.%, or 10 wt.% to 35 wt.%, or 15 wt.% to 30 wt.%, or 20 wt.% to 25 wt.%, or within any range using these endpoints, by weight of the composition.

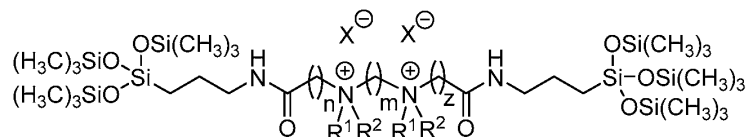
2. *Surfactant*

[0054] The pesticide formulations of the present disclosure comprise one or more surfactants of the disclosure, whereby the surfactants present in a given formulation can also be referred to as a surfactant system. The surfactant system is included to emulsify the composition, and/or to act as an adjuvant. The surfactant system comprises at least one surfactant, which may be an amphoteric surfactant, a zwitterionic surfactant, a cationic surfactant, a nonionic surfactant, and optionally at least one other surfactant, which may be an amphoteric surfactant, a zwitterionic surfactant, a cationic surfactant, a nonionic surfactant, or a combination thereof. Such surfactants and/or surfactant systems should be physically and chemically compatible with the essential components described herein, or should not otherwise unduly impair product stability, aesthetics, or performance.

[0055] Suitable surfactants for use in the pesticide formulations of the present disclosure include one or more surfactant molecule and/or co-surfactant molecule of Formula I or II,



Formula I



Formula II

wherein R^1 and R^2 may be the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R^3 may be selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_{12} linker attached to an additional surfactant molecule having a structure represented by Formula I, wherein the additional surfactant molecule of Formula I is the same or different from the surfactant molecule of Formula I;

n and z may be selected independently from any integer from 1 to 12;

m may be any integer from 1 to 12; and

X may be selected from the group consisting of chloride, bromide, and iodide;

and optionally a soil penetration agent; a foaming agent; a foam booster; a pH stabilizer; at least one thickener; a fragrance, and water.

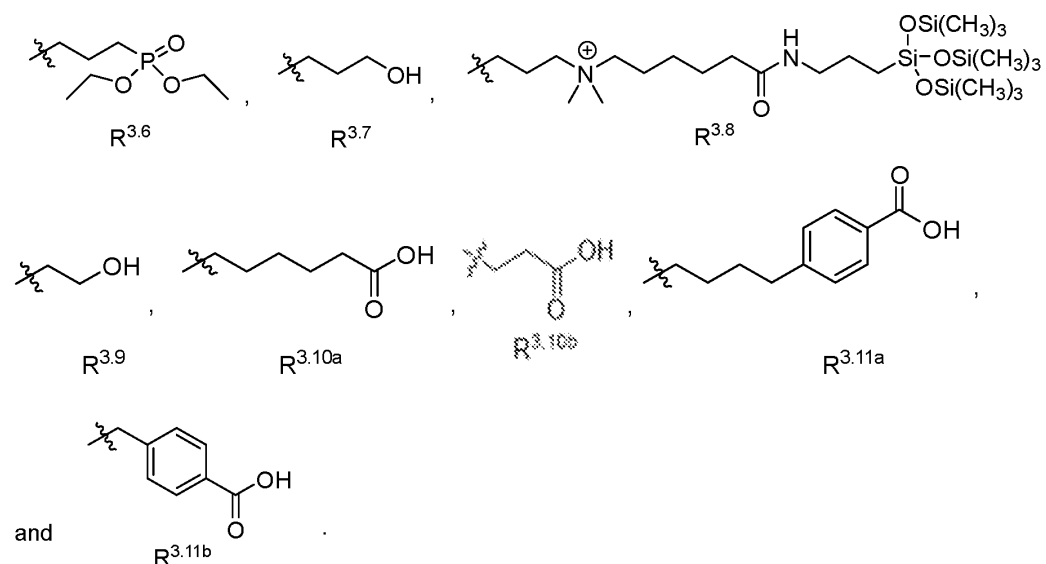
[0056] For clarity, as disclosed herein, and with respect to any of the formulations provided herein, the molecule of Formula II may represent a construct of the following structure:

Formula I – Linker – Formula I,

wherein one molecule of Formula I may be the same as, or different from, the other molecule of Formula I. In this exemplary construct, the Linker is R^3 in Formula I, a C_1 - C_{12} linker.

[0057] Specifically, R^3 may be selected from the group consisting of C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_2 - C_{12} ester, C_1 - C_{10} hydroxyl, benzyl, C_2 - C_{12} alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_5 alkyl benzoic acid, and a three-carbon linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same as the first molecule of Formula I.

[0058] More specifically, R^3 may be selected from the group consisting of the formulas below:



[0059] Suitable surfactants or co-surfactants, which may or may not be a part of a surfactant system, may include one or more of the Surfactants 1-12 described herein.

[0060] The surfactant system, which may comprise one or more surfactants of the same or different types, in the pesticide formulation may be present at a concentration of about 10 wt.% or greater, about 15 wt.% or greater, about 20 wt.% or greater, about 25 wt.% or greater, about 30 wt.% or greater, about 35 wt.% or

greater, about 40 wt.% or greater, even about 45 wt.% or greater, or at a concentration of about 50 wt.% or lower, about 55 wt.% or lower, about 60 wt.% or lower, about 65 wt.% or lower, about 70 wt.% or lower, about 75 wt.% or lower, or about 80 wt.% or lower, or within any range of 10 wt.% to 80 wt.%, or 15 wt.% to 75 wt.%, or 20 wt.% to 70 wt.%, or 25 wt.% to 65wt.%, or 30 wt.% to 60 wt.%, or 35 wt.% to 55 wt.%, or 40 wt.% to 50 wt.%, or 45 wt.% to 50 wt.%, or within any range using these endpoint, by weight of the composition.

3. *Water-Insoluble Solvent*

[0061] The pesticide formulations of the present disclosure may include a water-insoluble solvent. A solvent is considered water-insoluble if its water solubility is about 10 g/L of water or less, about 5 g/L of water or less, about 1 g/L of water or less, or about 0.1 g/L of water or less, at 20° C.

[0062] Suitable water-insoluble solvents may include aromatic solvents such as those sold under the tradename of Solvesso™, and water-insoluble alcohols, such as linear or branched, aliphatic or aromatic, saturated or unsaturated alcohols with, for example, 6 or more carbon atoms.

4. *Other additives*

[0063] The pesticide formulation may include other additives such as additional surfactants, water, thickeners, deposition enhancers, drift control agents, salts, stabilizers, penetrants, spreading agents, wetting agents, building agents, extending agents, emulsifiers, dispersants, suspending agents, plant penetrants, translocators, oils, activators, foliar nutrients, compatibility agents, drift retardants, foam retardants, buffers, inverting agents, soil penetrants, stabilizing agents, UV filters, feeding stimulants, washing agents, sinking agents, binders, liquid carriers, dry carriers such as attapulgite, kaolinite, vermiculite, starch polymers, corn cob, and combinations thereof. The pesticide formulation may also include additional chemical compounds that are not pesticides, such as activators, anti-feedants, anti-fouling agents, attractant agents, chemosterilants, disinfectant agents, fumigant agents, pheromones, repellent agents, defoliant, desiccants, insect growth regulators, plant growth regulators, synergists, adjuvants, and combinations thereof.

[0064] These additives may individually be present in the pesticidal formulation in an amount of about 0 wt.% or greater, about 5 wt.% or greater, about 10 wt.% or greater, about 15 wt.% or greater, or about 20 wt.% or lower, about 25

wt.% or lower, about 30 wt.% or lower, or within any range of 0 wt.% to 30 wt.%, or 5 wt.% to 25 wt.%, or 10 wt.% to 20 wt.%, or 15 wt.% to 20 wt.%, or within any range using these endpoints.

[0065] In addition to the surfactant system already present in the pesticide formulation of the present disclosure, and particularly for the formulation of concentrate, certain additional surfactants, such as additional anionic, non-ionic, cationic, amphoteric, and zwitterionic surfactants, may present in the concentrated composition at a concentration of about 5 wt.% or greater, about 10 wt.% or greater, about 15 wt.% or greater, about 20 wt.% or greater, or about 25 wt.% or lower, about 30 wt.% or lower, about 35 wt.% or lower, about 40 wt.% or lower, or within any range of 5 wt.% to 40 wt.%, or 10 wt.% to 35 wt.%, or 15 wt.% to 30 wt.%, or 20 wt.% to 25 wt.%, or within any range using these endpoints, by weight of the composition.

[0066] Water may be present in the concentrated composition at a concentration of about 0 wt.% or greater, about 5 wt.% or greater, about 10 wt.% or greater, about 20 wt.% or greater, about 30 wt.% or greater, or about 35 wt.% or lower, about 45 wt.% or lower, about 55 wt.% or lower, about 65 wt.% or lower, or within any range of 0 wt.% to 65 wt.%, or 5 wt.% to 55 wt.%, or 10 wt.% to 45 wt.%, or 20 wt.% to 35 wt.%, or 30 wt.% to 35 wt.%, or within any range using these endpoints, by weight of the composition.

[0067] Polymers may be included in the concentrated composition, as thickeners, deposition enhancers, or drift control agents. Suitable polymers may include polysaccharide ethers and synthetic polymers.

[0068] Water-soluble organic solvents, such as glycol ethers, butyl diglycol, N-formyl-morpholine, shorter aliphatic alcohols, propylene carbonate, may be present in the pesticidal formulation at a weight ratio water-soluble organic solvent:water-insoluble organic solvent of for example, 1:2.

5. *Method of Making*

[0069] The method includes the step of combining the surfactant system, the pesticide, and optionally the water insoluble solvent. This step may also include adding any additives described above. The aforementioned components and compounds may be added in any order to one or more of each other and in any amount and in one or more individual steps, e.g., in whole or in parts.

6. *Method of Use*

[0070] The concentrated pesticidal formulation of the present disclosure may be in liquid form at room temperature and/or atmospheric pressure, with the agriculturally active ingredient solubilized therein.

[0071] The concentrated pesticidal formulation may be intended to be mixed with an aqueous medium, typically tap water, before end use. The concentrated composition is added to a tank, before, simultaneously with, or after, addition of the aqueous medium (typically water) to the tank. The concentrated pesticidal composition is therewith diluted to a suitable concentration of the agriculturally active.

[0072] The water content in the diluted pesticidal formulation of the present disclosure may be from about 75 wt.% or greater, about 90 wt.% or greater, about 99 wt.% or greater, or about 99.9 wt.% or greater, based on the total weight of the diluted composition, and will ultimately depend on the amount of water needed to dilute the agriculturally active ingredient in the concentrated pesticidal formulation of the present disclosure to the desired concentration in the ready-to-use composition.

[0073] When mixed with and diluted in the aqueous medium, the agriculturally active is evenly distributed in the aqueous medium, in the form of a solution or a fine emulsion and can be further diluted substantially or otherwise handled in normal use conditions without causing any crystal growth in the resulting formulation.

[0074] Plants may be treated with the diluted, ready-to-use pesticidal formulation by contacting the plant to be treated with the composition or in its diluted form in any manner conventionally used. As used herein, the term "plant" refers not only to the individual stem, leaf and/or fruit of the plant, visible above ground, but also to the roots as well as the seed from which the plant may grow. The amount of active ingredient contacted with the plant is sufficient for the active ingredient to exercise its pesticidal or plant growth regulating activity, i.e. an effective amount.

II. Fungicide Formulations

[0075] The present disclosure provides formulations of fungicides. The fungicide formulation may be in solid or liquid form. Fungi against which the formulation may be employed include, without limitations, Basidiomycetes, Ascomycetes, Adalomyces or Fungi imperfecti-type fungi, especially heifers, oidia, eyespot, fusarioses, *Fusarium roseum*, *Fusarium nivale*, net blotch, leaf blotch,

Septoria spot and sin Rhizoctonia, etc. These harmful fungi can cause diseases in most vegetables and plants, but especially in cereals such as wheat, barley, rye, oats or their hybrids, and rice and corn crops of all varieties.

[0076] The fungicide formulation may include a fungicide, an emulsifier component, such as one or more surfactant molecules of the structure(s) of Formula I or II, an optional co-emulsifier, such as one or more additional surfactants or co-surfactants, and an optional carrier agent, such as a solvent or solid carrier.

[0077] The present disclosure provides the use as a surfactant of a compound of Formula I or II in a fungicide formulation. The compounds of Formula I or II and the fungicide formulation are as described herein.

1. Fungicide

[0078] The fungicidal formulation of the present disclosure includes at least one fungicidal compound that can be used to remove or otherwise clear fungal infections on a target plant or prevent the plant from getting a fungal infection. Suitable fungicides include, but are not limited to: azoxystrobin, benalaxyl, carbendazim, chlorothalonil, cupfer, cymoxanil, cyproconazol, diphenconazol, dinocap, epoxyconazol, fluazinam, flusilazol, flutriafol, folpel, fosetyl aluminum, kresoxim methyl, hexaconazol, mancozeb, metalaxyl, metconazol, myclobutanil, ofurace, phentimhydroxide, prochloraz, pyremethanil, soufre, tebuconazol and tetraconazol, and mixtures thereof.

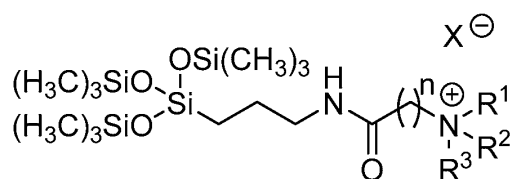
[0079] The fungicidal formulation may further include a herbicide. Suitable herbicides include, but are not limited to: alachlor, acetoniphen, acetochlor, amidosulfuron, aminotriazol, atrazin, bentazon, biphenox, bromoxyl octanoate, bromoxynil, clethodim, chlordinafop-propargyl, chloridazon, chlorsulfuron, chlortoluron, clomazon, cycloxydim, desmedipham, dicamba, dicyclofop-methyl, diurea, difluphenicanil, dimithenamid, ethofumesat, fluazifop, fluazifop-p-butyl, fluorochloridon, fluroxypyr, glufosinat, glyphosate, galoxyp-R, ioxynil octanoate, isoproturon, isoxaben, metamitron, metazachlor, metolachlor, metsulfuron-methyl, nicosulfuron, notflurazon, oryzalin, oxadiazon, oxyfluorphen, paraquat, pendimethalin, phenmedipham, phenoxyprop-p-ethyl, propaquizafop, prosulfocarb, quizalofop, sulcotrion, sulphosat, terbutylazin, triasulfuron, trichlorpyr, triflualin and triflusalforon-methyl which may be used individually or in admixture with one another.

[0080] The amount of fungicide in the fungicide formulation of the present disclosure may be about 1 wt.% or greater, about 5 wt.% or greater, about 10 wt.% or greater, about 15 wt.% or greater, about 20 wt.% or greater, about 25 wt.% or greater, about 30 wt.% or greater, about 35 wt.% or greater, about 40 wt.% or greater, about 45 wt.% or greater, or about 50 wt.% or less, about 55 wt.% or less, about 60 wt.% or less, about 65 wt.% or less, about 70 wt.% or less, about 75 wt.% or less, about 80 wt.% or less, about 85 wt.% or less, about 90 wt.% or less, or any range of 1 wt.% to 90 wt.%, or 5 wt.% to 85 wt.%, or 10 wt.% to 80 wt.%, or 15 wt.% to 75 wt.%, or 20 wt.% to 70 wt.%, or 25 wt.% to 65 wt.%, or 30 wt.% to 60 wt.%, or 35 wt.% to 55 wt.%, or 40 wt.% to 50 wt.%, or 45 wt.% to 50 wt.%, or any range combination using these endpoints, based on the total weight of the liquid fungicidal formulation.

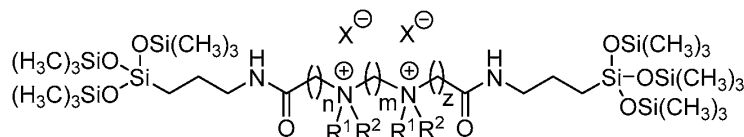
2. Surfactant

[0081] The fungicide formulations of the present disclose may comprise one or more surfactants of the disclosure., whereby the surfactants present in a given formulation may also be referred to as a surfactant system. The surfactant system may be used as a dispersing or wetting agent. The surfactant system may also be used as an emulsifier to form a stable emulsion of the liquid fungicide formation when prepared for agricultural applications. The emulsifier component may also be used to form a stable emulsifiable concentrate. In one embodiment, the surfactant system comprises at least one surfactant, which may be an amphoteric surfactant, a zwitterionic surfactant, a cationic surfactant, a nonionic surfactant, and optionally at least one other surfactant, which may be an amphoteric surfactant, a zwitterionic surfactant, a cationic surfactant, a nonionic surfactant, or in the event more than one other surfactant in the surfactant system, a combination thereof.

[0082] Suitable surfactants for use in the fungicidal formulations of the present disclosure include one or more surfactant molecule and/or co-surfactant molecule of Formula I or II,



Formula I



Formula II

wherein R^1 and R^2 may be the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R^3 may be selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_{12} linker attached to an additional surfactant molecule having a structure represented by Formula I, wherein the additional surfactant molecule of Formula I is the same or different from the surfactant molecule of Formula I;

n and z may be selected independently from any integer from 1 to 12;

m may be any integer from 1 to 12; and

X may be selected from the group consisting of chloride, bromide, and iodide.

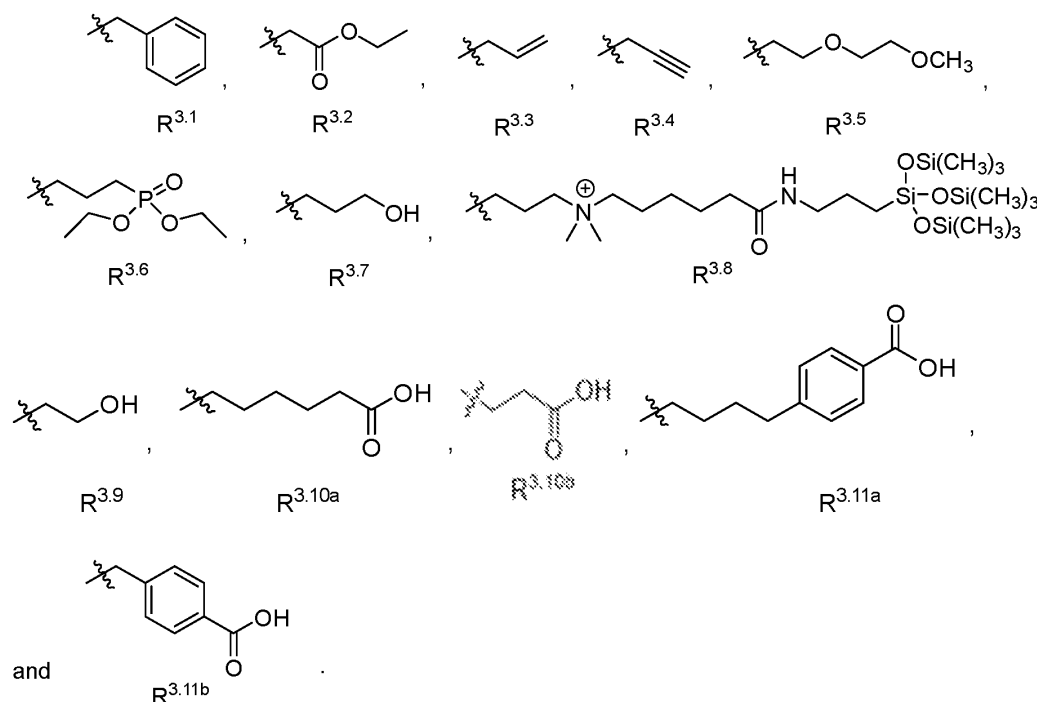
[0083] For clarity, as disclosed herein, and with respect to any of the formulations provided herein, the molecule of Formula II may represent a construct of the following structure:

Formula I – Linker – Formula I,

wherein one molecule of Formula I may be the same as, or different from, the other molecule of Formula I. In this exemplary construct, the Linker is R^3 in Formula I, a C_1 - C_{12} linker.

[0084] Specifically, R^3 may be selected from the group consisting of C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_2 - C_{12} ester, C_1 - C_{10} hydroxyl, benzyl, C_2 - C_{12} alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_5 alkyl benzoic acid, and a three-carbon linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same as the first molecule of Formula I.

[0085] More specifically, R^3 may be selected from the group consisting of the formulas below:



[0086] In particular, suitable surfactants or co-surfactants may include one or more of any of Surfactants 1-12 described herein below.

[0087] The total amount of the surfactant system, comprising a single or more than one surfactants of the present disclosure, in the fungicidal formulation may be about 1 wt.% or greater, about 5 wt.% or greater, about 10 wt.% or greater, or about 15 wt.% or less, about 20 wt.% or less, about 25 wt.% or less, about 30 wt.% or less, or about 35 wt.% or less, or about 40 wt.% or less, or about 50 wt.% or less, or within any range of 1 wt.% to 50 wt.%, or 5 wt.% to 40 wt.%, or 10 wt.% to 35 wt.%, or 10 wt.% to 30 wt.%, or 10 wt.% to 25 wt.%, or 10 wt.% to 15 wt.%, or within any range using these endpoints.

3. *Co-Emulsifier or Co-Surfactant*

[0088] The fungicide composition may include an optional co-emulsifier or co-surfactant. The optional co-surfactant may be an anionic surfactant and/or a non-ionic surfactant, and may include one or more of the surfactants presently disclosed or others. For example, the anionic surfactant may be one selected from the present disclosure or one known in the art, and it may be an alkali, alkaline earth or ammonium salts of fatty acids, such as potassium stearate, alkyl sulfates, alkyl ether sulfates, alkylsulfonates or iso-alkylsulfonates, alkylnaphthalenesulfonates, alkyl methyl ester sulfonates, acyl glutamates, alkylsulfosuccinates, sarcosinates such as sodium lauroyl sarcosinate or taurates, and combinations thereof. The anionic surfactant may be present in the emulsifier component in any amount.

[0089] The suitable non-ionic emulsifier may be selected from the surfactants of the present disclosure or from known emulsifiers in the art, such as alkoxyated animal or vegetable fats and oils such as corn oil ethoxylates, soybean oil ethoxylates, castor oil ethoxylates, tallow fatty ethoxylates, glycerol esters such as glycerol monostearate, fatty alcohol alkoxyates and oxoalcohol alkoxyates, fatty acid alkoxyates such as oleic acid ethoxylates, alkylphenol alkoxyates such as isononylphenol ethoxylates, fatty amine alkoxyates, fatty acid amide alkoxyates, sugar surfactants such as sorbitan fatty acid esters (e.g. sorbitan monooleate, and sorbitan tristearate), polyoxyethylene sorbitan fatty acid esters, alkyl polyglycosides, N-alkylgluconamides, alkylmethyl sulfoxides, alkyl dimethylphosphine oxides such as tetradecyldimethylphosphine oxide, and combinations thereof.

4. *Carrier Agent*

[0090] The fungicidal formulation of the present disclosure may include a carrier agent. As used herein, the term "carrier" refers to a material of natural or synthetic, organic or inorganic form which, when combined with the active ingredient, promotes its application to the plant, seeds or soil. Therefore, this carrier is usually inert, but must also be agriculturally acceptable, especially for the plant to be treated. The carrier may be solid (clay, natural or synthetic silicates, silicon dioxide, resins, waxes or solid fertilizers, etc.) or liquid (water, alcohols, ketones, petroleum fractions, aromatic or paraffinic hydrocarbons, chlorinated hydrocarbons, liquefied gases, etc.).

5. *Other Additives*

[0091] The fungicide formulation may include other additives such as stabilizers, penetrants, spreading agents, wetting agents, building agents, extending agents, emulsifiers, dispersants, suspending agents, plant penetrants, translocators, oils, activators, foliar nutrients, compatibility agents, drift retardants, foam retardants, buffers, inverting agents, soil penetrants, stabilizing agents, UV filters, feeding stimulants, washing agents, sinking agents, binders, liquid carriers, dry carriers such as attapulgite, kaolinite, vermiculite, starch polymers, corn cob, and combinations thereof. The pesticide formulation may also include additional chemical compounds that are not pesticides, such as activators, anti-feedants, anti-fouling agents, attractant agents, chemosterilants, disinfectant agents, fumigant agents, pheromones, repellent agents, defoliants, desiccants, insect growth regulators, plant growth regulators, synergists, adjuvants, and combinations thereof.

[0092] These additives may individually be present in the pesticidal formulation in an amount of about 0 wt.% or greater, about 5 wt.% or greater, about 10 wt.% or greater, about 15 wt.% or greater, or about 20 wt.% or lower, about 25 wt.% or lower, about 30 wt.% or lower, or within any range of 0 wt.% to 30 wt.%, or 5 wt.% to 25 wt.%, or 10 wt.% to 20 wt.%, or 15 wt.% to 20 wt.%, or within any range using these endpoints.

6. *Fungicidal Emulsion*

[0093] The liquid fungicidal formulation may be added to water and/or another solvent to form an agricultural emulsion at point of sale and/or use. Typically, well-formed agricultural emulsions can be milky in appearance, spontaneously bloom (i.e., form), and have sufficient stability for efficacious application. However, the fungicidal emulsions of the present disclosure are not limited to such parameters and may have other characteristics that are indicative of successful emulsion formation.

[0094] The present disclosure provides an aqueous fungicidal formulation that includes the aforementioned fungicidal formulation and water. The liquid fungicide formulation may be combined with the water in a spray tank or in an independent tank prior to addition to a spray tank. For example, the liquid fungicide formulation may be added to an independent container and/or a spray tank with the water or separate from the water. The terminology "diluted" describes that the agricultural liquid fungicidal formulation including the water.

[0095] The water used to prepare the diluted fungicidal formulation may be at a concentration of about 5 wt.% or greater, about 10 wt.% or greater, about 20 wt.% or greater, about 25 wt.% or greater, about 30 wt.% or greater, about 35 wt.% or greater, about 40 wt.% or greater, about 45 wt.% or greater, about 50 wt.% or greater, or about 60 wt.% or lower, about 65 wt.% or lower, about 70 wt.% or lower, about 75 wt.% or lower, about 80 wt.% or lower, about 85 wt.% or lower, about 90 wt.% or lower, about 99 wt.% or lower, about 99.5 wt.% or lower, or within any range of 5 wt.% to 99.5 wt.%, or 10 wt.% to 99 wt.%, or 20 wt.% to 90 wt.%, or 25 wt.% to 85 wt.%, or 30 wt.% to 80 wt.%, or 35 wt.% to 75 wt.%, or 40 wt.% to 70 wt.%, or 45 wt.% to 65 wt.%, or 50 wt.% to 60 wt.%, or within any range using these endpoints.

[0096] The fungicide may be present in the diluted fungicidal formulation in amounts from about 0.00001 wt.% or greater, about 0.0001 wt.% or greater, about 0.001 wt.% or greater, about 0.01 wt.% or greater, about 0.1 wt.% or greater, about 1 wt.% or greater, or about 2 wt.% or lower, about 4 wt.% or lower, about 6 wt.% or lower, about 8 wt.% or lower, about 10 wt.% or lower, or within any range of 0.00001 wt.% to 10 wt.%, or 0.0001 wt.% to 8 wt.%, or 0.001 wt.% to 6 wt.%, or 0.01 wt.% to 4 wt.%, or 0.1 wt.% to 2 wt.%, or 1 wt.% to 2 wt.%, or within any range using these endpoints.

[0097] After application to the target plants, the fungicide may be present on the plants in an amount (or in an amount equivalent to) of about 100 g/hectare or greater, about 200 g/hectare or greater, about 300 g/hectare or greater, about 400 g/hectare or greater, about 500 g/hectare or greater, or about 600 g/hectare or lower, about 700 g/hectare or lower, about 800 g/hectare or lower, about 900 g/hectare or lower, about 1000 g/hectare or lower, or within any range of 100 g/hectare to 1000 g/hectare, or 200 g/hectare to 900 g/hectare, or 300 g/hectare to 800 g/hectare, or 400 g/hectare to 700 g/hectare, or 500 g/hectare to 600 g/hectare, or within any range using these endpoints.

7. *Emulsifiable Concentrate*

[0098] The present disclosure provides a fungicidal emulsion that may be formed as an emulsifiable concentrate (also known in the art as an "EC"). To that end, the fungicidal composition comprising the one or more of the surfactants of the present disclosure may be deemed an EC because the formulation meets the required viscosity at ambient temperature, although not necessarily. The

emulsifiable concentrate may be a liquid that has a viscosity of about 1 cps or greater, 20 cps or greater, 40 cps or greater, 60 cps or greater, 80 cps or greater, 100 cps or greater, or 120 cps or lower, 140 cps or lower, 160 cps or lower, 180 cps or lower, 200 cps or lower, or within any range of 1 cps to 200 cps, or 20 cps to 180 cps, or 40 cps to 160 cps, or 60 cps to 140 cps, or 80 cps to 120 cps or 100 to 120 cps, or within any range using these endpoints, at 25 °C. for example, the emulsifiable concentrate may be a liquid that has a viscosity of 1 to 200, 50 to 200, 100 to 200, or less than or equal to about 200, cps at 25° C. Without intending to be bound by any particular theory, it is believed that a viscosity of less than or equal to about 200 cps at 25° C promotes blooming and efficient formation of an emulsion when the emulsifiable concentrate is used.

[0099] The emulsifiable concentrate itself may be anhydrous, i.e., free of water. Alternatively, the emulsifiable concentrate may include water. The emulsifiable concentrate may include water in an amount of 5 wt.% or less, 2.5 wt.% or less, 1 wt.% or less, 0.5 wt.% or less, or 0.1 wt.% or less. The emulsifiable concentrate may include less than 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, or 1, part by weight of water per 100 parts by weight of the emulsifiable concentrate. The emulsifiable concentrate is a single oil-like, e.g. hydrophobic, phase that does not include water. When added to water or another solvent, the emulsifiable concentrate may form a milky white agricultural emulsion that blooms and that has little to no phase separation, as is described in greater detail below.

[0100] The emulsifiable concentrate may include a single phase. In other words, the emulsifiable concentrate may not include a distinct non-polar phase and a distinct polar phase but instead a single phase that includes the active component (the fungicide), the surfactant system, the optional co-surfactant, and/or the optional water-insoluble solvent. It is to be appreciated that the single phase may include partial phase separation but does not typically include total phase separation. At low temperatures, phase separation may occur. The emulsifiable concentrate may be described as including or being the aforementioned surfactant system and the fungicide (e.g. without the optional solvent and/or without the optional co-surfactant).

8. Solid Formulation

[0101] The formulation for a fungicide as disclosed above can be in the form of a solid. In particular, the solid form composition can be a powder or dispersion

suitable for dusting, in particular the solid form composition can be a particulate composition which is extruded, extruded, or extruded. The solid formulations may be formed through impregnation of a carrier powder with the active agent and surfactant as disclosed, or by granulation of a powder comprising the active agent and a surfactant as disclosed herein.

[0102] The amount of active agent in these granular compositions may be about 1 wt.% or greater, 10 wt.% or greater, 20 wt.% or greater, 30 wt.% or greater, of about 40 wt.% or lower, about 50 wt.% or lower, about 60 wt.% or lower, about 70 wt.% or lower, about 80 wt.% or lower, or within any range of 1 wt.% to 80 wt.%, or 10 wt.% to 70 wt.%, or 20 wt.% to 60 wt.%, or 30 wt.% to 50 wt.%, or 30 wt.% to 40 wt.%, or within any range using these endpoints.

[0103] The formulation for a fungicide as disclosed above can be in the form of a wettable powder formulation (or spray powder) which may include the active agent in an amount of about 20 wt.% or greater, about 30 wt.% or greater, about 40 wt.% or greater, or about 50 wt.% or greater, about 60 wt.% or lower, about 70 wt.% or lower, about 80 wt.% or lower, about 90 wt.% or lower, about 95 wt.% or lower, or within any range of 20 wt.% to 95 wt.%, or 30 wt.% to 90 wt.%, or 40 wt.% to 80 wt.%, or 50 wt.% to 70 wt.%, or 50 wt.% to 60 wt.%, or within any range using these endpoints.

[0104] Wettable powder formulations may include wetting agents, which can be a surfactant selected from one or more of the surfactants described in the present disclosure, in an amount of about 0 wt.% or greater, about 1 wt.% or greater, about 2 wt.% or greater, or about 3 wt.% or lower, about 4 wt.% or lower, about 5 wt.% or lower, about 10 wt.% or lower, or within any range of 0 wt.% to 10 wt.%, or 1 wt.% to 5 wt.%, or 2 wt.% to 4 wt.%, or 2 wt.% to 3 wt.%, or within any range using these endpoints.

[0105] The wettable powder formulations may include a dispersant, which can be a surfactant, selected from one or more of the surfactants of the present disclosure, in an amount of about 3 wt.% or greater, about 4 wt.% or greater, about 5 wt.% or greater, about 6 wt.% or greater, or about 7 wt.% or lower, about 8 wt.% or lower, about 9 wt.% or lower, or about 10 wt.% or lower, or within any range of 3 wt.% to 10 wt.%, or 4 wt.% to 9 wt.%, or 5 wt.% to 8 wt.%, or 6 wt.% to 7 wt.%, or within any range using these endpoints.

[0106] The wettable powder formulations may include a solid carrier, which may include any solid carrier known in the art, in an amount or about 0 wt.% or greater, about 1 wt.% or greater, about 2 wt.% or greater, about 3 wt.% or greater, about 4 wt.% or greater, about 5 wt.% or greater, or about 6 wt.% or lower, about 7 wt.% or lower, about 8 wt.% or lower, about 9 wt.% or lower, about 10 wt.% or lower, or within any range of 0 wt.% to 10 wt.%, or 1 wt.% to 9 wt.%, or 2 wt.% to 8 wt.%, or 3 wt.% to 7 wt.%, or 4 wt.% to 6 wt.%, or 5 wt.% to 6 wt.%, or within any range using these endpoints.

[0107] The wettable powder formulations may contain one or more stabilizers and/or other additives, such as pigments, colorants, permeation agents, adhesion promoters or anti-caking agents.

[0108] In order to produce these wettable powder formulations or sprayable powders, the active agent(s) are intimately mixed with the other components in a suitable mixing apparatus, and the resulting mixture is milled with mills or other suitable grinding equipment. Thus, sprayable powders are obtained which have a wettability and suspendability. Thus, they can be suspended in arbitrary concentrations in water, and these suspensions are particularly useful for treating seeds in particular.

[0109] In addition, the formulation for a fungicide as disclosed herein can be in the form of a paste. The conditions and methods of preparation and use of the pastes are similar to those for wettable powders or spray powders.

[0110] In addition, the formulation for a fungicide as disclosed herein can be in the form of a dispersible granular composition, which may be prepared by agglomeration in a suitable granulation system to provide powder compositions similar to wettable powder formulations.

III. Herbicide formulation

[0111] The present disclosure further provides formulations of herbicides. Herbicides are commonly known as weed killers, and, generally, are substances used to control undesired plants, also known as weeds. Selective herbicides control specific weed species while leaving the desired crop relatively unharmed, while non-selective herbicides (sometimes called total weed killers in commercial products) can be used to clear waste ground, industrial and construction sites, railways and railway

embankments as they kill all plant material with which they come into contact. Apart from selective/non-selective, other important distinctions include persistence or residual action, i.e., how long the product stays in place and remains active, and whether the herbicide is absorbed by above-ground foliage only, through the roots, or by other means. Historically, products such as common salt and other metal salts were used as herbicides, however, these have gradually fallen out of favor, and in some countries, a number of these are banned due to their persistence in soil, and toxicity and groundwater contamination concerns.

[0112] The herbicide formulations disclosed herein may be applied to a plant in a herbicidally effective amount, and can effectively control one or more plant species of one or more of the following genera without restriction: *Abutilon*, *Amaranthus*, *Artemisia*, *Asclepias*, *Avena*, *Axonopus*, *Borreria*, *Brachiaria*, *Brassica*, *Bromus*, *Chenopodium*, *Cirsium*, *Commelina*, *Convolvulus*, *Cynodon*, *Cyperus*, *Digitaria*, *Echinochloa*, *Eleusine*, *Elymus*, *Equisetum*, *Erodium*, *Helianthus*, *Imperata*, *Ipomoea*, *Kochia*, *Lolium*, *Malva*, *Oryza*, *Ottlochloa*, *Panicum*, *Paspalum*, *Phalaris*, *Phragmites*, *Polygonum*, *Portulaca*, *Pteridium*, *Pueraria*, *Rubus*, *Salsola*, *Setaria*, *Sida*, *Sinapis*, *Sorghum*, *Triticum*, *Typha*, *Ulex*, *Xanthium* and *Zea*.

[0113] The herbicidal formulations of the present disclosure may include an herbicide, and optional second herbicide, one or more surfactants one or more surfactant molecules of the structure(s) of Formula I or II, a water-insoluble solvent, and water.

[0114] The present disclosure provides the use as a surfactant of a compound of Formula I or II in a herbicide formulation. The compounds of Formula I or II and the herbicide formulation are as described herein.

1. *Herbicide*

[0115] The herbicide formulation of the present disclosure may include herbicides or their water-soluble salts. Suitable herbicides may include 2,4-D (2,4-dichlorophenoxyacetic acid), 2,4-DB (4-(2,4-dichlorophenoxy)butyric acid), aminocyclopyrachlor, aminopyralid, clopyralid, dicamba, glyphosate, MCPA, MCPB, picloram, triclopyr, or mixtures thereof.

[0116] The water-soluble salts of the herbicides may include salts containing one or more cations selected from the class of organo ammonium cations, wherein

the organo ammonium cations may have from 1 to about 12 carbon atoms, such as organo ammonium cations include, for example, isopropyl ammonium, diglycol ammonium (2-(2-aminoethoxy)ethanol ammonium), dimethyl ammonium, diethyl ammonium, triethyl ammonium, monoethanol ammonium, dimethylethanol ammonium, diethanol ammonium, triethanol ammonium, triisopropanol ammonium, tetramethyl ammonium, tetraethylammonium, N,N,N-trimethylethanol ammonium (choline), and N,N-bis-(3-aminopropyl)methyl ammonium (BAPMA).

[0117] Additionally, the water-soluble salts of the herbicides may include salts containing one or more cations selected from inorganic cations such as, for example, sodium and/or potassium.

[0118] In the case of acidic herbicides, such as auxin herbicides, the herbicide active ingredient may be present in the herbicide formulation at an amount of about 100 grams acid equivalent per liter (g ae/L) or greater, about 200 g ae/L or greater, about 300 g ae/L or greater, or about 400 g ae/L or lower, about 500 g ae/L or lower, about 600 g ae/L or lower, about 625 g ae/L or lower, or within any range of 100 g ae/L to 625 g ae/L, or 200 g ae/L to 600 g ae/L, or 300 g ae/L to 500 g ae/L, or 300 g ae/L to 400 g ae/L, or within any range using these endpoints.

[0119] Some herbicide active agents described herein do not contain an acid-type functional group and, for these active ingredients, the terms “acid equivalent” and “acid equivalent basis” are not accurate to describe the amount of the second herbicide present. Generally, in such instances, the terms “active ingredient” or “active ingredient basis” can be used to describe the amount of the second herbicide active ingredient present. For example, grams active ingredient per liter (g ai/L) may be used in place of grams acid equivalent per liter (g ae/L), or grams active ingredient per kilogram (g ai/kg) may be used in place of grams acid equivalent per kilogram (g ae/kg) when the active ingredient does not have an acid equivalent.

2. *Optional Second Herbicide*

[0120] Suitable second herbicides may be for example, without limitation, esters of 4-CPA, 4-CPB, 4-CPP, 2,4-D, 3,4-DA, 2,4-DB, 3,4-DB, 2,4-DEB, 2,4-DEP, 3,4-DP, 2,4,5-T, 2,4,5-TB, and 2,3,6-TBA, allidochlor, acetochlor, acifluorfen, aclonifen, alachlor, alloxymid, alorac, ametrifone, ametryn, amibuzin, amicarbazone, amidosulfuron, aminocyclopyrachlor esters, aminopyralid esters, amiprofos-methyl, amitrole, anilofos, anisuron, asulam, atraton, atrazine, azafenidin,

azimsulfuron, aziprotryne, barban, BCPC, beflubutamid, benazolin, bencarbazone, benfluralin, benfuresate, bensulfuron, bensulide, bentazone, benzadox, benzfendizone, benzipram, benzobicyclon, benzofenap, benzofluor, benzoylprop, benzthiazuron, bicylopyrone, bifenox, bilanafos, bispyribac, bromacil, bromobonil, bromobutide, bromofenoxim, bromoxynil, brompyrazon, butachlor, butafenacil, butamifos, butenachlor, buthidazole, buthiuron, butralin, butroxydim, buturon, butylate, cafenstrole, cafenstrole, cambendichlor, carbasulam, carbasulam, carbetamide, carboxazole chlorprocarb, carfentrazone, CDEA, CEPC, chlomethoxyfen, chloramben, chloranocryl, chlorazifop, chlorazine, chlorbromuron, chlorbufam, chloreturon, chlorfenac, chlorfenprop, chlorflurazole, chlorflurenol, chloridazon, chlorimuron, chlornitrofen, chloropon, chlorotoluron, chloroxuron, chloroxynil, chlorpropham, chlorsulfuron, chlorthal, chlorthiamid, cinidon-ethyl, cinmethylin, cinosulfuron, cisanilide, clethodim, clidinate, clodinafop, clofop, clomazone, clomeprop, clomeprop, cloprop, cloproxydim, clopyralid esters, cloransulam, CPMF, CPPC, credazine, cumyluron, cyanatryn, cyanazine, cycloate, cyclosulfamuron, cycloxydim, cycluron, cyhalofop, cyperquat, cyprazine, cyprazole, cypromid, daimuron, dalapon, dazomet, delachlor, desmedipham, desmetryn, di-allate, dicamba esters, dichlobenil, dichloralurea, dichlormate, dichlorprop, dichlorprop-P, diclofop, diclosulam, diethamquat, diethatyl, difenopenten, difenoxuron, difenzoquat, diflufenican, diflufenzopyr, dimefuron, dimepiperate, dimethachlor, dimethametryn, dimethenamid, dimethenamid-P, dimexano, dimidazon, dinitramine, dinitramine, dinofenate, dinoprop, dinosam, dinoseb, dinoterb, diphenamid, dipropetryn, diquat, disul, dithiopyr, diuron, DMPA, DNOC, EBEP, eglinazine, endothal, epronaz, epronaz, EPTC, erbon, esprocarb, ethalfluralin, ethametsulfuron, ethidimuron, ethiolate, ethofumesate, ethoxyfen, ethoxysulfuron, etinofen, etnipromid, etnipromid, etnipromid, etobenzanid, EXD, fenasulam, fenasulam, fenasulam, fenoprop, fenoxaprop, fenoxaprop-P, fenoxasulfone, fenteracol, fenthiafop, fentrazamide, fenuron, flamprop, flamprop-M, flazasulfuron, florasulam, fluazifop, fluazifop-P, fluazolate, flucarbazone, flucetosulfuron, fluchloralin, flufenacet, flufenican, flufenpyr, flumetsulam, flumezin, flumiclorac, flumioxazin, flumipropyn, fluometuron, fluorodifen, fluoroglycofen, fluoromidine, fluoronitrofen, fluothiuron, flupoxam, flupoxam, flupropacil, flupropanate, flupyrsulfuron, fluridone, fluorochloridone, non-liquid fluoroxypyr esters,

fluoroxypyr-meptyl, flurtamone, fluthiacet, fomesafen, fomesafen, foramsulfuron, fosamine, furyloxyfen, glyphosate, halauxfen, halauxfen-methyl, halosafen, halosafen, halosulfuron, haloxydine, haloxyfop, haloxyfop-P, hexazinone, imazamethabenz, imazamox, imazapic, imazapyr, imazaquin, imazethapyr, imazosulfuron, indanofan, indaziflam, iodobonil, iodosulfuron, ioxynil, ipazine, ipfencarbazone, iprymidam, isocarbamid, isocil, isomethiozin, isonoruron, isopollinate, isopropalin, isoproturon, isouron, isoxaben, isoxachlortole, isoxaflutole, isoxapyrifop, karbutilate, ketospiradox, lactofen, lenacil, linuron, MCPA esters, MCPA-thioethyl, MCPA-EHE, MCPB esters, mecoprop, mecoprop-P, medinoterb, mefenacet, mefluidide, mesoprazine, mesosulfuron, mesotrione, metam, metamifop, metamifop, metamidron, metazachlor, metazosulfuron, metflurazon, methabenzthiazuron, methalpropalin, methazole, methiobencarb, methiozinol, methiuron, methiuron, methometon, methoprotrotyne, methylidymron, metobenzuron, metobromuron, metolachlor, S-metolachlor, metosulam, metoxuron, metribuzin, metsulfuron, molinate, monalide, monisouron, monolinuron, monuron, morfamquat, naproanilide, napropamide, naptalam, neburon, nicosulfuron, nipyraclufen, nitratin, nitrofen, nitrofluorfen, norflurazon, noruron, OCH, orbencarb, orthosulfamuron, oryzalin, oryzalin, oxadiargyl, oxadiazon, oxapyrazon, oxasulfuron, oxaziclonofone, oxyfluorfen, parafluoron, paraquat, pebulate, pelargonic acid, pendimethalin, penoxsulam, pentanochlor, pentoxazone, perfluidone, pethoxamid, phenisopham, phenmedipham, phenmedipham-ethyl, phenobenzuron, picloram esters, picolinafen, pinoxaden, piperophos, pretilachlor, primisulfuron, procyazine, prodiamine, prodiamine, profluzol, profluralin, profoxydim, proglinazine, prometon, prometryn, propachlor, propanil, propaquizafop, propazine, propham, propisochlor, propoxycarbazone, propyrisulfuron, propyzamide, prosulfalin, prosulfocarb, prosulfuron, proxan, prynachlor, pydanon, pyraclonil, pyraflufen, pyrasulfotole, pyrazolynate, pyrazosulfuron, pyrazoxyfen, pyribenzoxim, pyributicarb, pyriclor, pyridafol, pyridate, pyrifthalid, pyriminobac, pyrimisulfan, pyriothiobac, pyrosulfotole, pyroxasulfone, pyroxsulam, quinclorac, quinmerac, quinclamine, quinonamid, quizalofop, quizalofop-P, rhodethanil, rimsulfuron, saflufenacil, sebuthylazine, sebumeton, sethoxydim, siduron, simazine, simeton, simetryn, sulcotrione, sulfallate, sulfentrazone, sulfometuron, sulfosulfuron, sulglycapin, swep, tebutam, tebuthiuron, tefuryltrione, tembotrione, tepraloxydim, terbacil, terbucarb, terbutylchlor,

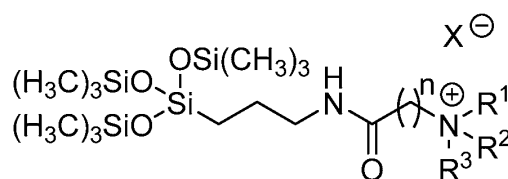
terbumeton, terbuthylazine, terbutryn, tetrafluron, thenylchlor, thiazafluron, thiazopyr, non-liquid triclopyr esters, thidiazimin, thidiazuron, thidiazuron, thiencarbazone-methyl, thifensulfuron, thiobencarb, tiocarbazil, tioclorim, topramezone, tralkoxydim, tri-allate, triasulfuron, triaziflam, tribenuron, tricamba, tridiphane, trietazine, trifloxysulfuron, trifluralin, triflusulfuron, trifop, trifopsime, trihydroxytriazine, trimeturon, tripropindan, tritac, tritosulfuron, vernolate, xylachlor and mixtures and derivatives thereof.

[0121] If present, the second herbicide can be present at a concentration of about 0 g ae/L or greater, 0.1 g ae/L or greater, 10 g ae/L or greater, 50 g ae/L or greater, 100 g ae/L or greater, or 200 g ae/L or lower, about 300 g ae/L or lower, about 400 g ae/L or lower, or within any range of 0 g ae/L to 400 g ae/L, or 0.1 g ae/L to 300 g ae/L, or 10 g ae/L to 200 g ae/L, or 50 g ae/L to 200 g ae/L, or 100 g ae/L to 200 g ae/L, or within any range using these endpoints.

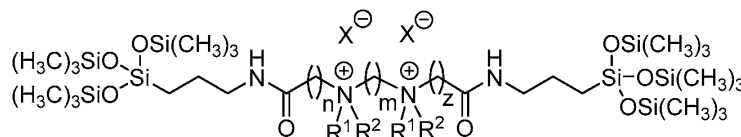
[0122] Some second herbicide active agents described herein do not contain an acid-type functional group and, for these active ingredients, the terms “acid equivalent” and “acid equivalent basis” are not accurate to describe the amount of the second herbicide present. Generally, in such instances, the terms “active ingredient” or “active ingredient basis” can be used to describe the amount of the second herbicide active ingredient present. For example, grams active ingredient per liter (g ai/L) may be used in place of grams acid equivalent per liter (g ae/L), or grams active ingredient per kilogram (g ai/kg) may be used in place of grams acid equivalent per kilogram (g ae/kg) when the active ingredient does not have an acid equivalent

3. *Surfactant*

[0123] Suitable surfactants for use in the herbicide formulations of the present disclosure include one or more surfactant molecule and/or co-surfactant molecule of Formula I or II,



Formula I



Formula II

wherein R^1 and R^2 may be the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R^3 may be selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_{12} linker attached to an additional surfactant molecule having a structure represented by Formula I, wherein the additional surfactant molecule of Formula I is the same or different from the surfactant molecule of Formula I;

n and z may be selected independently from any integer from 1 to 12;

m may be any integer from 1 to 12; and

X may be selected from the group consisting of chloride, bromide, and iodide.

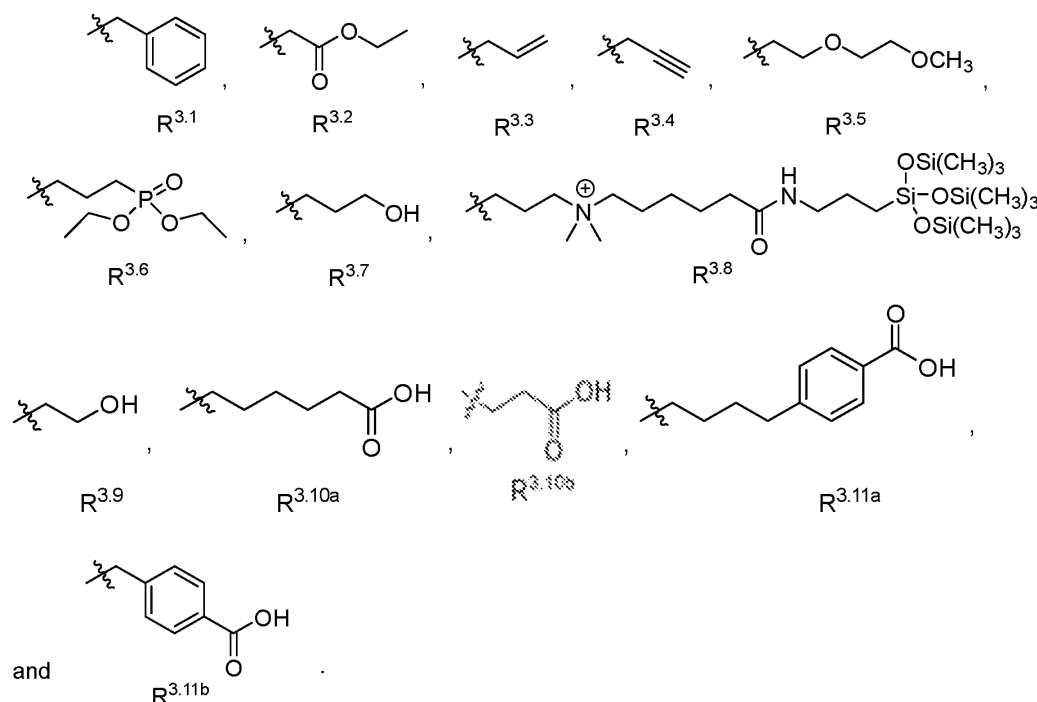
[0124] For clarity, as disclosed herein, and with respect to any of the formulations provided herein, the molecule of Formula II may represent a construct of the following structure:

Formula I – Linker – Formula I,

wherein one molecule of Formula I may be the same as, or different from, the other molecule of Formula I. In this exemplary construct, the Linker is R^3 in Formula I, a C_1 - C_{12} linker.

[0125] Specifically, R^3 may be selected from the group consisting of C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_2 - C_{12} ester, C_1 - C_{10} hydroxyl, benzyl, C_2 - C_{12} alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_5 alkyl benzoic acid, and a three-carbon linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same as the first molecule of Formula I.

[0126] More specifically, R^3 may be selected from the group consisting of the formulas below:



[0127] In particular, suitable surfactants or co-surfactants may include one or more of any of Surfactants 1-12 described herein.

[0128] The herbicidal formulations may include one or more surfactants of the present disclosure in an amount of about 0 wt.% or greater, about 2 wt.% or greater, about 4 wt.% or greater, about 6 wt.% or greater, about 8 wt.% or greater, or about 10 wt.% or lower, about 12 wt.% or lower, about 14 wt.% or lower, about 16 wt.% or lower, or within any range of 0 wt.% to 16 wt.%, or 2 wt.% to 14 wt.%, or 4 wt.% to 12 wt.%, or 6 wt.% to 10 wt.%, or 8 wt.% to 10 wt.%, or within any range using these endpoints.

4. *Water-Insoluble Solvents*

[0129] Suitable water-insoluble immiscible organic solvents include those derived from or made from natural, non-petroleum sources such as, for example, plants and animals, and include, vegetable oils, seed oils, animal oils and the like, such N,N-dimethylcaprylamide (N,N-dimethyloctanamide), N,N-dimethylcapramide (N,N-dimethyldecanamide), and mixtures thereof, which are available commercially as Agnique® AMD 810 and Agnique® AMD 10, from BASF Corp. (Florham Park, N.J.), Genegen® 4166, Genegen® 4231 and Genegen® 4296, from Clariant (Charlotte, N.C.), Hallcomid M-8-10 and Hallcomid M-10, from Stepan (Northfield, Ill.), and Amid DM10 and DM810 from AkzoNobel (Chicago, Ill.). Additional examples of naturally derived organic solvents include the morpholine amides of caprylic/capric fatty acids (C₈/C₁₀) which are commercially available as JEFFSOL® AG-1730 Solvent from Huntsman International LLC (The Woodlands, Tex.).

[0130] Other suitable water-insoluble solvents may include aromatic hydrocarbons, mixed naphthalene and alkyl naphthalene fractions, aromatic solvents, particularly alkyl substituted benzenes such as xylene or propylbenzene fractions, and the like; C₁-C₆ esters of fatty acids derived from vegetable, seed or animal oils such as, methyl caproate, methyl caprylate, methyl caprate, methyl laurate, methyl myristate, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, methyl linolenate, and the like; ketones such as isophorone and trimethylcyclohexanone (dihydroisophorone); acetate esters such as, methyl, ethyl, propyl, butyl, pentyl, hexyl, or heptyl acetate, and the like; and cyclic alkyl carbonates such as propylene carbonate and butylene carbonate, which are available as the JEFFSOL® alkylene carbonates from Huntsman (The Woodlands, Tex.), and dibutyl carbonate, also from Huntsman, and mixtures of any of the water immiscible organic solvents described herein.

[0131] The water-insoluble solvent may be present in the herbicidal formulation in an amount of about 0 wt.% or greater, about 10 wt.% or greater, about 20 wt.% or greater, or about 30 wt.% or lower, about 40 wt.% or lower, about 50 wt.% or lower, or within any range of 0 wt.% to 50 wt.%, or 10 wt.% to 40 wt.%, or 20 wt.% to 30 wt.%, or within any range using these endpoints.

5. *Water*

[0132] Water may be present in the herbicidal formulations of the present disclosure to serve as both an aqueous solvent and a carrier for the ingredients in the described compositions.

[0133] The herbicidal formulation of the present disclosure may include water in an amount of about 200 g/L or greater, about 300 g/L or greater, about 400 g/L or greater, or about 500 g/L or lower, about 600 g/L or lower, about 700 g/L or lower, about 800 g/L or lower, or within any range of 200 g/L to 800 g/L, or 300 g/L to 700 g/L, or 400 g/L to 600 g/L, or 400 g/L to 500 g/L, or within any range using these endpoints.

6. *Other Additives*

[0134] The herbicidal formulation may include one or more additional compatible ingredients. These additional ingredients may include, for example, one or more pesticides or other ingredients, which may be dissolved or dispersed in the composition and may be selected from acaricides, algicides, antifeedants, avicides, bactericides, bird repellents, chemosterilants, defoliants, desiccants, disinfectants, fungicides, herbicide safeners, herbicides, insect attractants, insecticides, insect repellents, mammal repellents, mating disrupters, molluscicides, nematocides, plant activators, plant growth regulators, rodenticides, semiochemicals, synergists, and virucides. Also, any other additional ingredients providing functional utility such as, for example, antifoam agents, antimicrobial agents, buffers, corrosion inhibitors, dispersing agents, dyes, fragrances, freezing point depressants, neutralizing agents, odorants, penetration aids, sequestering agents, spray drift control agents, spreading agents, stabilizers, sticking agents, viscosity-modifying additives, water soluble solvents and the like, may be included in these compositions.

[0135] When the described herbicidal formulations are used in combination with the additional active ingredients such as, for example, herbicide active ingredients, the compositions described herein can be formulated with the other active ingredient or active ingredients as premix concentrates, tank-mixed in water with the other active ingredient or active ingredients for spray application or applied sequentially with the other active ingredient or active ingredients in separate spray applications.

7. *Method of Making*

[0136] The herbicide formulations of the present disclosure may be prepared by the steps of: 1) preparing a solution of the one or more second herbicide in the organic solvent and a surfactant; 2) adding the solution prepared in step 1) to a concentrated solution of a water-soluble salt of an herbicide in water with good mixing to form a clear solution; and 3) optionally, adding any additional compatible active or inert ingredients.

[0137] Alternatively, the herbicide formulations of the present disclosure may be prepared by the steps of: 1) providing a second herbicide that is a liquid and, optionally, mixing it with the organic solvent and a surfactant; 2) adding the composition prepared in step 1) to a concentrated solution of a water-soluble salt of an herbicide in water with good mixing to form a clear solution; and 3) optionally, adding any additional compatible active or inert ingredients.

[0138] Suitable water compatible ingredients that may be added to the herbicide formulations include, but are not limited to, water soluble or water insoluble dispersing surfactants, such as the surfactants of the present disclosure, water insoluble active ingredients and optionally, other inert ingredients such as pH buffers, wetting agents, antifreeze agents, antifoam agents, and biocides.

8. *Method of Use*

[0139] The aqueous herbicidal formulations described herein may optionally be diluted in an aqueous spray mixture for agricultural application such as for weed control in crop fields or in turf. Such herbicidal formulations are typically diluted with an inert carrier, such as water, before application. The diluted herbicidal formulations, which are usually applied, for example, to weeds, the locus of weeds, or the locus of where weeds may eventually emerge, may contain the agriculturally active agent (the herbicide) in an amount of about 0.0001 wt.% or greater, about 0.001 wt.% or greater, about 0.01 wt.% or greater, about 0.1 wt.% or greater, about 1 wt.% or greater, or about 2 wt.% or lower, about 3 wt.% or lower, about 4 wt.% or lower, or about 5 wt.% or lower, or within any range of 0.0001 wt.% to 5 wt.%, or 0.001 wt.% to 4 wt.%, or 0.01 wt.% to 3 wt.%, or 0.1 wt.% to 2 wt.% or lower, or 1 wt.% to 2 wt.%, or within any range using these endpoints. The herbicide formulations of the present disclosure can be applied, for example, to weeds or their

locus by the use of conventional ground or aerial sprayers, by addition to irrigation water and by other conventional means known to those skilled in the art.

[0140] The herbicide formulations of the present disclosure may be used in controlling undesirable vegetation in crops possessing single, multiple or stacked genomic traits conferring tolerance to one or more herbicide chemistries and/or inhibitors with single or multiple modes of action.

IV. Insecticide formulations

[0141] The present disclosure also provides formulations of insecticides. Insecticides are pesticides used to kill insects. They include ovicides and larvicides used against insect eggs and larvae, respectively. Insecticides are used in agriculture, medicine, industry and by consumers, and may significantly improve agricultural productivity. Insecticides can be classified into two major groups: systemic insecticides, which have residual or long-term activity; and contact insecticides, which have no residual activity.

[0142] Such formulations may be in liquid or solid forms, such as emulsifiable concentrates, oil in water (O/W) emulsions, suspension concentrates, and wettable powders.

[0143] The insecticide formulation may include an insecticide, one or more surfactants of the structure(s) of Formula I or II, chosen from one or more surfactant classes, an optional antifoaming agent, an optional antifreezing agent, and water.

[0144] The present disclosure provides the use as a surfactant of a compound of Formula I or II in an insecticide formulation. The compounds of Formula I or II and the insecticide formulation are as described herein.

1. Insecticide

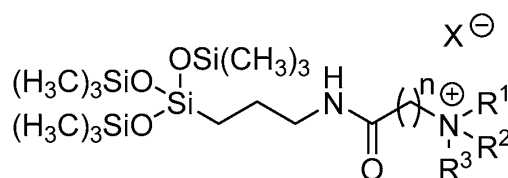
[0145] Suitable insecticides may include one or more of pyrethroids, such as a synthetic pyrethroid; an organophosphate compound, such as chlorpyrifos-ethyl, chlorpyrifos-methyl, pirimiphos-methyl, fenitrothion; a phenyl ether such as pyriproxyfen; a benzoylurea, such as flufenoxuron; a carbamate, such as fenoxycarb, carbosulfan; nicotinoids, such as acetamiprid; pyridinecarboxamides, such as flonicamid; and/or others. The pyrethroid may be selected from one or more of bifenthrin, zeta-cypermethrin, alpha-cypermethrin, tetra-methrin, lambda-cyhalothrin, fenvalerate, cyfluthrin, bio-resmethrin, permethrin, delta-methrin.

[0146] The insecticide active ingredient may be present in the insecticide formulation in an amount, measured in weight per volume, of about 1% or greater, about 5% or greater, about 10% or greater, or about 15% or less, about 20% or less, about 30% or less, or within any range of 1% to 30%, or 5% to 20%, or 10% to 15%, or within any range using these endpoints.

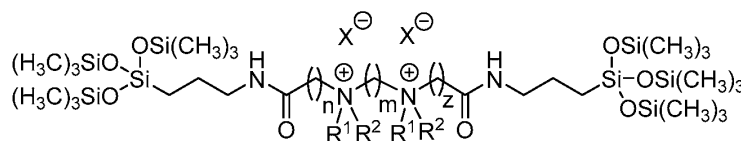
2. Surfactants

[0147] The insecticide formulation may include one or more surfactants chosen from one or more surfactant classes, collectively referred to as the surfactant system.

[0148] Suitable surfactants for use in the insecticide formulations of the present disclosure include one or more surfactant molecules and/or co-surfactant molecules of Formula I or II,



Formula I



Formula II

wherein R¹ and R² may be the same or different, and comprise at least one group selected from the group consisting of C₁-C₆ alkyl, optionally the C₁-C₆ alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R³ may be selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C₃-C₈ carboxylic acid, C₁-C₁₀ alkyl benzoic acid, and a C₁-C₁₂ linker attached to an additional surfactant molecule having a structure represented by Formula I, wherein

the additional surfactant molecule of Formula I is the same or different from the surfactant molecule of Formula I;

n and z may be selected independently from any integer from 1 to 12;

m may be any integer from 1 to 12; and

X may be selected from the group consisting of chloride, bromide, and iodide.

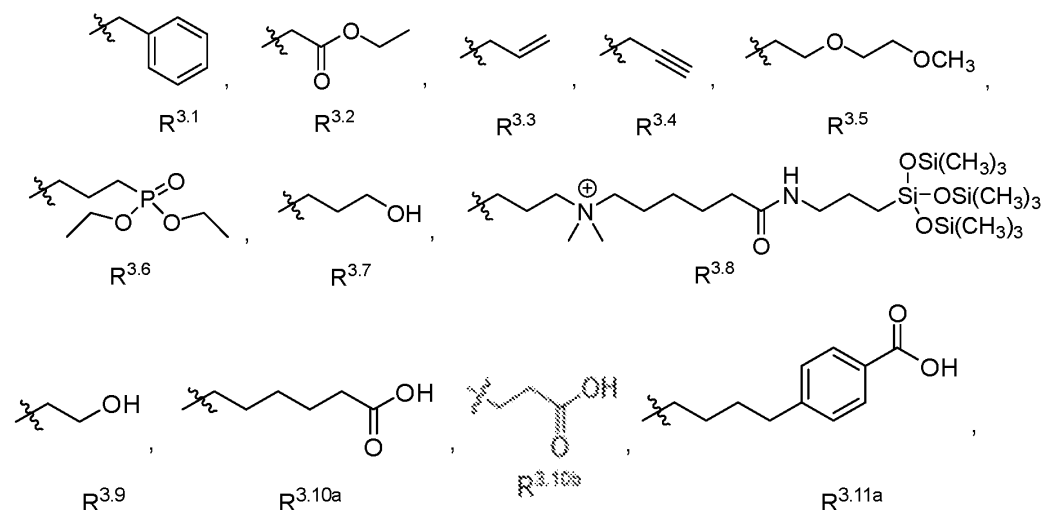
[0149] For clarity, as disclosed herein, and with respect to any of the formulations provided herein, the molecule of Formula II may represent a construct of the following structure:

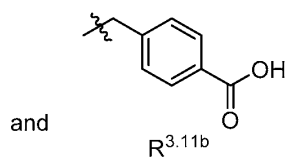
Formula I – Linker – Formula I,

wherein one molecule of Formula I may be the same as, or different from, the other molecule of Formula I. In this exemplary construct, the Linker is R^3 in Formula I, a C_1 - C_{12} linker.

[0150] Specifically, R^3 may be selected from the group consisting of C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_2 - C_{12} ester, C_1 - C_{10} hydroxyl, benzyl, C_2 - C_{12} alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_5 alkyl benzoic acid, and a three-carbon linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same as the first molecule of Formula I.

[0151] More specifically, R^3 may be selected from the group consisting of the formulas below:





[0152] Suitable surfactants or co-surfactants may be one or more of any of Surfactants 1-12 described herein.

[0153] The surfactant system may be present in the insecticide formulation in an amount, measured in weight per volume, of about 0.1% or greater, about 1% or greater, about 5% or greater, about 10% or greater, about 15% or greater, or about 20% or less, about 25% or less, about 30% or less, about 35% or less, about 40% or less, or within any range of 0.1% to 40%, or 1% to 35%, or 5% to 30%, or 10% to 25%, or 15% to 20%, or within any range using these endpoints.

3. *Optional Antifoaming Agent*

[0154] The optional antifoaming agent in the insecticide formulation may include silicone emulsions, and/or surfactants, such as the surfactants of the present disclosure.

[0155] The antifoaming agent may be present in the insecticide formulation in an amount, measured in weight per volume, of about 0.0% or greater, about 0.1% or greater, about 0.2% or greater, about 0.3% or greater, about 0.4% or greater, about 0.5% or greater, or about 0.6% or lower, about 0.7% or lower, about 0.8% or lower, about 0.9% or lower, about 1.0% or lower, or within any range of 0.0% to 1.0%, or 0.1% to 0.9%, or 0.2% to 0.8%, or 0.3% to 0.7%, or 0.4% to 0.6%, or 0.5% to 0.6%, or within any range using these endpoints.

4. *Optional Antifreezing Agent*

[0156] The insecticide formulation may include an optional antifreezing agent. Suitable antifreezing agents may include diols, such as alkyldiols or dialkyldiols.

[0157] The insecticide formulation may include an antifreezing agent in an amount, measured in weight per volume, of about 0% or greater, about 1% or greater, about 2% or greater, about 3% or greater, about 4% or greater, about 5% or greater, or about 6% or lower, about 7% or lower, about 8% or lower, about 9% or lower, about 10% or lower, or within any range of 0% to 10%, or 1% to 9%, or 2% to 8%, or 3% to 7%, or 4% to 6%, or 5% to 6%, or within any range using these endpoints.

5. *Water*

[0158] The insecticide formulation may include water in an amount, measured in weight per volume, of about 25% or greater, about 30% or greater, about 35% or greater, about 40% or greater, about 45% or greater, about 50% or greater, about 55% or greater, or about 60% or lower, about 65% or lower, about 70% or lower, about 75% or lower, about 80% or lower, about 85% or lower, about 90% or lower, about 95% or lower, about 98% or lower, or within any range of 25% to 98%, or 30% to 95%, or 35% to 90%, or 40% to 85%, or 45% to 80%, or 50% to 75%, or 55% to 70%, or 55% to 65%, or 55% to 60%, or within any range using these endpoints.

6. *Other Additives*

[0159] The insecticide formulations of the present disclosure may include viscosity modifiers. Such viscosity modifiers may include thickening agents, such as cellulose derivatives, polyacrylamides, polyvinyl alcohols, polyvinyl pyrrolidones, and natural gums.

[0160] Viscosity modifiers may be present in the insecticidal formulation in any amount suitable to modify the viscosity to the desired level.

[0161] The insecticide formulations of the present disclosure may also include preservatives. Suitable preservatives include methylparaben.

[0162] Preservatives may be present in the insecticide formulation in an amount, measured as weight per volume, of 0.0% or greater, 0.1% or greater, or 0.2% or less, or within any range of 0.0% to 0.2%, or 0.1% to 0.2%, or within any range using these endpoints.

V. Adjuvants

[0163] In addition to the uses described above, the surfactants of the present disclosure may be used as adjuvants in formulations of agriculturally active agents, such as pesticides, plant growth regulators, herbicides, fungicides, and insecticides. Adjuvant compounds may be employed to improve one or more properties of formulations of agriculturally active agents, such as for example, storage stability, ease of handling, pesticide efficacy against a target organism.

VI. Spray drift reducing agents

[0164] Spray drift refers to the unintentional diffusion of pesticides and other agriculturally active agents, including off-target contamination. This can lead to damage in human health, environmental contamination, and property damage. The present disclosure therefore relates to the use of the surfactants of the present disclosure to reduce the amount of driftable fines of formulations of agriculturally active agents in both aerial and ground spray applications.

[0165] The surfactants of the present disclosure, and mixtures thereof, can be incorporated into an aqueous spray mixture, for example, by being tank-mixed directly with a diluted formulation of an agriculturally active agent, such as a pesticide, plant growth regulator, fungicide, herbicide, or insecticide.

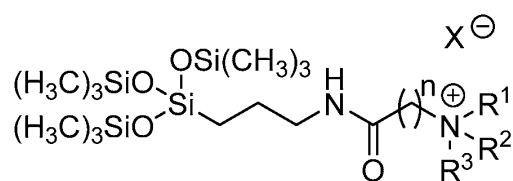
[0166] The optimum spray droplet size depends on the application for which the composition is used. If droplets are too large, there will be less coverage by the spray, e.g., large droplets will land in certain areas while areas in between will receive little or no spray coverage. The maximum acceptable droplet size may depend on the amount of composition being applied per unit area and the need for uniformity in spray coverage. Smaller droplets provide more even coverage, but are more prone to drift during spraying. Thus, application parameters such as uniformity in spray coverage must be balanced against the tendency for smaller droplets to drift. For example, if it is particularly windy during spraying, larger droplets may be needed to reduce drift, whereas on a calmer day, smaller droplets may be acceptable. In addition to the physical properties of a particular aqueous composition, spray droplet size may also depend on the spray apparatus, e.g., nozzle size and configuration.

[0167] The reduction in spray drift may result from a variety of factors including a reduction in the production of fine spray droplets (<150 μm minimum diameter) and an increase in the volume median diameter (VMD) of the spray droplets. In any event, for a given spray apparatus, application, and conditions, and based on the surfactant used, the median diameter of the plurality of spray droplets created using the surfactants described herein is increased above that of a spray composition that does not include the surfactants of the present disclosure.

VII. Surfactants

[0168] The present disclosure provides surfactants for use in agricultural products in the form of siloxane derivatives of amino acids. Thus, there is disclosed herein, the use as a surfactant of a compound of Formula I or II in an agricultural product. The amino acids may be naturally occurring or synthetic, or they may be obtained from ring-opening reactions of lactams, such as caprolactam. The compounds of the present disclosure have been shown to have surface-active properties, and may be used as surfactants and wetting agents, for example.

[0169] In particular, the present disclosure provides compounds of Formula I, shown below:



Formula I

wherein R^1 and R^2 may be the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

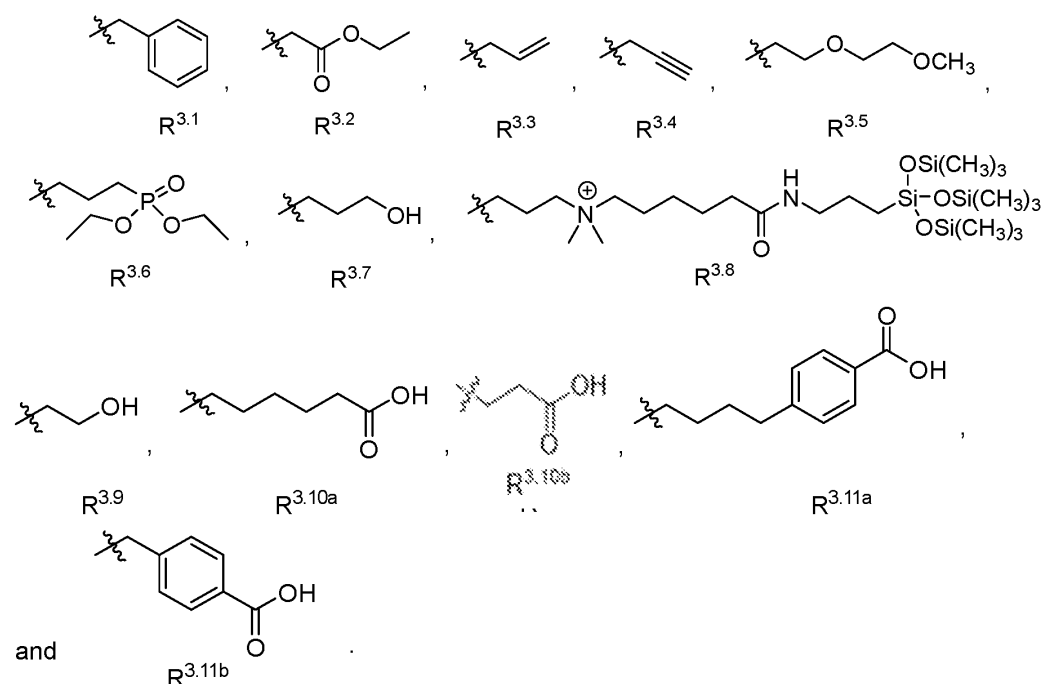
R^3 may be selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, C_3 - C_8 carboxylic acid, alkyl phosphate, alkyl phosphonate, or a C_1 - C_{12} linker attached to a second molecule of Formula I, wherein the second molecule is the same or different;

n may be an integer from 1 to 12; and

X may be selected from the group consisting of chloride, bromide, and iodide.

[0170] Specifically, R^3 may be selected from the group consisting of C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, C_2 - C_{12} ester, C_1 - C_{10} hydroxyl, benzyl, C_2 - C_{12} alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_5 alkyl benzoic acid, and a three-carbon linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same as the first molecule of Formula I.

[0171] More specifically, R^3 may be selected from the group consisting of the formulas below:



[0172] There is set out above the disclosure of formulations comprising at least one surfactant of Formula I or II for use in various agricultural products. The following disclosure of the compounds of Formula I and II applies to the compounds of Formula I and II in any of the disclosed uses and formulations set out herein.

[0173] Further compounds provided by the present disclosure are those compounds of Formula I wherein R^1 and R^2 are methyl.

[0174] Other compounds provided by the present disclosure are compounds of Formula I, wherein n is 5.

[0175] As used herein, the phrase “ n may be an integer from 1 to 12” means that n may be equal to 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and/or 12.

[0176] As used herein, the phrase “ C_1 - C_6 alkyl” means a straight chain or branched alkyl group containing 1, 2, 3, 4, 5, and/or 6 carbons.

[0177] As used herein, the phrase “ C_1 - C_6 linker” means a straight chain or branched alkyl chain containing 1, 2, 3, 4, 5, and/or 6 carbons.

[0178] As used herein, the phrase “C₂-C₁₀ alkenyl” means a straight chain or branched alkenyl group containing 2, 3, 4, 5, 6, 7, 8, 9, and/or 10 carbons.

[0179] As used herein, the phrase “C₂-C₁₀ alkynyl” means a straight chain or branched alkynyl group containing 2, 3, 4, 5, 6, 7, 8, 9, and/or 10 carbons.

[0180] As used herein, the phrase “C₂-C₁₂ ester” means a straight chain or branched ester group having a total of 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and/or 12 carbons.

[0181] As used herein, the phrase “C2-C12 alkoxy alkyl ether” means a straight chain or branched alkoxy alkyl ether group having a total of 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and/or 12 carbons.

[0182] As used herein, the phrase “C1-C10 hydroxyl” means a hydroxyl attached to a straight chain or branched alkyl group containing 1, 2, 3, 4, 5, 6, 7, 8, 9, and/or 10 carbons.

[0183] As used herein, the phrase “C3-C8 carboxylic acid” means a carboxylic acid group attached to a straight chain or branched alkyl group with a containing 3, 4, 5, 6, 7, and/or 8, carbons.

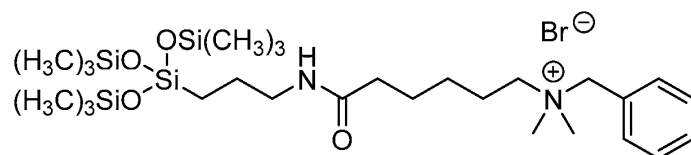
[0184] As used herein, the phrase “C1-C10 alkyl benzoic acid” means a benzoic acid group attached to a straight chain or branched alkyl group containing 1, 2, 3, 4, 5, 6, 7, 8, 9, and/or 10 carbons.

[0185] As used herein, the phrase “n and z may be selected independently from any integer from 1 to 12” means that n and z may be independently 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and/or 12.

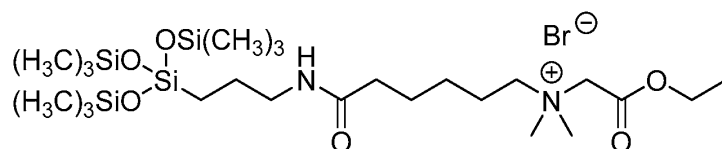
[0186] As used herein, the phrase “m may be any integer from 1 to 12” means that m may be 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and/or 12.

[0187] As used herein, the phrase “q may be any integer from 1 to 10” means that q may be 1, 2, 3, 4, 5, 6, 7, 8, 9, and/or 10.

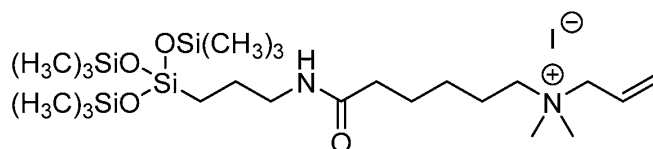
[0188] One specific compound provided by the present disclosure and referred to herein as **Surfactant 1** is N-benzyl-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide, having the following formula:



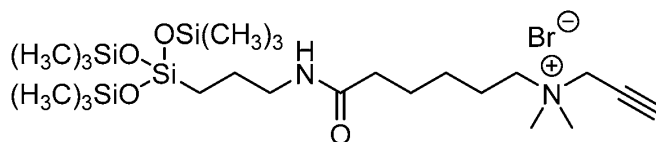
[0189] A second specific compound provided by the present disclosure and referred to herein as **Surfactant 2** is N-(2-ethoxy-2-oxoethyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide, having the following formula:



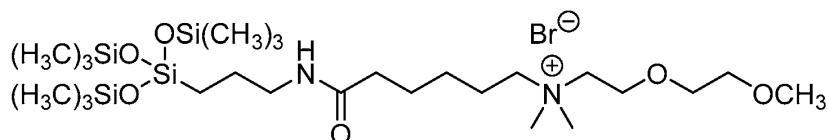
[0190] A third specific compound provided by the present disclosure and referred to herein as **Surfactant 3** is N-allyl-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium iodide, having the following formula:



[0191] A fourth specific compound provided by the present disclosure and referred to herein as **Surfactant 4** is 6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxo-N-(prop-2-yn-1-yl)hexan-1-aminium bromide, having the following formula:

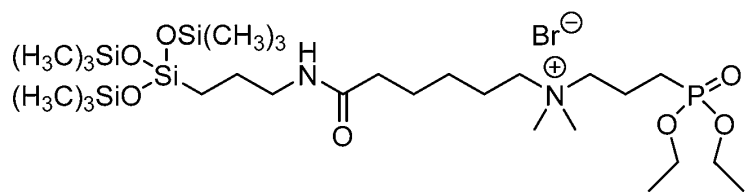


[0192] A fifth specific compound provided by the present disclosure and referred to herein as **Surfactant 5** is 6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N-(2-(2-methoxyethoxy)ethyl)-N,N-dimethyl-6-oxohexan-1-aminium bromide, having the following formula:

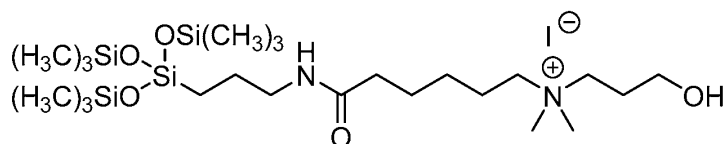


[0193] A sixth specific compound provided by the present disclosure and referred to herein as **Surfactant 6** is N-(3-(diethoxyphosphoryl)propyl)-6-((3-

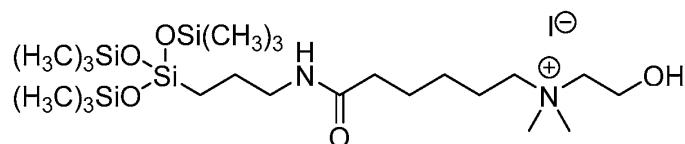
(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide, having the following formula:



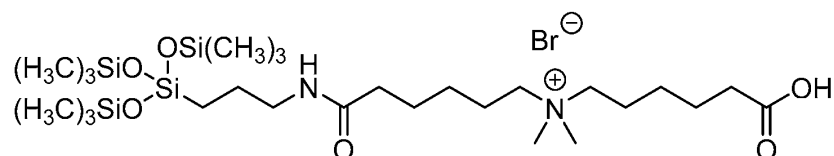
[0194] A seventh specific compound provided by the present disclosure and referred to herein as **Surfactant 7** is 6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N-(3-hydroxypropyl)-N,N-dimethyl-6-oxohexan-1-aminium iodide, having the following formula:



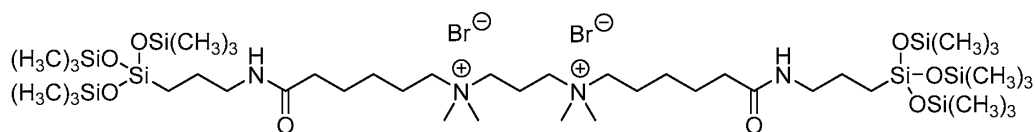
[0195] An eighth specific compound provided by the present disclosure and referred to herein as **Surfactant 8** is 6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N-(2-hydroxyethyl)-N,N-dimethyl-6-oxohexan-1-aminium iodide, having the following formula:



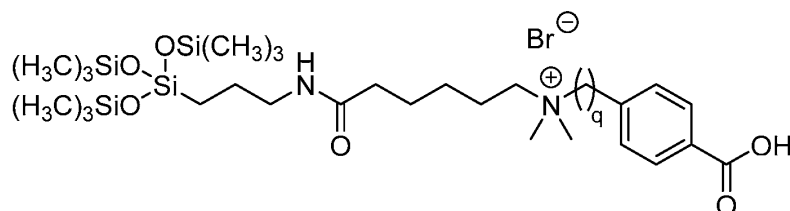
[0196] A ninth specific compound provided by the present disclosure and referred to herein as **Surfactant 9** is N-(5-carboxypentyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide, having the following formula:



[0197] An tenth specific compound provided by the present disclosure and referred to herein as **Surfactant 10** is N¹,N³-bis(6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-6-oxohexyl)-N¹,N¹,N³,N³-tetramethylpropane-1,3-diaminium dibromide, having the formula:

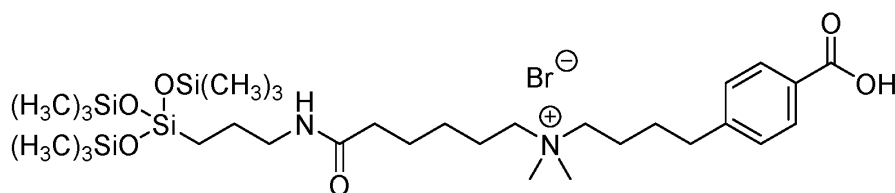


[0198] A further group of specific compounds provided by the present disclosure and referred to herein as **Surfactant 11-12** have the general formula:

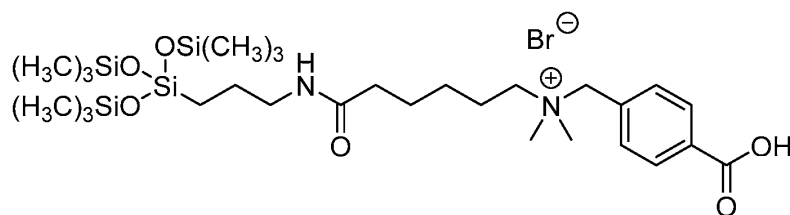


wherein q may be an integer from 1 to 10.

[0199] An eleventh specific compound provided by the present disclosure and referred to herein as **Surfactant 11** is N-(4-(4-carboxyphenyl)butyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide, having the formula:



[0200] A twelfth specific compound provided by the present disclosure and referred to herein as **Surfactant 12** is N-(4-carboxybenzyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide, having the formula:

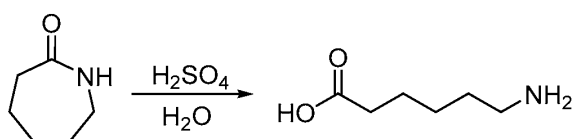


[0201] These compounds may be synthesized by various methods. One such method includes reacting an amino acid, such as an *N*-alkylated or *N*-acylated amino acid, with a siloxane to convert the amino acid C-terminus to the desired siloxane

derivative. The amino acid N-terminus may be further alkylated to yield a quaternary amine, for example.

[0202] The amino acid may be naturally occurring or synthetic or may be derived from a ring opening reaction of a lactam, such as caprolactam. The ring-opening reaction may be either an acid or alkali catalyzed reaction, and an example of an acid catalyzed reaction is shown below in Scheme 1.

SCHEME 1

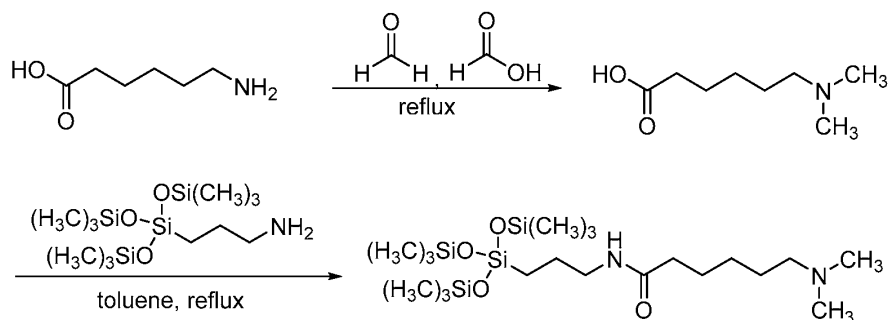


[0203] The amino acid may have as few as 1 or as many as 12 carbons between the N- and C-termini, such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 carbons. The alkyl chain may be branched or straight. The alkyl chain may be interrupted with nitrogen, oxygen, or sulfur. The alkyl chain may be further substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carboxyl, and carboxylate. The N-terminal nitrogen may be acylated or alkylated with one or more alkyl groups. For example, the amino acid may be 6-(dimethylamino)hexanoic acid.

[0204] The siloxane may be substituted with one or more alkoxy groups, such as methoxy, ethoxy, isopropoxy, tertiary butoxy, and others. The siloxane may be further substituted with one or more alkyl groups, such as propyl, wherein the alkyl group may yet be further substituted with an appropriate functional group to permit coupling of the siloxane to the amino acid, such as a nitrogen. For example, the siloxane may be 3-aminopropyltris(trimethylsiloxy)silane.

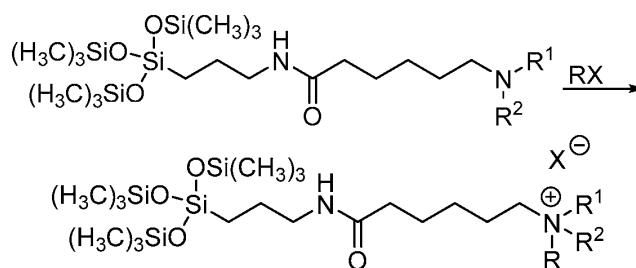
[0205] The siloxane derivative of the amino acid may be synthesized as shown below in Scheme 2. As shown, 6-aminohexanoic acid may be alkylated at the N-terminus by treatment with formaldehyde in formic acid at reflux to give 6-(dimethylamino)hexanoic acid. The free carboxylic acid is then coupled to 3-aminopropyl(trimethylsiloxy)silane in refluxing toluene to give the desired siloxane derivative.

SCHEME 2



[0206] The N-terminal nitrogen may be further derivatized to modify or improve water solubility and surface-active properties. A sample synthetic scheme is shown below in Scheme 3, in which the N-terminal nitrogen is alkylated to provide a quaternary amine.

SCHEME 3



[0207] Suitable alkylating agents may include benzyl bromide, ethyl bromoacetate, allyl iodide, propargyl bromide, 1-bromo-2-(2-methoxyethoxy)ethane, bromo phosphonate, 3-iodopropanol, 3-bromopropanol, 2-iodoethanol, 2-bromoethanol, 6-bromohexanoic acid, 4-(4-bromobutyl)benzoic acid, and 4-(bromomethyl)benzoic acid, for example. Two molecules of Formula I may be linked by treating the N-terminal nitrogen with a difunctional alkylating agent, such as 1,3-dibromopropane for example.

[0208] The compounds of the present disclosure demonstrate surface-active properties. These properties may be measured and described by various methods. One method by which surfactants may be described is by the molecule's critical micelle concentration (CMC). CMC may be defined as the concentration of a

surfactant at which micelles form, and above which all additional surfactant is incorporated into micelles.

[0209] As surfactant concentration increases, surface tension decreases. Once the surface is completely overlaid with surfactant molecules, micelles begin to form. This point represents the CMC, as well as the minimum surface tension. Further addition of surfactant will not further affect the surface tension. CMC may therefore be measured by observing the change in surface tension as a function of surfactant concentration. One such method for measuring this value is the Wilhelmy plate method. A Wilhelmy plate is usually a thin iridium-platinum plate attached to a balance by a wire and placed perpendicularly to the air-liquid interface. The balance is used to measure the force exerted on the plate by wetting. This value is then used to calculate the surface tension (γ) according to Equation 1:

$$\text{Equation 1: } \gamma = F/l \cos \theta$$

wherein l is equal to the wetted perimeter ($2w + 2d$, in which w and d are the plate thickness and width, respectively) and $\cos \theta$, the contact angle between the liquid and the plate, is assumed to be 0 in the absence of an extant literature value.

[0210] Another parameter used to assess the performance of surfactants is dynamic surface tension. The dynamic surface tension is the value of the surface tension for a particular surface or interface age. In the case of liquids with added surfactants, this can differ from the equilibrium value. Immediately after a surface is produced, the surface tension is equal to that of the pure liquid. As described above, surfactants reduce surface tension; therefore, the surface tension drops until an equilibrium value is reached. The time required for equilibrium to be reached depends on the diffusion rate and the adsorption rate of the surfactant.

[0211] One method by which dynamic surface tension is measured relies upon a bubble pressure tensiometer. This device measures the maximum internal pressure of a gas bubble that is formed in a liquid by means of a capillary. The measured value corresponds to the surface tension at a certain surface age, the time from the start of the bubble formation to the occurrence of the pressure maximum. The dependence of surface tension on surface age can be measured by varying the speed at which bubbles are produced.

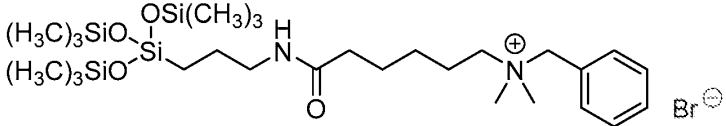
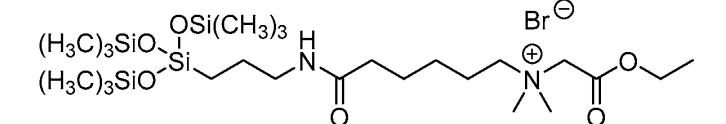
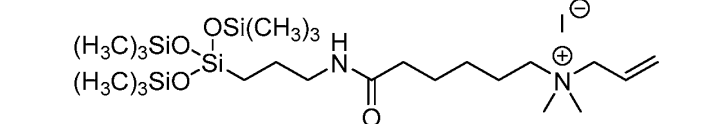
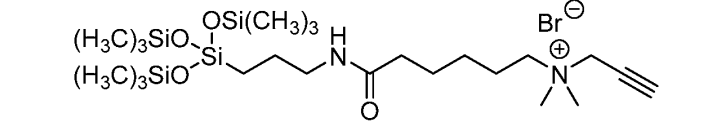
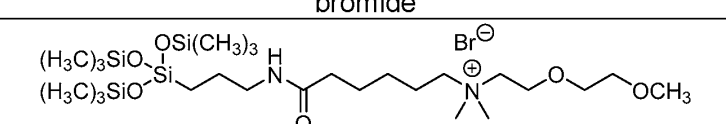
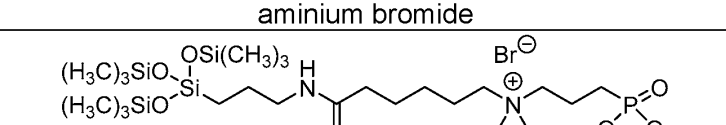
[0212] Surface-active compounds may also be assessed by their wetting ability on solid substrates as measured by the contact angle. When a liquid droplet comes in contact with a solid surface in a third medium, such as air, a three-phase line forms among the liquid, the gas and the solid. The angle between the surface tension unit vector, acting at the three-phase line and tangent at the liquid droplet, and the surface is described as the contact angle. The contact angle (also known as wetting angle) is a measure of the wettability of a solid by a liquid. In the case of complete wetting, the liquid is completely spread over the solid and the contact angle is 0°. Wetting properties are typically measured for a given compound at the concentration of 1-100x CMC; however, it is not a property that is concentration-dependent. Therefore, measurements of wetting properties can be measured at concentrations that are higher or lower.

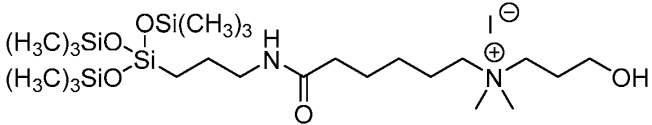
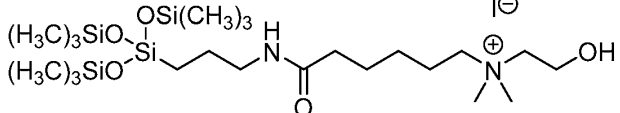
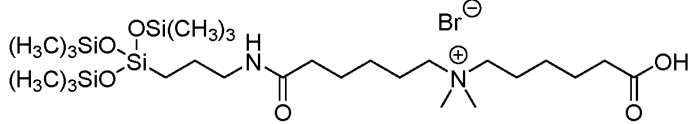
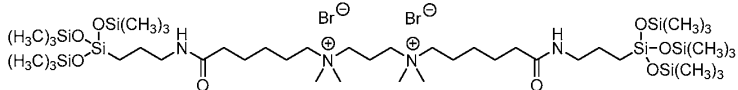
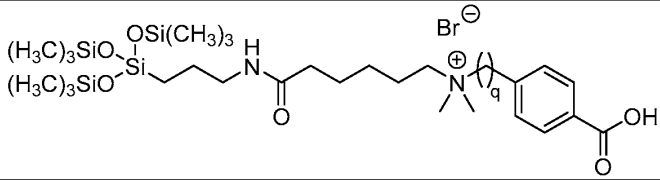
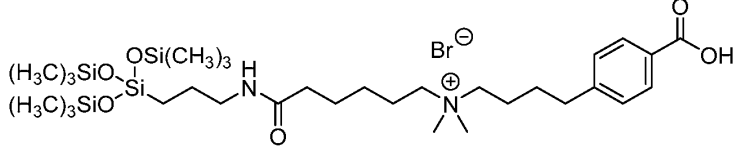
[0213] In one method, an optical contact angle goniometer may be used to measure the contact angle. This device uses a digital camera and software to extract the contact angle by analyzing the contour shape of a sessile droplet of liquid on a surface.

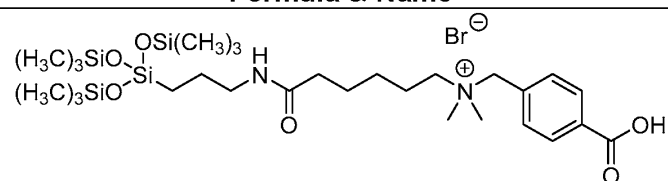
[0214] It will be understood by one skilled in the art that small differences between compounds may lead to substantially different surfactant properties, such that different compounds may be used with different substrates, in different applications. It will be further understood by one skilled in the art that surfactant properties may not be predictable on the basis of chemical structure, as further demonstrated below. For example, Surfactant 9 and the Comparative Surfactant, which differ only in the number of methylene groups in R3, demonstrate different surfactant properties. Surprisingly, Surfactant 9 demonstrates excellent activity, as described further below, while the Comparative Surfactant demonstrates inferior surfactant properties.

[0215] The following non-limiting embodiments are provided to demonstrate the different properties of the different surfactants. In Table 1 below, short names for the surfactants are correlated with their corresponding chemical structures.

TABLE 1

Surfactant	Formula & Name
Surfactant 1	 N-benzyl-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide
Surfactant 2	 N-(2-ethoxy-2-oxoethyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide
Surfactant 3	 N-allyl-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium iodide
Surfactant 4	 6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxo-N-(prop-2-yn-1-yl)hexan-1-aminium bromide
Surfactant 5	 6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N-(2-(2-methoxyethoxy)ethyl)-N,N-dimethyl-6-oxohexan-1-aminium bromide
Surfactant 6	 N-(3-(diethoxyphosphoryl)propyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide

Surfactant	Formula & Name
Surfactant 7	 6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium iodide
Surfactant 8	 6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium iodide
Surfactant 9	 N-(5-carboxypentyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide
Surfactant 10	 N¹,N³-bis(6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-6-oxohexyl)-N¹,N¹,N³,N³-tetramethylpropane-1,3-diaminium dibromide
Surfactant 11-12	
Surfactant 11	 N-(4-(4-carboxyphenyl)butyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide

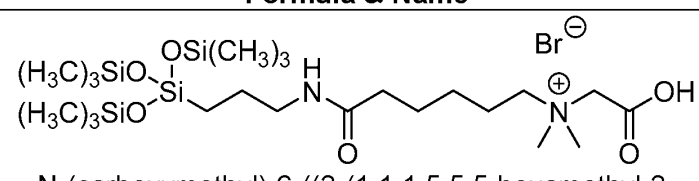
Surfactant	Formula & Name
Surfactant 12	 N-(4-carboxybenzyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide

[0216] These compounds may be effective as surface-active agents, useful for wetting or foaming agents, dispersants, emulsifiers, and detergents, in any of the formulations contemplated by this disclosure.

[0217] The amount of the compounds disclosed herein used in a formulation may be as low as about 0.001 wt.%, about 0.05 wt.%, about 0.1 wt.%, about 0.5 wt.%, about 1 wt.%, about 2 wt.%, or about 5 wt.%, or as high as about 8 wt.%, about 10 wt.%, about 15 wt.%, about 20 wt.%, or about 25 wt.%, about 30 wt.%, about 40 wt.%, about 50 wt.%, about 80 wt.%, or within any range of 0.001 wt.% to 80 wt.%, or 0.05 wt.% to 50 wt.%, or 0.1 wt.% to 20 wt.%, or 0.5 wt.% to 10 wt.%, or 1 wt.% to 8 wt.%, or 2 wt.% to 8 wt.%, or 5 wt.% to 8 wt.%, or within any range using any two of the foregoing values.

[0218] Table 2 includes a comparative surfactant, including name and structure.

TABLE 2

Surfactant	Formula & Name
Comparative Surfactant	 N-(carboxymethyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide

[0219] The surfactants useful in the formulations disclosed herein may have a critical micelle concentration (CMC) of less than about 15 mmol, less than about 10 mmol, less than about 5 mmol, less than about 1 mmol, less than about 0.8 mmol, less than about 0.7 mmol, less than about 0.6 mmol, less than about 0.5 mmol, less

than about 0.4 mmol, less than about 0.3 mmol, less than about 0.2 mmol, less than about 0.1 mmol, less than about 0.05 mmol, or less than about 0.01 mmol, or may have any CMC that falls within a range encompassed by the foregoing endpoints. For example, the surfactant may have a CMC of from about 0.01 to about 15 mmol, from about 0.05 to about 10 mmol, or from about 0.1 to about 5 mmol.

[0220] The surfactants useful in the formulations disclosed herein may have a plateau value of minimum surface tension of less than about 25 mN/m, less than about 24 mN/m, less than about 23 mN/m, less than about 22 mN/m, less than about 21 mN/m, less than about 20 mN/m, less than about 19 mN/m, less than about 18 mN/m, less than about 17 mN/m, less than about 16 mN/m, or less than about 15 mN/m, or may have any plateau value of minimum surface tension that falls within a range encompassed by the foregoing endpoints. For example, the surfactant may have a plateau value of minimum surface tension of from about 15 to about 25 mN/m, from about 18 to about 22 mN/m or from about 20 to about 21 mN/m.

[0221] Surfactants with Antimicrobial Activities

[0222] Cells are fundamental units of all living organisms, which all have individual set of organelles that are responsible for the respective cell's ability to perform various kinds of functions, store genetic information for the development and functioning of the organisms. The outside boundaries of cells are called cell membranes, which serve as barriers and regulate the transport of materials between the inside and outside of the cells. Cell membranes can be destroyed through a process called lysis, resulting in cell deaths, which fundamentally underlie all antimicrobial processes. The use of surfactants which have an intrinsic biocidal activities for incorporation into agricultural products, such as tank spray formulations, can be highly important especially in situations where plants cannot tolerate the use of chemical biocidal agents.

[0223] Traditionally cationic surfactants have been used as antimicrobial agents in industries such as the food industry and hospitals. Unlike traditional antimicrobial chemicals, which rely on a "lock-key" mechanism, cationic surfactants are known to exert antimicrobial activities by disintegrating bacterial membranes via electrostatic and hydrophobic interactions. Zhou & Wang, Structure-activity relationship of cationic surfactants as antimicrobial agents., Current Opinion in Colloids & Interface Science, 45:28-43 (2020). To serve as a good antimicrobial

agent a surfactant would need to sufficiently kill bacteria or other unwanted pathogenic microbes without perturbing mammalian cells. Today, with the rising awareness of potential cytotoxicity and environmental hazards caused by certain chemicals, there has also been concerted efforts to develop surfactants that have reduced cytotoxicity concerns that may arise due to the lack of selectivity of conventional quaternary ammonium type of surfactants which are known to indiscriminately disrupt the bio-membranes, regardless of cell types.

[0224] Surfactants of the present disclosure have been shown in a standard protocol to assess antimicrobial activities called minimum inhibitory concentration (MIC) tests. The tables below shows the MIC results of examples of surfactants of the present disclosure.

Surfactant 6	Interval	Result
Inoculum: <i>P. aeruginosa</i> (9027), serial dilution 1:10; 2000 ppm max	24 hours	Not determined
Inoculum: <i>S. aureus</i> (6538), serial dilution 1.7 fold; 400 ppm max	24 hours	138 +/- 57 ppm
Inoculum: <i>E. coli</i> (8739), serial dilution 1:10; 2000 ppm max	24 hours	Not determined
Inoculum: <i>S. mutans</i> (25715) serial dilution 1.7 fold; 400 ppm max	24 hours	81 +/- 34 ppm
Surfactant 7		
Inoculum: <i>P. aeruginosa</i> (9027), serial dilution 1.7 fold; 400 ppm max	24 hours	81 +/- 34 ppm
Inoculum: <i>S. aureus</i> (6538), serial dilution 1:10; 2000 ppm max	24 hours	Not determined
Inoculum: <i>E. coli</i> (8739), serial dilution 1.7 fold; 400 ppm max	24 hours	81 +/- 34 ppm
Inoculum: <i>S. mutans</i> (25715) serial dilution 1:10; 2000 ppm max	24 hours	Not determined
Surfactant 9		
Inoculum: <i>P. aeruginosa</i> (9027), serial dilution 1:10; 2000 ppm max	24 hours	Not determined
Inoculum: <i>S. aureus</i> (6538), serial dilution 1.7 fold; 400 ppm max	24 hours	138 +/- 57 ppm
Inoculum: <i>E. coli</i> (8739), serial dilution 1:10; 2000 ppm max	24 hours	Not determined
Inoculum: <i>S. mutans</i> (25715) serial dilution 1.7 fold; 400 ppm max	24 hours	81 +/- 34 ppm

ADBAC control		
Inoculum: <i>P. aeruginosa</i> (9027), serial dilution 1.7 fold; 400 ppm max	24 hours	48 +/- 20 ppm
Inoculum: <i>S. aureus</i> (6538), serial dilution 1.7 fold; 20 ppm max	24 hours	7 +/- 3 ppm
Inoculum: <i>E. coli</i> (8739), serial dilution 1.7 fold; 20 ppm max	24 hours	16 +/- 7 ppm
Inoculum: <i>S. mutans</i> (25715) serial dilution 1.7 fold; 20 ppm max	24 hours	7 +/- 3 ppm

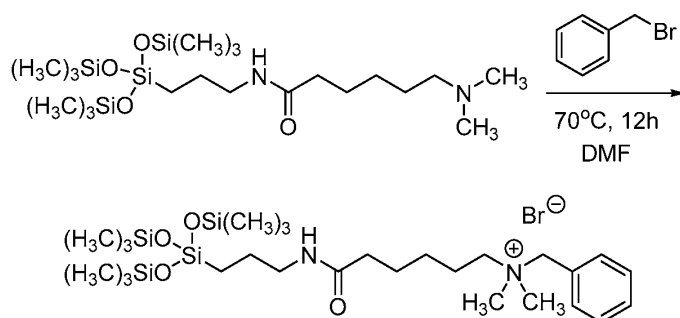
EXAMPLES

[0225] Nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker 500 MHz spectrometer. The critical micelle concentration (CMC) was determined by the Wilhelmy plate method at 23° C with a tensiometer (DCAT 11, DataPhysics Instruments GmbH) equipped with a Pt-Ir plate. Dynamic surface tension was determined with a bubble pressure tensiometer (Krüss BP100, Krüss GmbH), at 23° C. Contact angle was determined with the optical contact angle goniometer (OCA 15 Pro, DataPhysics GmbH) equipped with a digital camera.

Example 1: Synthesis of 6-(dimethylamino)-N-(3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)hexanamide

[0226] 6-(Dimethylamino)hexanoic acid (2.00 g, 12.56 mmol, 1 equiv.) was dissolved in toluene (50 mL) in a 100 mL round bottom boiling flask equipped with a Dean Stark trap, then 3-aminopropyltris(trimethylsiloxy)silane (5.48 mL, 13.81 mmol, 1.1 equiv.) was added. The reaction vessel was heated, and the reaction refluxed for 24 hours until no more water separated in the Dean Stark tube. The solvent was removed under vacuum to give the desired siloxane derivative as a yellow oil in 94% yield. ¹H NMR (500 MHz, DMSO) δ: 0.09 (s, 27H), 0.28-0.31 (m, 2H), 1.12-1.26 (m, 2H), 1.27-1.30 (m, 4H), 1.38-1.41 (m, 2H), 1.94 (t, *J* = 7.3 Hz, 2H), 2.00 (s, 6H), 2.06 – 2.03 (m, 2H), 2.89 (dd, *J* = 12.9, 6.8 Hz, 2H).

Example 2a: Synthesis of N-benzyl-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide (Surfactant 1)

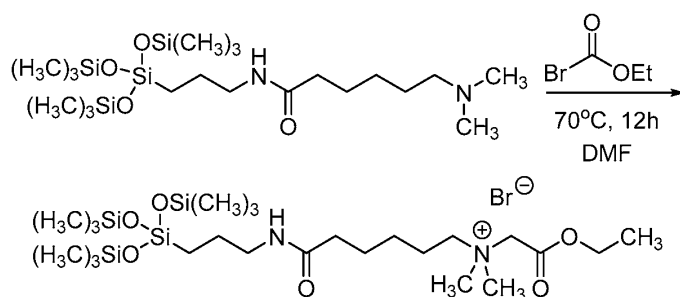


[0227] The siloxane derivative described in Example 1 (1 g, 2.02 mmol) was dissolved in dimethylformamide (DMF) (15 mL). Benzyl bromide (518 mg, 3.03 mmol) was added, and the mixture was heated to 70°C for 12 hours. The solvent was removed under vacuum and the crude product was washed twice with acetone to remove excess benzyl bromide and give Surfactant 1 as a yellow solid (1.1 g).

Example 2b: Determination of physical properties of Surfactant 1

[0228] The critical micelle concentration (CMC) for Surfactant 1 was measured. From the surface tension change with concentration in water, the CMC was determined to be about 9.883 mmol at pH 8. The plateau value of minimum surface tension that can be reached by this surfactant was around 20.67 mN/m, indicating that the surfactant has outstanding interfacial activity. These results are plotted as surface tension versus concentration in Fig. 1.

Example 3a: Synthesis of N-(2-ethoxy-2-oxoethyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide (Surfactant 2)



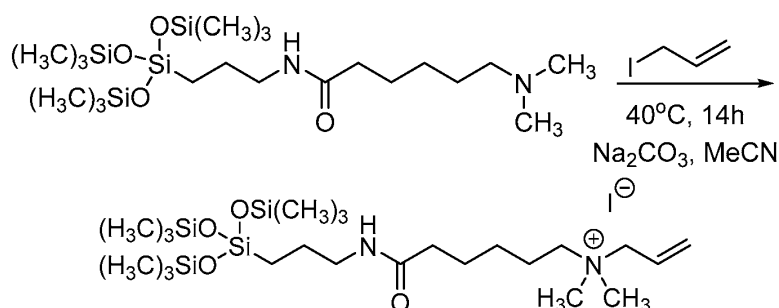
[0229] The siloxane derivative described in Example 1 (1g, 2.02 mmol) was dissolved in DMF (15 mL), and ethyl bromoacetate (0.25 mL, 2.4 mmol) was added.

The mixture was stirred for 12 hours at 70°C. The solvent was removed under vacuum, and the crude product was washed twice with hexane two times to give Surfactant 2 as a brown liquid (900 mg).

Example 3b: Determination of physical properties of Surfactant 2

[0230] The critical micelle concentration (CMC) for Surfactant 2 was measured. From the surface tension change with concentration in water, the CMC was determined to be about 0.2171 mmol. The plateau value of minimum surface tension that can be reached by this surfactant was around 20.36 mN/m, indicating that the surfactant has outstanding interfacial activity. These results are plotted as surface tension versus concentration in Fig. 2.

Example 4a: Synthesis of N-allyl-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium iodide (Surfactant 3)



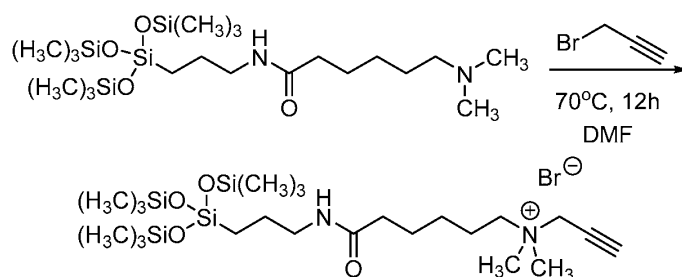
[0231] The siloxane derivative described in Example 1 (1.00 g, 2.02 mmol) was added to acetonitrile (10 mL), followed by sodium carbonate (0.26 g), then allyl iodide (674 mg). The reaction was refluxed for 14 hours at 40°C. Residual sodium carbonate was removed via filtration and the filtrate was concentrated. The crude product was washed twice with hexane to remove excess allyl iodide to give Surfactant 3 as a brown liquid (850 mg).

Example 4b: Determination of physical properties of Surfactant 3

[0232] The critical micelle concentration (CMC) for Surfactant 3 was measured. From the surface tension change with concentration in water, the CMC was determined to be about 1.3599 mmol. The plateau value of minimum surface tension that can be reached by this surfactant was about 20.67 mN/m, indicating that

the surfactant has outstanding interfacial activity. These results are plotted as surface tension versus concentration in Fig. 3.

Example 5a: Synthesis of 6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxo-N-(prop-2-yn-1-yl)hexan-1-aminium bromide (Surfactant 4)

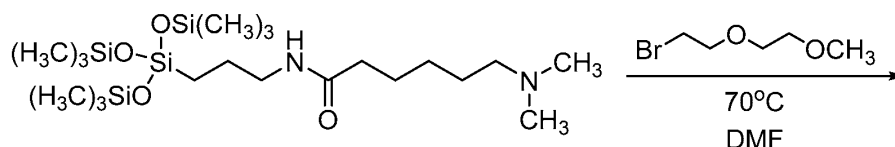


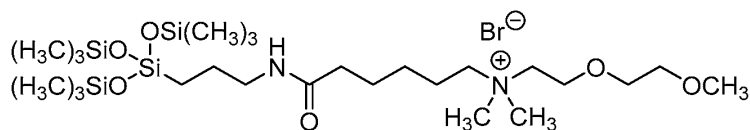
[0233] The siloxane derivative described in Example 1 (1.00 g, 2.02 mmol) was dissolved in dimethylformamide (DMF) (15 mL). Propargyl bromide (674 mg, 2.4 mmol) was added, and the mixture was stirred for 12 hours at 70°C. The solvent was removed under vacuum, and the crude product was washed twice with hexanes to give Surfactant 4 as a brown liquid (850 mg).

Example 5b: Determination of physical properties of Surfactant 4

[0234] The critical micelle concentration (CMC) for Surfactant 4 was measured. From the surface tension change with concentration in water, the CMC was determined to be about 0.2419 mmol. The plateau value of minimum surface tension that can be reached by this surfactant was about 20.54 mN/m, indicating that the surfactant has outstanding interfacial activity. These results are plotted as surface tension versus concentration in Fig. 4.

Example 6a: Synthesis of 6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N-(2-(2-methoxyethoxy)ethyl)-N,N-dimethyl-6-oxohexan-1-aminium bromide (Surfactant 5)



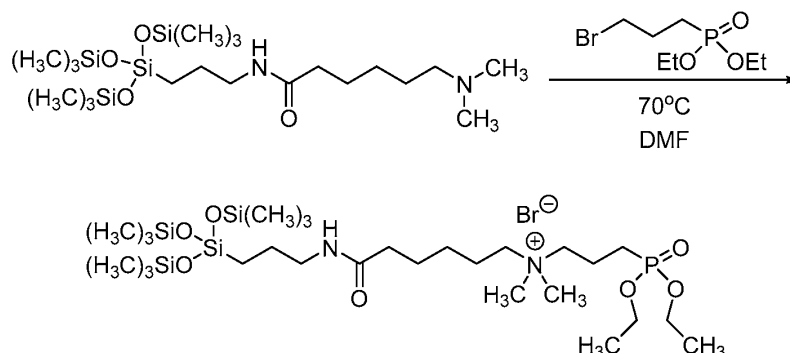


[0235] The siloxane derivative described in Example 1 (1.00 g, 2.02 mmol) was dissolved in dimethylformamide (DMF) (15 mL). 1-Bromo-2-(2-methoxyethoxy)ethane (2.4 mmol) was added, and the mixture was stirred for 12 hours at 70°C. The solvent was removed under vacuum, and the crude product was washed twice with hexanes to give Surfactant 5 as a brown liquid (800 mg).

Example 6b: Determination of physical properties of Surfactant 5

[0236] The critical micelle concentration (CMC) for Surfactant 5 was measured. From the surface tension change with concentration in water, the CMC was determined to be about 0.4622 mmol. The plateau value of minimum surface tension that can be reached by this surfactant was about 20.40 mN/m, indicating that the surfactant has outstanding interfacial activity. These results are plotted as surface tension versus concentration in Fig. 5.

Example 7a: Synthesis of N-(3-(diethoxyphosphoryl)propyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide (Surfactant 6)

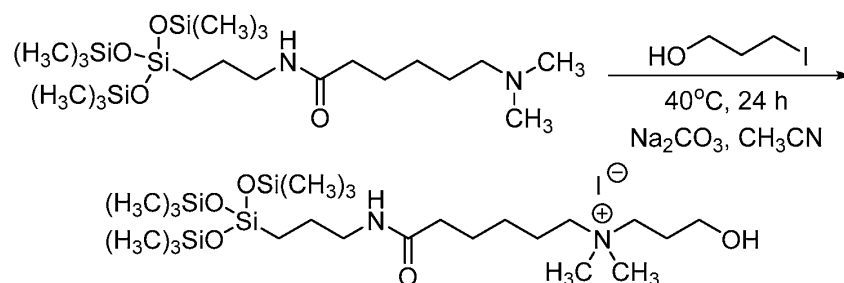


[0237] The siloxane derivative described in Example 1 (1.00 g, 2.02 mmol) was dissolved in dimethylformamide (DMF) (20 mL). Bromo phosphonate (4.04 mmol) was added, and the mixture was stirred for 12 hours at 70°C. The solvent was removed under vacuum, and the crude product was washed twice with hexanes to give Surfactant 6 as a brown liquid (900 mg).

Example 7b: Determination of physical properties of Surfactant 6

[0238] The critical micelle concentration (CMC) for Surfactant 6 was measured. From the surface tension change with concentration in water, the CMC was determined to be about 0.3989 mmol. The plateau value of minimum surface tension that can be reached by this surfactant was about 20.48 mN/m, indicating that the surfactant has outstanding interfacial activity. These results are plotted as surface tension versus concentration in Fig. 6.

Example 8a: Synthesis of 6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N-(3-hydroxypropyl)-N,N-dimethyl-6-oxohexan-1-aminium iodide (Surfactant 7)

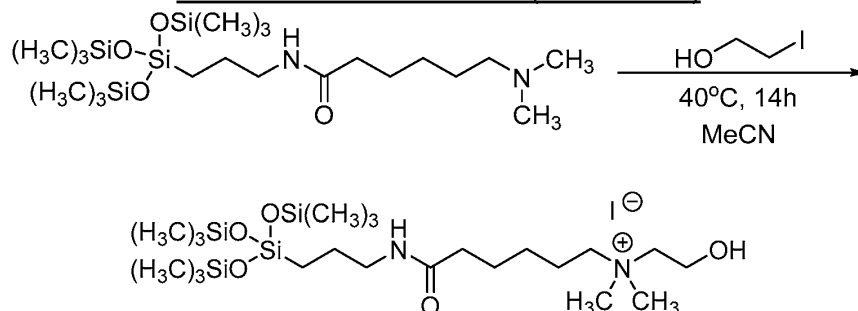


[0239] The siloxane derivative described in Example 1 (1.00 g, 2.02 mmol) was dissolved in acetonitrile (10 mL). Sodium carbonate (0.26 g) was added, followed by 3-iodopropanol (674 mg). The mixture was stirred for 24 hours at 40°C. Residual base was removed via filtration and the filtrate was concentrated. The crude product was washed twice with hexanes to remove excess iodopropanol and give Surfactant 7 as a brown liquid (780 mg).

Example 8b: Determination of physical properties of Surfactant 7

[0240] The critical micelle concentration (CMC) for Surfactant 7 was measured. From the surface tension change with concentration in water, the CMC was determined to be about 0.4568 mmol. The plateau value of minimum surface tension that can be reached by this surfactant was about 20.61 mN/m, indicating that the surfactant has outstanding interfacial activity. These results are plotted as surface tension versus concentration in Fig. 7.

Example 9a: Synthesis of 6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium iodide (Surfactant 8)

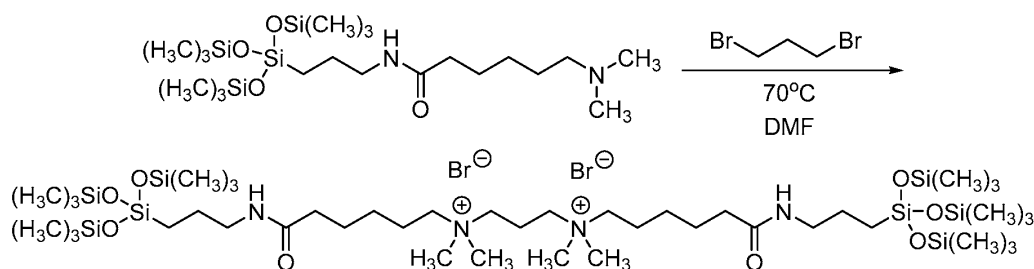


[0241] The siloxane derivative described in Example 1 (1.00 g, 2.02 mmol) was dissolved in acetonitrile (10 mL). 2-Iodoethanol (4.04 mmol) was added, and the mixture was stirred for 14 hours at 40°C. The solvent was removed, and the crude product was washed twice with hexanes to give Surfactant 8 (910 mg).

Example 9b: Determination of physical properties of Surfactant 8

[0242] The critical micelle concentration (CMC) for Surfactant 8 was measured. From the surface tension change with concentration in water, the CMC was determined to be about 0.9986 mmol. The plateau value of minimum surface tension that can be reached by this surfactant was about 20.41 mN/m, indicating that the surfactant has outstanding interfacial activity. These results are plotted as surface tension versus concentration in Fig. 8.

Example 10a: Synthesis of N¹,N³-bis(6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-6-oxohexyl)-N¹,N¹,N³,N³-tetramethylpropane-1,3-diaminium dibromide (Surfactant 10)



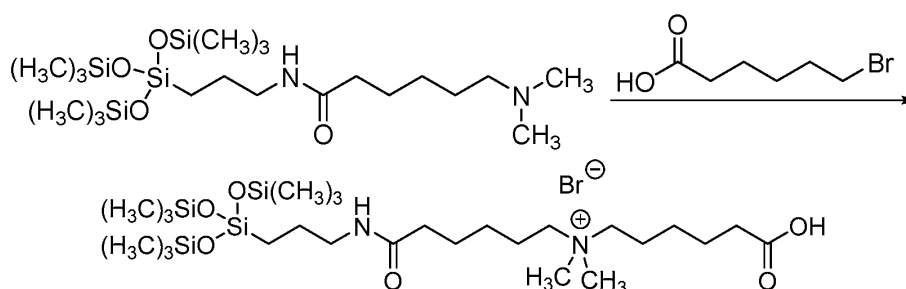
[0243] The siloxane derivative described in Example 1 (1.00 g, 2.02 mmol) was dissolved in dimethylformamide (DMF) (20 mL). 1,2-Dibromopropane (1 mmol) was added, and the mixture was stirred for 12 hours at 70°C. The solvent was

removed, and the crude product was washed twice with hexanes to give Surfactant 10 as a brown liquid (900 mg).

Example 10b: Determination of physical properties of Surfactant 10

[0244] The critical micelle concentration (CMC) for Surfactant 10 was measured. From the surface tension change with concentration in water, the CMC was determined to be about 0.0631 mmol. The plateau value of minimum surface tension that can be reached by this surfactant was about 22.12 mN/m, indicating that the surfactant has interfacial activity. These results are plotted as surface tension versus concentration in Fig. 10.

Example 11a: Synthesis of N-(5-carboxypentyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide (Surfactant 9)



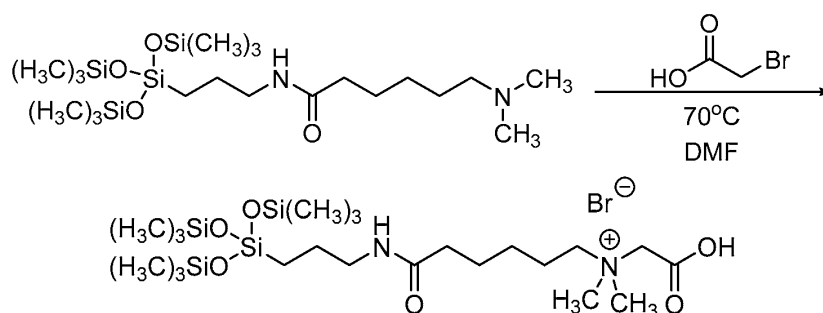
[0245] The siloxane derivative described in Example 1 (1 g, 2.02 mmol) was dissolved in dimethylformamide (DMF) (15 mL) and 6-bromohexanoic acid (2.02 mmol) was added. The mixture was stirred for 12 hours at 70°C, after which the solvent was removed under vacuum. The crude product was washed twice with hexane to provide N-(5-carboxypentyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide as a sticky brown liquid (650 mg).

Example 11b: Determination of physical properties of Surfactant 9

[0246] The critical micelle concentration (CMC) for Surfactant 9 was measured. From the surface tension change with concentration in water, the CMC was determined to be about 0.2237 mmol. The plateau value of minimum surface tension that can be reached by this surfactant was about 20.52 mN/m, indicating that

the surfactant has excellent interfacial activity. These results are plotted as surface tension versus concentration in Fig. 9.

Comparative Example A1: Synthesis of N-(carboxymethyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide (Comparative Surfactant)

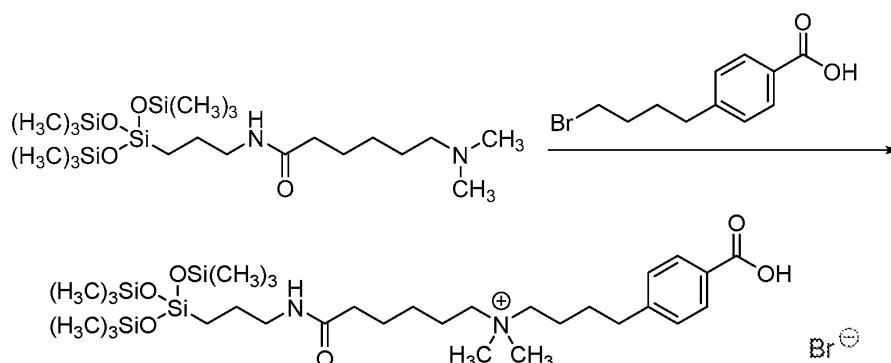


[0247] The siloxane derivative described in Example 1 (1.00 g, 2.02 mmol) was dissolved in dimethylformamide (DMF) (15 mL). Bromoacetic acid (2.02 mmol) was added, and the mixture was stirred for 12 hours at 70°C. The solvent was removed, and the crude product was washed twice with hexanes to give Comparative Surfactant as a brown liquid (700 mg).

Comparative Example A2: Determination of physical properties of Comparative Surfactant

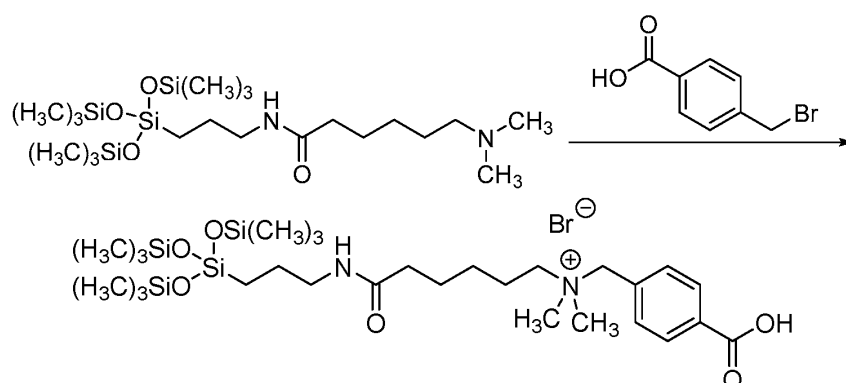
[0248] The critical micelle concentration (CMC) for Comparative Surfactant was measured. From the surface tension change with concentration in water, the CMC was determined to be about 17.28 mmol. The plateau value of minimum surface tension that can be reached by this surfactant was about 29.16 mN/m. These results are plotted as surface tension versus concentration in Fig. 11. The results show the difficulty in predicting surfactant activity on the basis of chemical structure; Surfactant 9, which differs only in the number of methylene groups in the carboxylic acid, displays excellent activity.

Example 12: Synthesis of N-(4-(4-carboxyphenyl)butyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide (Surfactant 11)



[0249] To the siloxane derivative described in Example 1 is added 4-(4-bromobutyl)benzoic acid to provide N-(4-(4-carboxyphenyl)butyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide.

Example 13: Synthesis of N-(4-carboxybenzyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide (Surfactant 12)



[0250] To the siloxane derivative described in Example 1 is added 4-(bromomethyl)benzoic acid to provide N-(4-carboxybenzyl)-6-((3-(1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxan-3-yl)propyl)amino)-N,N-dimethyl-6-oxohexan-1-aminium bromide.

Example 14:

Formulation for pesticides

[0251] In this Example, a concentrated formulation for use as a pesticide is provided. The components of the formulation are shown below in Table 3. The

formulation may also include additional surfactants, water, thickeners, deposition enhancers, drift control agents, and salts.

Table 3

Component	Function	Weight %
Pesticide	Agriculturally Active Agent	5-40
Any of Surfactants 1-12	Emulsifier	20-80
Water-Insoluble Solvent	Solvent	0.1-50

Example 15:Formulation for liquid fungicidal composition

[0252] In this Example, a formulation for use as liquid fungicidal composition is provided. The formulation is shown below in Table 4.

TABLE 4

Component	Function	Weight %
Fungicide	Agriculturally Active Agent	1-90
Any of Surfactants 1-12	Emulsifier	1-30
Co-Surfactant	Co-Emulsifier	0-20
Water-Insoluble Solvent	Solvent	0-90

Example 16:Formulation for herbicide

[0253] In this Example, a formulation for use as an herbicide is provided. The formulation is shown below in Table 5.

TABLE 5

Component	Function	Weight %
Herbicide Salt	Agriculturally Active Agent	5-70
Second Herbicide	Agriculturally Active Agent	0.1-40
Any of Surfactants 1-12	Emulsifier	0-15
Water-Insoluble Solvent	Solvent	0-50
Water		20-80

Example 17:Formulation for insecticide

[0254] In this Example, a formulation for use as an insecticide is provided. The formulation is shown below in Table 6.

TABLE 6

Component	Function	Weight %
Insecticide	Agriculturally Active Agent	5-70
Any of Surfactants 1-12		0.1-40
Surfactant	Antifoaming Agent	0-15
Thickener	Viscosity Modifier	0-50
Water		20-80

[0255] Example 18 Antimicrobial MIC Studies

[0256] The antimicrobial properties of surfactants were examined using known methods and standard protocols, and various types of microorganisms as treatment targets. More specifically a minimum inhibitory concentration (MIC) test protocol was applied, using serial dilution method, giving concentration-dependent microorganism growth inhibition measurements against gram positive (e.g., *Streptococcus mutans*, which is anaerobic, and *Staphylococcus aureus*, which is usually aerobic but can grow also anaerobically), gram negative (e.g., *Escherichia coli*, which is anaerobic, or *Pseudomonas aeruginosa*, which is aerobic).

[0257] Bacteria were propagated overnight in a suitable growth medium, which was a Tryptic Soy Broth. Prior to testing, the concentrations of the test organisms were established using a spectrophotometer that can measure optical density. Those bacterial samples were then diluted to about 1E3 to 1E4 CFU/mL. Thereafter, 10 mL of the bacterial cultures thus prepared were inoculated into test wells of a 96-well plate, each containing suitable growth media, which was Tryptic Soy Agar, and once the bacterial cultures were inoculated, these wells were then treated with the test specimen, serially diluted, incubated at a temperature of 37 +/- 1oC and relative humidity of not less than 90% for about 24 +/- 1 hour.

[0258] Test surfactants were prepared into dilution series. All dilutions were conducted serially using a multichannel pipetter into 96-well microtiter plates. The dilution series were previously established by range-finding exercises so as to determine a high concentration ceiling and a series of diluted, lower concentrations

so as to ensure that the test substance would at no time completely inhibit bacterial growth but still show effects.

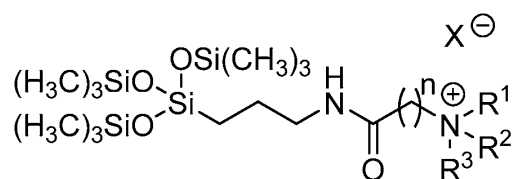
[0259] The MIC was then used to determine the approximate concentration of the test surfactant at which there was inhibition of bacterial growth.

[0260] A reference substance was typically used as a positive control in this antimicrobial testing protocol, in this case, ADBAC, a quarternary amine having a CAS number of 139-08-2 was applied as a suitable test reference.

[0261] Test measurements were made on replicate 96-well plates, and reported as the rounded whole number average of the determined MIC. Replicate data were averaged by determination of the mean value (arithmetic average) for a selected measure using the equation: Arithmetic mean = the sum of the numbers in the set of interest/the number of terms. Measurement variability was then reported based on the determined average in the form of MIC +/-.

ASPECTS

[0262] Aspect 1 is a formulation for a pesticide, comprising:
at least one surfactant of Formula I:



Formula I

wherein R¹ and R² are the same or different, and comprise at least one group selected from the group consisting of C₁-C₆ alkyl, optionally the C₁-C₆ alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R³ is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C₃-C₈ carboxylic acid, C₁-C₁₀ alkyl benzoic acid, and a C₁-C₁₂ linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same or different form the first molecule of Formula I;

n is an integer from 1 to 12; and

X is selected from the group consisting of chloride, bromide, and iodide;
and a pesticide or a plant growth regulator.

[0263] Aspect 2 is the formulation of Aspect 1, further comprising a water-insoluble solvent.

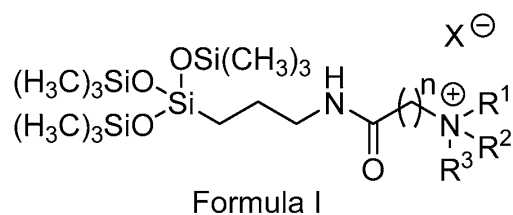
[0264] Aspect 3 is the formulation of Aspect 1, wherein the pesticide is an insecticide.

[0265] Aspect 4 is the formulation of Aspect 3, further comprising an antifoaming agent.

[0266] Aspect 5 is the formulation of Aspect 3 or Aspect 4, further comprising an antifreezing agent.

[0267] Aspect 6 is the formulation of any of Aspects 3-5, further comprising water.

[0268] Aspect 7 is a formulation for a fungicide, comprising:
at least one surfactant of Formula I:



wherein R¹ and R² are the same or different, and comprise at least one group selected from the group consisting of C₁-C₆ alkyl, optionally the C₁-C₆ alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R³ is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C₃-C₈ carboxylic acid, C₁-C₁₀ alkyl benzoic acid, and a C₁-C₂ linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same or different from the first molecule of Formula I;

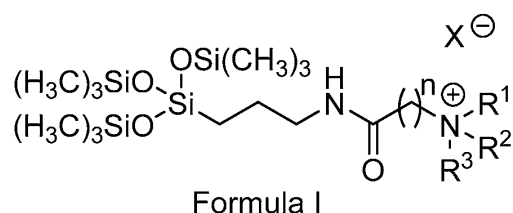
n is an integer from 1 to 12; and

X is selected from the group consisting of chloride, bromide, and iodide; and a fungicide.

[0269] Aspect 8 is the formulation of Aspect 7, further comprising a co-surfactant.

[0270] Aspect 9 is the formulation of either of Aspect 7 or Aspect 8, further comprising a carrier agent.

[0271] Aspect 10 is a formulation for an herbicide, comprising: at least one surfactant of Formula I:



wherein R¹ and R² are the same or different, and comprise at least one group selected from the group consisting of C₁-C₆ alkyl, optionally the C₁-C₆ alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R³ is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C₃-C₈ carboxylic acid, C₁-C₁₀ alkyl benzoic acid, and a C₁-C₁₂ linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same or different from the first molecule of Formula I;

n is an integer from 1 to 12; and

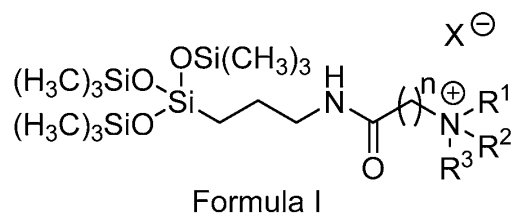
X is selected from the group consisting of chloride, bromide, and iodide; and an herbicide.

[0272] Aspect 11 is the formulation of Aspect 10, further comprising a second herbicide.

[0273] Aspect 12 is the formulation of either Aspect 10 or Aspect 11, further comprising a water-insoluble solvent.

[0274] Aspect 13 is the formulation of any of Aspects 10-12, further comprising water.

[0275] Aspect 14 is a formulation for an insecticide, comprising:
at least one surfactant of Formula I:



wherein R¹ and R² are the same or different, and comprise at least one group selected from the group consisting of C₁-C₆ alkyl, optionally the C₁-C₆ alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R³ is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C₃-C₈ carboxylic acid, C₁-C₁₀ alkyl benzoic acid, and a C₁-C₁₂ linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same or different from the first molecule of Formula I;

n is an integer from 1 to 12; and

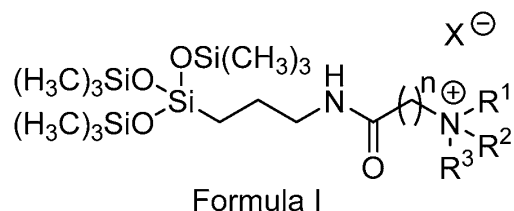
X is selected from the group consisting of chloride, bromide, and iodide;
and an insecticide.

[0276] Aspect 15 is the formulation of Aspect 14, further comprising an antifoaming agent.

[0277] Aspect 16 is the formulation of either of Aspect 14 or Aspect 15, further comprising an antifreezing agent.

[0278] Aspect 17 is the formulation of any of Aspects 14-16, further comprising water.

[0279] Aspect 18 is the use as a surfactant of a compound of Formula I



wherein R^1 and R^2 are the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R^3 is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_{12} linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same or different from the first molecule of Formula I;

n is an integer from 1 to 12; and

X is selected from the group consisting of chloride, bromide, and iodide; in a pesticide formulation, where the formulation comprises at least one surfactant of Formula I and a pesticide.

[0280] Aspect 19 is the use of Aspect 18, wherein the formulation further comprises a water-insoluble solvent.

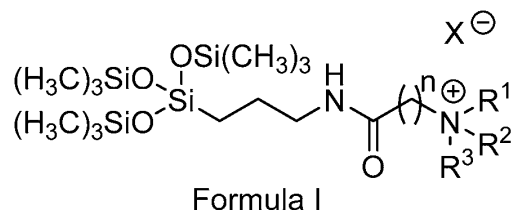
[0281] Aspect 20 is the use of Aspect 18, wherein the pesticide is an insecticide.

[0282] Aspect 21 is the use of Aspect 20, wherein the formulation further comprises an antifoaming agent.

[0283] Aspect 22 is the use of Aspect 20 or Aspect 21, wherein the formulation further comprises an antifreezing agent.

[0284] Aspect 23 is the use of any of Aspects 20-22, wherein the formulation further comprises water.

[0285] Aspect 24 is the use as a surfactant of a compound of Formula I:



wherein R^1 and R^2 are the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R^3 is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_2 linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same or different from the first molecule of Formula I;

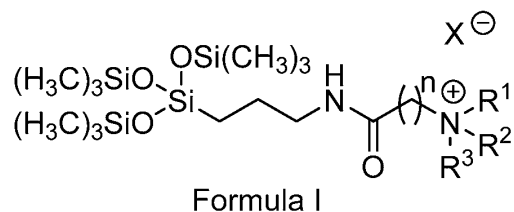
n is an integer from 1 to 12; and

X is selected from the group consisting of chloride, bromide, and iodide;
in a fungicide formulation, wherein the fungicide formulation comprises at least one surfactant of formula (I) and a fungicide.

[0286] Aspect 25 is the use of Aspect 24, wherein the formulation further comprises a co-surfactant.

[0287] Aspect 26 is the use of either of Aspect 24 or Aspect 25, wherein the formulation further comprises a carrier agent.

[0288] Aspect 27 is the use as a surfactant of a compound of Formula I:



wherein R^1 and R^2 are the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R³ is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C₃-C₈ carboxylic acid, C₁-C₁₀ alkyl benzoic acid, and a C₁-C₁₂ linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same or different from the first molecule of Formula I;

n is an integer from 1 to 12; and

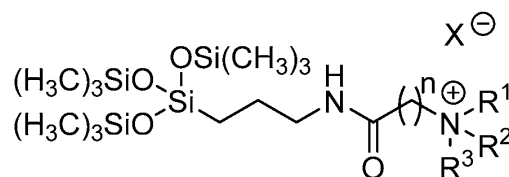
X is selected from the group consisting of chloride, bromide, and iodide; in a herbicide formulation, wherein the herbicide formulation comprises at least one surfactant of formula (I) and an herbicide.

[0289] Aspect 28 is the use of Aspect 27, wherein the formulation further comprises a second herbicide.

[0290] Aspect 29 is the use of either Aspect 27 or Aspect 28, wherein the formulation further comprises a water-insoluble solvent.

[0291] Aspect 30 is the use of any of Aspects 27-29, wherein the formulation further comprises water.

[0292] Aspect 31 is the use as a surfactant of a compound of Formula I:



Formula I

wherein R¹ and R² are the same or different, and comprise at least one group selected from the group consisting of C₁-C₆ alkyl, optionally the C₁-C₆ alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R³ is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C₃-C₈ carboxylic acid, C₁-C₁₀ alkyl benzoic acid, and a C₁-C₁₂ linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same or different from the first molecule of Formula I;

n is an integer from 1 to 12; and

X is selected from the group consisting of chloride, bromide, and iodide; in an insecticide formulation where the formulation comprises at least one surfactant of formula (I) and an insecticide.

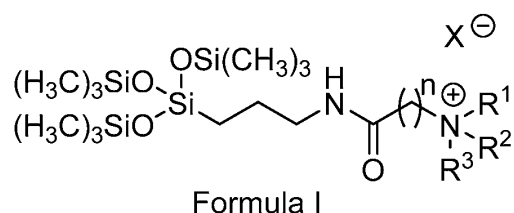
[0293] Aspect 32 is the use of Aspect 31, wherein the formulation further comprises an antifoaming agent.

[0294] Aspect 33 is the use of either of Aspect 31 or Aspect 32, wherein the formulation further comprises an antifreezing agent.

[0295] Aspect 34 is the use of any of Aspects 31-33, wherein the formulation further comprises water.

[0296] Aspect 35 is a pesticide, fungicide, herbicide or insecticide formulation as disclosed in any one of aspects 1 to 17.

[0297] Aspect 36 is the use as a pesticide of a formulation comprising at least one surfactant of a compound of Formula (I)



wherein R^1 and R^2 are the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R^3 is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_{12} linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same or different from the first molecule of Formula I;

n is an integer from 1 to 12; and

X is selected from the group consisting of chloride, bromide, and iodide; a pesticide.

[0298] Aspect 37 is the use of Aspect 36, wherein the formulation further comprises a water-insoluble solvent.

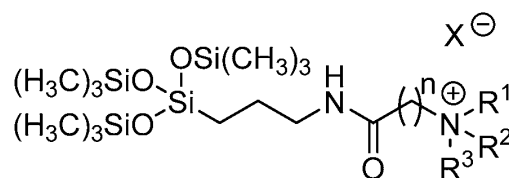
[0299] Aspect 38 is the use of Aspect 36, wherein the pesticide is an insecticide.

[0300] Aspect 39 is the use of Aspect 38, wherein the formulation further comprises an antifoaming agent.

[0301] Aspect 40 is the use of Aspect 38 or Aspect 39, wherein the formulation further comprises an antifreezing agent.

[0302] Aspect 41 is the use of any of Aspects 38-40, wherein the formulation further comprises water.

[0303] Aspect 42 is the use as a fungicide of a formulation comprising at least one surfactant of Formula I:



Formula I

wherein R¹ and R² are the same or different, and comprise at least one group selected from the group consisting of C₁-C₆ alkyl, optionally the C₁-C₆ alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R³ is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C₃-C₈ carboxylic acid, C₁-C₁₀ alkyl benzoic acid, and a C₁-C₂ linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same or different from the first molecule of Formula I;

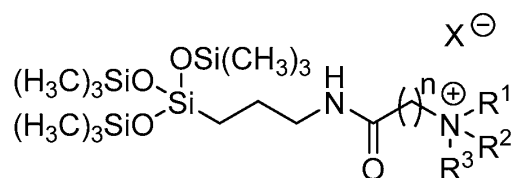
n is an integer from 1 to 12; and

X is selected from the group consisting of chloride, bromide, and iodide; and a fungicide.

[0304] Aspect 43 is the use of Aspect 42, wherein the formulation further comprises a co-surfactant.

[0305] Aspect 44 is the use of either of Aspect 42 or Aspect 43, wherein the formulation further comprises a carrier agent.

[0306] Aspect 45 is the use as a herbicide of a formulation comprising at least one surfactant of Formula I:



Formula I

wherein R^1 and R^2 are the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R^3 is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_{12} linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same or different from the first molecule of Formula I;

n is an integer from 1 to 12; and

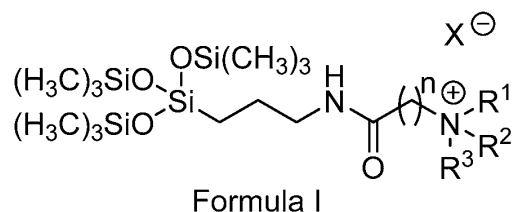
X is selected from the group consisting of chloride, bromide, and iodide; and an herbicide.

[0307] Aspect 46 is the use of Aspect 45, wherein the formulation further comprises a second herbicide.

[0308] Aspect 47 is the use of either Aspect 45 or Aspect 46, wherein the formulation further comprises a water-insoluble solvent.

[0309] Aspect 48 is the use of any of Aspects 45-47, wherein the formulation further comprises water.

[0310] Aspect 49 is the use as an insecticide of a formulation comprising at least one surfactant of Formula I:



wherein R^1 and R^2 are the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R^3 is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, alkyl phosphonate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_{12} linker attached to a second molecule of Formula I, wherein the second molecule of Formula I is the same or different from the first molecule of Formula I;

n is an integer from 1 to 12; and

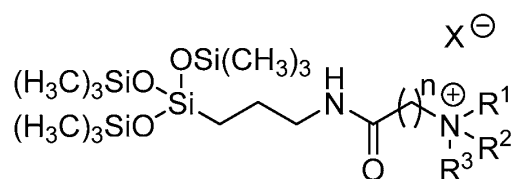
X is selected from the group consisting of chloride, bromide, and iodide; and an insecticide.

[0311] Aspect 50 is the use of Aspect 49, wherein the formulation further comprises an antifoaming agent.

[0312] Aspect 52 is the use of either of Aspect 49 or Aspect 50, wherein the formulation further comprises an antifreezing agent.

[0313] Aspect 53 is the use of any of Aspects 49-51, wherein the formulation further comprises water.

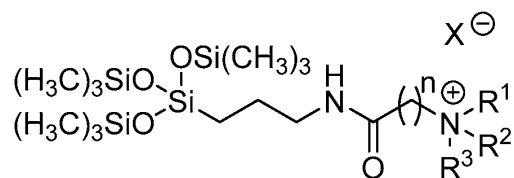
[0314] Aspect 54 is a method of preparing the formulation of any one of Aspects 1-6 comprising:
synthesizing a compound of Formula I



Formula I

wherein R^1 and R^2 are the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate; R^3 is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_6 linker attached to a second molecule of Formula I, wherein the second molecule is the same or different; n is an integer from 1 to 12; and X is selected from the group consisting of chloride, bromide, and iodide, the method comprising: a ring opening step to open lactam ring to provide an amino acid having an N-terminus and a C-terminus; a first alkylation step, to alkylate the N-terminus to provide a tertiary amine; a coupling step, to react the C-terminus with 3-aminopropyltris(trimethylsiloxy)silane to provide siloxane derivative; and a second alkylation step, to alkylate the N-terminus to provide a quaternary amine of Formula I, and adding a pesticide.

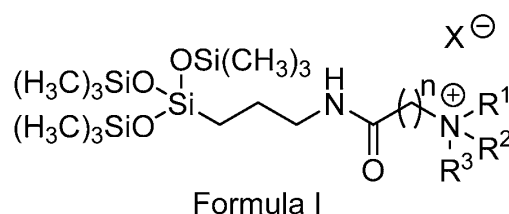
[0315] Aspect 55 is a method of preparing the formulation of any one of Aspects 7-9 comprising:
synthesizing a compound of Formula I



Formula I

wherein R¹ and R² are the same or different, and comprise at least one group selected from the group consisting of C₁-C₆ alkyl, optionally the C₁-C₆ alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate; R³ is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, C₃-C₈ carboxylic acid, C₁-C₁₀ alkyl benzoic acid, and a C₁-C₆ linker attached to a second molecule of Formula I, wherein the second molecule is the same or different; n is an integer from 1 to 12; and X is selected from the group consisting of chloride, bromide, and iodide, the method comprising: a ring opening step to open lactam ring to provide an amino acid having an N-terminus and a C-terminus; a first alkylation step, to alkylate the N-terminus to provide a tertiary amine; a coupling step, to react the C-terminus with 3-aminopropyltris(trimethylsiloxy)silane to provide siloxane derivative; and a second alkylation step, to alkylate the N-terminus to provide a quaternary amine of Formula I, and adding a fungicide.

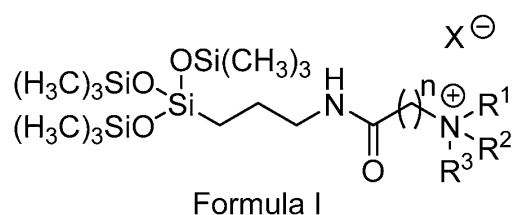
[0316] Aspect 56 is a method of preparing the formulation of any one of Aspects 10 - 13 comprising:
synthesizing a compound of Formula I



wherein R¹ and R² are the same or different, and comprise at least one group selected from the group consisting of C₁-C₆ alkyl, optionally the C₁-C₆ alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate; R³ is selected from the

group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, C₃-C₈ carboxylic acid, C₁-C₁₀ alkyl benzoic acid, and a C₁-C₆ linker attached to a second molecule of Formula I, wherein the second molecule is the same or different; n is an integer from 1 to 12; and X is selected from the group consisting of chloride, bromide, and iodide, the method comprising: a ring opening step to open lactam ring to provide an amino acid having an N-terminus and a C-terminus; a first alkylation step, to alkylate the N-terminus to provide a tertiary amine; a coupling step, to react the C-terminus with 3-aminopropyltris(trimethylsiloxy)silane to provide siloxane derivative; and a second alkylation step, to alkylate the N-terminus to provide a quaternary amine of Formula I, and adding a herbicide.

[0317] Aspect 57 is a method of preparing the formulation of any one of Aspects 14-17 comprising: synthesizing a compound of Formula I



wherein R¹ and R² are the same or different, and comprise at least one group selected from the group consisting of C₁-C₆ alkyl, optionally the C₁-C₆ alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate; R³ is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, C₃-C₈ carboxylic acid, C₁-C₁₀ alkyl benzoic acid, and a C₁-C₆ linker attached to a second molecule of Formula I, wherein the second molecule is the same or different; n is an integer from 1 to 12; and X is selected from the group consisting of chloride, bromide, and iodide, the method comprising: a ring opening step to open lactam ring to provide an amino acid having an N-terminus and a C-

terminus; a first alkylation step, to alkylate the N-terminus to provide a tertiary amine; a coupling step, to react the C-terminus with 3-aminopropyltris(trimethylsiloxy)silane to provide siloxane derivative; and a second alkylation step, to alkylate the N-terminus to provide a quaternary amine of Formula I, and adding an insecticide.

[0318] Aspect 58 is the method of any of Aspects 54 to 57, wherein the lactam is caprolactam.

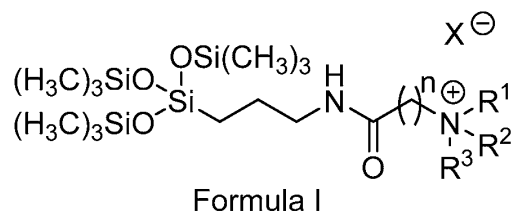
[0319] Aspect 59 is the method of any of Aspects 54 to 58, wherein in the first alkylation step, the tertiary amine is 6-(dimethylamino)hexanoic acid.

[0320] Aspect 60 is the method of any one of Aspects 54 to 59, wherein in the second alkylation step, the N-terminus is alkylated with an alkylating agent selected from the group consisting of benzyl bromide, ethyl bromoacetate, allyl iodide, propargyl bromide, 1-bromo-2-(2-methoxyethoxy)ethane, bromo phosphonate, 3-iodopropanol, 3-bromopropanol, 2-iodoethanol, 2-bromoethanol, 6-bromohexanoic acid, and 1,3-dibromopropane.

CLAIMS

1. A formulation for a pesticide, comprising:

at least one surfactant of Formula I:



wherein R^1 and R^2 are the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R^3 is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_6 linker attached to a second molecule of Formula I, wherein the second molecule is the same or different;

n is an integer from 1 to 12; and

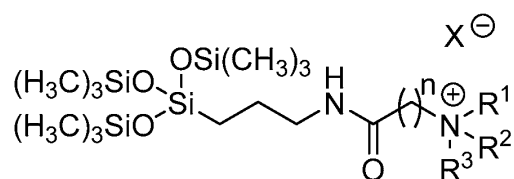
X is selected from the group consisting of chloride, bromide, and iodide;

and

a pesticide.

2. The formulation of Claim 1, further comprising water, a water-insoluble solvent, an antifoaming agent or an antifreezing agent.
3. The formulation of Claim 1 or claim 2, wherein the pesticide is an insecticide.
4. A formulation for a fungicide, comprising:

at least one surfactant of Formula I:



Formula I

wherein R^1 and R^2 are the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R^3 is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, C_3 - C_8 carboxylic acid, C_1 - C_{10} alkyl benzoic acid, and a C_1 - C_6 linker attached to a second molecule of Formula I, wherein the second molecule is the same or different;

n is an integer from 1 to 12; and

X is selected from the group consisting of chloride, bromide, and iodide;

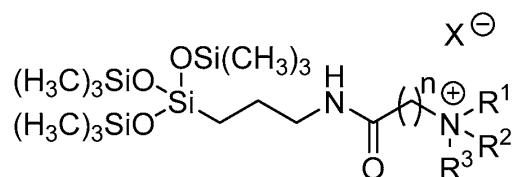
and

a fungicide.

5. The formulation of Claim 4, further comprising a co-surfactant or a carrier agent.

6. A formulation for an herbicide, comprising:

at least one surfactant of Formula I:



Formula I

wherein R^1 and R^2 are the same or different, and comprise at least one group selected from the group consisting of C_1 - C_6 alkyl, optionally the C_1 - C_6 alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at

least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate;

R³ is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, C₃-C₈ carboxylic acid, C₁-C₁₀ alkyl benzoic acid, and a C₁-C₆ linker attached to a second molecule of Formula I, wherein the second molecule is the same or different;

n is an integer from 1 to 12; and

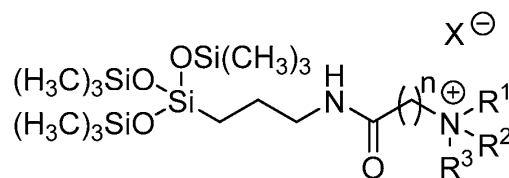
X is selected from the group consisting of chloride, bromide, and iodide;

and

an herbicide.

7. The formulation of Claim 6, further comprising water, a second herbicide, or a water-insoluble solvent.

8. A method of preparing the formulation of any of claims 1 - 7 comprising: synthesizing a compound of Formula I



Formula I

wherein R¹ and R² are the same or different, and comprise at least one group selected from the group consisting of C₁-C₆ alkyl, optionally the C₁-C₆ alkyl may include one or more of oxygen, nitrogen, or sulfur atoms or groups that include at least one of these atoms, and the alkyl chain may be optionally substituted with one or more substituents selected from the group consisting of hydroxyl, amino, amido, sulfonyl, sulfonate, carbonyl, carboxyl, and carboxylate; R³ is selected from the group consisting of alkenyl, alkynyl, ester, alcohol, aryl alkyl, alkoxy alkyl ether, alkyl phosphate, C₃-C₈ carboxylic acid, C₁-C₁₀ alkyl benzoic acid, and a C₁-C₆ linker attached to a second molecule of Formula I, wherein the second molecule is the

same or different; n is an integer from 1 to 12; and X is selected from the group consisting of chloride, bromide, and iodide, the method comprising:

a ring opening step to open lactam ring to provide an amino acid having an N-terminus and a C-terminus;

a first alkylation step, to alkylate the N-terminus to provide a tertiary amine;

a coupling step, to react the C-terminus with 3-aminopropyltris(trimethylsiloxy)silane to provide siloxane derivative; and

a second alkylation step, to alkylate the N-terminus to provide a quaternary amine of Formula I; and

adding a further component selected from a pesticide, a fungicide, a herbicide or an insecticide, and optionally, water.

9. The method of claim 8 wherein the lactam is caprolactam.

10. The method of claim 8 or claim 9, wherein in the first alkylation step, the tertiary amine is 6-(dimethylamino)hexanoic acid.

11. The method of and of claim 8 to claim 10, wherein in the second alkylation step, the N-terminus is alkylated with an alkylating agent selected from the group consisting of benzyl bromide, ethyl bromoacetate, allyl iodide, propargyl bromide, 1-bromo-2-(2-methoxyethoxy)ethane, bromo phosphonate, 3-iodopropanol, 3-bromopropanol, 2-iodoethanol, 2-bromoethanol, 6-bromohexanoic acid, and 1,3-dibromopropane.

12. The use of the formulation of any of claims 1 to 3 as a pesticide.

13. The use of the formulation of claim 4 or claim 5 as a fungicide.

14. The use of the formulation of claim 6 or claim 7 as a herbicide.