C_{12}) unsaturated fatty portions. Metathesis chemistry provides an opportunity to generate precursors having shorter chains and mostly *trans-* isomers, which could impart improved performance when the precursors are converted to downstream compositions (e.g., in surfactants).

Sulfation of alcohols produces alcohol sulfates, which have an C-O-SO_3X group, where X is typically an alkali metal or ammonium ion from a subsequent neutralization step. Sulfonation of unsaturated hydrocarbons gives sulfonates, which have a C-SO_3X group. When an unsaturated alcohol is the starting material, the unsaturated sulfate can be produced under some conditions (see, e.g., WO91/13057). With other reagents, alcohol sulfation and carbon-carbon double bond sulfonation may compete, with most of the reaction product resulting from sulfation, although the nature of the sulfonated by-products is generally not well understood (see, e.g., U.S. Pat. No. 5,446,188). Because of the competing side reactions, unsaturated alcohols are usually avoided when the goal is to make an alcohol sulfate or ether sulfate.

SUMMARY OF THE INVENTION

The present disclosure relates to sulfate and sulfonate derivatives made by one or more of alkoxylating, sulfating, sulfonating, and sulfitating monounsaturated fatty alcohol compositions. In one ~~aspect~~embodiment, the ~~invention~~ present disclosure relates to a sulfate and sulfonate derivative made by one or more of alkoxylating, sulfating, sulfonating, and sulfitating a monounsaturated fatty alcohol composition, wherein the fatty alcohol compositions are obtained by reducing a metathesis-derived monounsaturated alkyl ester. Of particular interest are the sulfate and ether sulfate derivatives. Microscopy studies indicate that the unsaturated sodium sulfates in particular have a lamellar phase that should enable formulation at high actives levels. ~~In another aspect, the invention relates to a fatty alcohol ethoxylate sulfate as disclosed herein. In another aspect, the invention relates to a mixture comprising water and from 1 to 80 wt.%, based on the amount of mixture, of the derivative as disclosed above. In another aspect, the invention relates to a liquid surfactant composition comprising the derivative as disclosed above, wherein the surfactant can be processed, formulated, or both at a higher actives level compared with that of a similar composition comprising a~~

~~saturated analog of the derivative. In another aspect, the invention relates to a process which comprises reducing a metathesis-derived monounsaturated alkyl ester to produce a monounsaturated fatty alcohol composition, and making a sulfate or sulfonate derivative by one or more of alkoxylating, sulfating, sulfonating, and sulfitating the monounsaturated fatty alcohol composition.~~

In ~~another~~ aspect, the ~~invention~~ present disclosure relates to a sulfate ~~compositions~~ comprising: (a) from 40 to 60 wt.% of a monounsaturated fatty primary alcohol sulfate; and (b) from 40 to 60 wt.% of a secondary hydroxyalkyl fatty primary alcohol sulfate, wherein (a) and (b) derive from a C_{11}-C_{17} monounsaturated alcohol. In another aspect, the ~~invention~~ present disclosure relates to a mixture comprising water and from 1 to 80 wt.%, based on the amount of mixture, of the composition as disclosed above.

In another aspect, the ~~invention~~ present disclosure relates to a composition comprising a monounsaturated fatty alcohol alkali metal sulfate having at least one lamellar phase at an actives level within the range of 65-80% actives.

In another aspect, the ~~invention~~ present disclosure relates to a process for making an internally monounsaturated fatty alcohol sulfate, the process comprising reacting a terminally monounsaturated fatty alcohol, preferably a metathesis-derived terminally monounsaturated fatty alcohol, with sulfur trioxide in a falling-film reactor, followed by neutralization.

The derivatives and sulfate compositions are valuable for many end-use applications, including, for example, agricultural dispersants, water-soluble herbicides, anionic emulsifiers for agricultural use, hard surface cleaners, light-duty liquid detergents, personal cleansers, gas well foamers for oilfield applications, laundry detergents, enhanced oil recovery compositions, latex paints, and specialty foams.

In an aspect~~s~~, there is provided a dispersant for agricultural compositions comprising the ~~derivative or ethoxylate sulfate or sulfate~~ composition as disclosed above.

In an aspect~~s~~, there is provided a water-soluble herbicide composition comprising the ~~derivative or ethoxylate sulfate or sulfate~~ composition as disclosed above.

In an aspects, there is provided an anionic emulsifier for agricultural compositions comprising the ~~derivative or ethoxylate sulfate or sulfate~~ composition as disclosed above.

In an aspects, there is provided an aqueous hard-surface cleaner comprising the ~~derivative or ethoxylate sulfate or sulfate~~ composition as disclosed above.

In an aspects, there is provided a personal cleanser comprising the ~~derivative or ethoxylate sulfate or sulfate~~ composition as disclosed above.

In an aspects, there is provided a foamer, foam additive, or dispersant for use in gypsum, concrete, or fire-fighting applications comprising the ~~derivative or ethoxylate sulfate or sulfate~~ composition as disclosed above.

In an aspects, there is provided a gas well foamer for use in oilfield applications comprising the ~~derivative or ethoxylate sulfate or sulfate~~ composition as disclosed above.

In an aspects, there is provided a light-duty liquid detergent comprising the ~~derivative or ethoxylate sulfate or sulfate~~ composition as disclosed above, wherein the ~~fatty alcohol~~ composition derives from ~~is made by reducing~~ a ~~metathesis-derived~~ C_{14}-C_{17} monounsaturated ~~lower alkyl ester~~alcohol.

In an aspects, there is provided a laundry detergent comprising the ~~derivative or ethoxylate sulfate or sulfate~~ composition as disclosed above.

In an aspects, there is provided a surfactant composition for use in enhanced oil recovery, comprising the ~~derivative or ethoxylate sulfate or sulfate~~ composition as disclosed above.

In an aspects, there is provided a surfactant composition for use in emulsion polymerization, comprising the ~~derivative or ethoxylate sulfate or sulfate~~ composition as disclosed above.

In an aspect, there is provided a sulfate derivative having the general structure: $R\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CH_2O\text{-}(AO)_n\text{-}SO_3X$ wherein R is H or C_2-C_7 alkyl; X is a mono- or divalent cation or an ammonium or substituted ammonium cation; AO is an oxyalkylene group; and n, which is the average number of oxyalkylene groups, has a value within the range of 0 to 20.

In an aspect, there is provided a process which comprises reducing a metathesis-derived monounsaturated alkyl ester, preferably a C_{10}-C_{17} monounsaturated lower alkyl ester, to produce a monounsaturated fatty alcohol composition, and making a sulfate or sulfonate derivative by one or more of alkoxylating, sulfating, sulfonating, and sulfitating the monounsaturated fatty alcohol composition, wherein the derivative comprises: (a) an alkyl sulfate, a sulfonated alkyl sulfate, an alcohol sulfonate, a sulfated alcohol sulfonate, or a mixture thereof; or (b) an ether sulfate, a sulfonated ether sulfate, an alkoxylate sulfonate, a sulfated alkoxylate sulfonate, or a mixture thereof.

In aspects, the present disclosure provides a dispersant for agricultural compositions; a water-soluble herbicide composition; an anionic emulsifier from agricultural compositions; an aqueous hard-surface cleaner; a personal cleanser; a foamer, foam additive or dispersant for use in gypsum, concrete or fire-fighting applications; a gas well foamer for use in oilfield applications; a laundry detergent; a light-duty liquid detergent; a surfactant composition for use in enhanced oil recovery; or a surfactant composition for use in emulsion polymerization comprising the sulfate derivative as disclosed above.

Claims

1. A sulfate composition comprising:

(a) from 40 to 60 wt.% of a monounsaturated fatty primary alcohol sulfate;

and

(b) from 40 to 60 wt.% of a secondary hydroxyalkyl fatty primary alcohol sulfate, wherein (a) and (b) derive from a C_{11}-C_{17} monounsaturated alcohol.

2. The composition of claim 1 further comprising 0.1 to 20 wt.% of sulfonated products.

3. The composition of claim 1 wherein the monounsaturated alcohol is metathesis-derived.

4. The composition of claim 1 wherein (a) has the structure:

$$R\text{-}O\text{-}SO_3X$$

wherein R is a linear or branched C_8-C_{30} monounsaturated hydrocarbyl group, and X is a mono- or divalent cation or an ammonium or substituted ammonium cation.

5. The composition of claim 4 wherein R is a linear C_{11}-C_{17} monounsaturated hydrocarbyl group.

6. The composition of claim 1 wherein (a) is a mixture of cis- and trans- isomers.

7. The composition of claim 1 wherein (b) has the structure:

$$CH_3\text{-}(CH_2)_y\text{-}CHOH\text{-}(CH_2)_z\text{-}O\text{-}SO_3X$$

wherein y= 0 to 28, z= 0 to 28, y+z = 6 to 28, and X is a mono- or divalent cation or an ammonium or substituted ammonium cation.

8. The composition of claim 7 wherein y+z = 9 to 15.

9. The composition of claim 1 made by sulfating a monounsaturated fatty alcohol with sulfur trioxide in a falling-film reactor, followed by neutralization.

10. A mixture comprising water and from 1 to 80 wt.%, based on the amount of mixture, of the composition of claim 1.

11. A composition comprising a monounsaturated fatty alcohol alkali metal sulfate having at least one lamellar phase at an actives level within the range of 65-80% actives.

12. The composition of claim 11 having an isotropic clear phase over a broader % actives range compared with that of a composition comprising a saturated analog of the monounsaturated fatty alcohol alkali metal sulfate.

13. The composition of claim 11 further comprising a hydroxyalkyl alcohol sulfate and sulfonates, the composition having an isotropic clear phase at up to 50% actives.

14. A dispersant for agricultural compositions comprising the composition of claim 1.

15. A water-soluble herbicide composition comprising the composition of claim 1.

16. An anionic emulsifier for agricultural compositions comprising the composition of claim 1.

17. An aqueous hard-surface cleaner comprising the composition of claim 1.

18. A personal cleanser comprising the composition of claim 1.

19. A foamer, foam additive, or dispersant for use in gypsum, concrete, or fire-fighting applications comprising the composition of claim 1.

20. A gas well foamer for use in oilfield applications comprising the composition of claim 1.

21. A light-duty liquid detergent comprising the composition of claim 1, wherein the composition derives from a C_{14}-C_{17} monounsaturated alcohol.

22. A laundry detergent comprising the composition of claim 1.

23. A surfactant composition for use in enhanced oil recovery, comprising the composition of claim 1.

24. A surfactant composition for use in emulsion polymerization, comprising the composition of claim 1.

25. A sulfate derivative having the general structure:

$$R\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CH_2O\text{-}(AO)_n\text{-}SO_3X$$

wherein R is H or C_2-C_7 alkyl; X is a mono- or divalent cation or an ammonium or substituted ammonium cation; AO is an oxyalkylene group; and n, which is the average number of oxyalkylene groups, has a value within the range of 0 to 20.

26. The derivative of claim 25 wherein R is C_2-C_7 alkyl and the derivative has at least 1 mole % of trans-Δ^9 unsaturation.

27. The derivative of claim 25 or claim 26 comprising a fatty alcohol ethoxylate sulfate.

28. A process which comprises reducing a metathesis-derived monounsaturated alkyl ester, preferably a C_{10}-C_{17} monounsaturated lower alkyl ester, to produce a monounsaturated fatty alcohol composition, and making a sulfate or sulfonate derivative by one or more of alkoxylating, sulfating, sulfonating, and sulfitating the monounsaturated fatty alcohol composition, wherein the derivative comprises: (a) an alkyl sulfate, a sulfonated alkyl sulfate, an alcohol sulfonate, a sulfated alcohol sulfonate, or a mixture thereof; or (b) an ether sulfate, a sulfonated ether sulfate, an alkoxylate sulfonate, a sulfated alkoxylate sulfonate, or a mixture thereof.

29. A process for making an internally monounsaturated fatty alcohol sulfate, the process comprising reacting a terminally monounsaturated fatty alcohol, preferably a metathesis-derived terminally monounsaturated fatty alcohol, with sulfur trioxide in a falling-film reactor, followed by neutralization.

30. A dispersant for agricultural compositions; a water-soluble herbicide composition; an anionic emulsifier from agricultural compositions; an aqueous hard-surface cleaner; a personal cleanser; a foamer, foam additive or dispersant for use in gypsum, concrete or fire-fighting applications; a gas well foamer for use in oilfield applications; a laundry detergent; a light-duty liquid detergent; a surfactant composition for use in enhanced oil recovery; or a surfactant composition for use in emulsion polymerization comprising the sulfate derivative of claim 25.

31. A dispersant for agricultural compositions; a water-soluble herbicide composition; an anionic emulsifier from agricultural compositions; an aqueous hard-surface cleaner; a personal cleanser; a foamer, foam additive or dispersant for use in gypsum, concrete or fire-fighting applications; a gas well foamer for use in oilfield applications; a laundry detergent; a light-duty liquid detergent; a surfactant composition for use in enhanced oil recovery; or a surfactant composition for use in emulsion polymerization comprising the sulfate derivative of claim 27.

We claim:

1. A sulfate or sulfonate derivative made by one or more of alkoxylating, sulfating, sulfonating, and sulfitating a monounsaturated fatty alcohol composition, wherein the fatty alcohol composition is made by reducing a metathesis-derived monounsaturated alkyl ester.

2. The derivative of claim **1** wherein the fatty alcohol composition is made by reducing a metathesis-derived C_5-C_{35} monounsaturated alkyl ester.

3. The derivative of claim **1** wherein the fatty alcohol composition is made by reducing a metathesis-derived C_{10}-C_{17} monounsaturated lower alkyl ester.

4. The derivative of claim **1** comprising an alkyl sulfate, a sulfonated alkyl sulfate, an alcohol sulfonate, a sulfated alcohol sulfonate, or a mixture thereof.

5. The derivative of claim **1** comprising an ether sulfate, a sulfonated ether sulfate, an alkoxylate sulfonate, a sulfated alkoxylate sulfonate, or a mixture thereof.

6. The derivative of claim **1** wherein the metathesis-derived alkyl ester has at least 1 mole % of *trans*-Δ^9 unsaturation.

7. The derivative of claim **1** made by reacting the fatty alcohol composition with one or more alkylene oxides to give an alkoxylate, followed by one or more of sulfation, sulfonation, and sulfitation.

8. The derivative of claim **7** wherein the alkoxylate is reacted with a sulfating agent to give an ether sulfate.

9. A fatty alcohol ethoxylate sulfate of claim **8**.

10. The derivative of claim **1** made by reacting the fatty alcohol composition with a sulfating agent to give an alkyl sulfate.

11. The derivative of claim **1** made by reacting the fatty alcohol composition with a sulfitating or sulfonating agent to give a sulfonate.

12. The derivative of claim **1** wherein the fatty alcohol composition has the general structure:

$$R\text{-}C_9H_{16}\text{-}CH_2OH$$

wherein R is H or C_2-C_7 alkyl.

13. The derivative of claim **12** wherein the fatty alcohol composition has the general structure:

$$R\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CH_2OH$$

wherein R is H or C_2-C_7 alkyl.

14. The derivative of claim **1** having the general structure:

$$R\text{-}C_9H_{16}\text{-}CH_2O\text{-}(AO)_n\text{-}SO_3X$$

wherein R is H or C_2-C_7 alkyl; X is a mono- or divalent cation or an ammonium or substituted ammonium cation; AO is an oxyalkylene group; and n, which is the average number of oxyalkylene groups, has a value within the range of 0 to 200.

15. The derivative of claim **14** having the general structure:

$$R\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CH_2O\text{-}(AO)_n\text{-}SO_3X$$

wherein R is H or C_2-C_7 alkyl; X is a mono- or divalent cation or an ammonium or substituted ammonium cation; AO is an oxyalkylene group; and n, which is the average number of oxyalkylene groups, has a value within the range of 0 to 200.

16. The derivative of claim **1** wherein the alkyl ester is made by cross-metathesis of a natural oil with an olefin, followed by stripping to remove unsaturated hydrocarbons from a modified oil component, followed by transesterification of the modified oil component with an alkanol under basic conditions to generate the alkyl ester.

17. The derivative of claim **1** wherein the natural oil is selected from the group consisting of soybean oil, palm oil, rapeseed oil, algal oil, and mixtures thereof.

18. A mixture comprising water and from 1 to 80 wt.%, based on the amount of mixture, of the derivative of claim **1**.

19. A liquid surfactant composition comprising the derivative of claim **1**, wherein the surfactant can be processed, formulated, or both at a higher actives level compared with that of a similar composition comprising a saturated analog of the derivative.

20. A process which comprises reducing a metathesis-derived monounsaturated alkyl ester to produce a monounsaturated fatty alcohol composition, and making a sulfate or sulfonate derivative by one or more of alkoxylating, sulfating, sulfonating, and sulfitating the monounsaturated fatty alcohol composition.

21. The process of claim **20** wherein the metathesis-derived alkyl ester is a C_5-C_{35} monounsaturated alkyl ester.

22. The process of claim **20** wherein the metathesis-derived alkyl ester is a C_{10}-C_{17} monounsaturated lower alkyl ester.

23. The process of claim **20** wherein the derivative comprises an alkyl sulfate, a sulfonated alkyl sulfate, an alcohol sulfonate, a sulfated alcohol sulfonate, or a mixture thereof.

24. The process of claim **20** wherein the derivative comprises an ether sulfate, a sulfonated ether sulfate, an alkoxylate sulfonate, a sulfated alkoxylate sulfonate, or a mixture thereof.

25. The process of claim **20** comprising sulfating the fatty alcohol composition to give an alkyl sulfate.

26. The process of claim **20** comprising alkoxylating the fatty alcohol composition with one or more alkylene oxides to give an alkoxylate, followed by one or more of sulfation, sulfonation, and sulfitation.

27. The process of claim **26** wherein the alkoxylate is sulfated to give an ether sulfate.

28. The process of claim **20** comprising sulfonating or sulfitating the monounsaturated alcohol to give a sulfonate.

29. A sulfate composition comprising:

(a) from 40 to 60 wt.% of a monounsaturated fatty primary alcohol sulfate;

and

(b) from 40 to 60 wt.% of a secondary hydroxyalkyl fatty primary alcohol sulfate.

30. The composition of claim **29** further comprising 0.1 to 20 wt.% of sulfonated products.

31. The composition of claim **29** wherein (a) and (b) derive from a C_8-C_{30} monounsaturated alcohol.

32. The composition of claim **31** wherein (a) and (b) derive from a C_{11}-C_{17} monounsaturated alcohol.

33. The composition of claim **31** wherein the monounsaturated alcohol is metathesis-derived.

34. The composition of claim **29** wherein (a) has the structure:

$$R\text{-}O\text{-}SO_3X$$

wherein R is a linear or branched C_8-C_{30} monounsaturated hydrocarbyl group, and X is a mono- or divalent cation or an ammonium or substituted ammonium cation.

35. The composition of claim **34** wherein R is a linear C_{11}-C_{17} monounsaturated hydrocarbyl group.

36. The composition of claim **29** wherein (a) is a mixture of *cis*- and *trans*-isomers.

37. The composition of claim **29** wherein (b) has the structure:

$$CH_3\text{-}(CH_2)_y\text{-}CHOH\text{-}(CH_2)_z\text{-}O\text{-}SO_3X$$

wherein y= 0 to 28, z= 0 to 28, y+z = 6 to 28, and X is a mono- or divalent cation or an ammonium or substituted ammonium cation.

38. The composition of claim **37** wherein y+z = 9 to 15.

39. The composition of claim **29** made by sulfating a monounsaturated fatty alcohol with sulfur trioxide in a falling-film reactor, followed by neutralization.

40. A mixture comprising water and from 1 to 80 wt.%, based on the amount of mixture, of the composition of claim **29**.

41. A composition comprising a monounsaturated fatty alcohol alkali metal sulfate having at least one lamellar phase at an actives level within the range of 65-80% actives.

42. The composition of claim **41** having an isotropic clear phase over a broader % actives range compared with that of a composition comprising a saturated analog of the monounsaturated fatty alcohol alkali metal sulfate.

43. The composition of claim **41** further comprising a hydroxyalkyl alcohol sulfate and sulfonates, the composition having an isotropic clear phase at up to 50% actives.

44. A process for making an internally monounsaturated fatty alcohol sulfate, the process comprising reacting a terminally monounsaturated fatty alcohol with sulfur trioxide in a falling-film reactor, followed by neutralization.

45. The process of claim **44** wherein the monounsaturated fatty alcohol is metathesis-derived.

46. A dispersant for agricultural compositions comprising the derivative of claim **1**.

47. A dispersant for agricultural compositions comprising the ethoxylate sulfate of claim **9**.

48. A dispersant agricultural compositions comprising the composition of claim **29**.

49. A water-soluble herbicide composition comprising the derivative of claim **1**.

50. A water-soluble herbicide composition comprising the ethoxylate sulfate of claim **9**.

51. A water-soluble herbicide composition comprising the composition of claim **29**.

52. An anionic emulsifier for agricultural compositions comprising the derivative of claim **1**.

53. An anionic emulsifier for agricultural compositions comprising the ethoxylate sulfate of claim **9**.

54. An anionic emulsifier for agricultural compositions comprising the composition of claim **29**.

55. An aqueous hard-surface cleaner comprising the derivative of claim **1**.

56. An aqueous hard-surface cleaner comprising the ethoxylate sulfate of claim **9**.

57. An aqueous hard-surface cleaner comprising the composition of claim **29**.

58. A personal cleanser comprising the derivative of claim **1**.

59. A personal cleanser comprising the ethoxylate sulfate of claim **9**.

60. A personal cleanser comprising the composition of claim **29**.

61. A foamer, foam additive, or dispersant for use in gypsum, concrete, or fire-fighting applications comprising the derivative of claim **1**.

62. A foamer, foam additive, or dispersant for use in gypsum, concrete, or fire-fighting applications comprising the ethoxylate sulfate of claim **9**.

63. A foamer, foam additive, or dispersant for use in gypsum, concrete, or fire-fighting applications comprising the composition of claim **29**.

64. A gas well foamer for use in oilfield applications comprising the derivative of claim **1**.

65. A gas well foamer for use in oilfield applications comprising the ethoxylate sulfate of claim **9**.

66. A gas well foamer for use in oilfield applications comprising the composition of claim **29**.

67. A light-duty liquid detergent comprising the derivative of claim **1**, wherein the fatty alcohol composition is made by reducing a metathesis-derived C_{14}-C_{17} monounsaturated lower alkyl ester.

68. A light-duty liquid detergent comprising the ethoxylate sulfate of claim **9**, wherein the fatty alcohol composition is made by reducing a metathesis-derived C_{14}-C_{17} monounsaturated lower alkyl ester.

69. A light-duty liquid detergent comprising the composition of claim **29**, wherein the composition derives from a C_{14}-C_{17} monounsaturated alcohol.

70. A laundry detergent comprising the derivative of claim **1**.

71. A laundry detergent comprising the ethoxylate sulfate of claim **9**.

72. A laundry detergent comprising the composition of claim **29**.

73. A surfactant composition for use in enhanced oil recovery, comprising the derivative of claim **1**.

74. A surfactant composition for use in enhanced oil recovery, comprising the ethoxylate sulfate of claim **9**.

75. A surfactant composition for use in enhanced oil recovery, comprising the composition of claim **29**.

76. A surfactant composition for use in emulsion polymerization, comprising the derivative of claim **1**.

77. A surfactant composition for use in emulsion polymerization, comprising the ethoxylate sulfate of claim **9**.

78. A surfactant composition for use in emulsion polymerization, comprising the composition of claim **29**.