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(54) USE OF A PARTICULAR CARBOXYLIC AMINO ACID IN ORDER TO LIMIT THE FORMATION AND/OR AGGLOMERATION OF GAS HYDRATES

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(57) **ABSTRACT**

Provided is a process for limiting or preventing the formation and/or agglomeration of gas hydrates, comprising combining (1) a production fluid comprising an aqueous phase and one or more gasses and (2) at least one compound represented by formula (I) or a salt thereof as defined herein.

USE OF A PARTICULAR CARBOXYLIC AMINO ACID IN ORDER TO LIMIT THE FORMATION AND/OR AGGLOMERATION OF GAS HYDRATES

[0001] The present invention relates to the use of one or more carboxylic amino acids of particular structure for limiting, or even preventing, the formation and/or agglomeration of gas hydrates.

[0002] The present invention also relates to a process for limiting, or even preventing, the formation and/or agglomeration of gas hydrates, using such carboxylic amino acids.

[0003] Petroleum and/or gas and/or condensates are produced in various environments, and especially in offshore sites and/or in sites that are subject to cold meteorological periods, which leads to substantial cooling of the fluids produced on contact with the cold walls of the transportation pipes.

[0004] The term "fluids produced" means fluids comprising petroleum, gases, condensates, water and mixtures thereof.

[0005] For the purposes of the present invention, the term "petroleum" means crude oil, i.e. unrefined oil, originating from an oilfield.

[0006] For the purposes of the present invention, the term "gas" means crude natural gases, i.e. untreated gases, extracted directly from a gasfield, for instance hydrocarbons such as methane, ethane, propane or butane, hydrogen sulfide, carbon dioxide and other compounds that are gaseous under the exploitation conditions, and also mixtures thereof. The composition of the natural gas extracted varies considerably depending on the well. Thus, the gas may comprise gaseous hydrocarbons, water and other gases.

[0007] For the purposes of the present invention, the term "condensates" means hydrocarbons of intermediate density. The condensates generally comprise mixtures of hydrocarbons, which are liquid under the exploitation conditions.

[0008] It is known that these production fluids, or fluids produced, usually comprise an aqueous phase. The origin of this aqueous phase may be endogenous and/or exogenous to the underground reservoir containing the hydrocarbons, the exogenous aqueous phase generally originating from injection of water (injection water).

[0009] The depletion of the old sites discovered is nowadays leading the petroleum and gas industry to perform production, especially on new sites, often with increasingly great depths for the offshore sites and with ever more extreme meteorological conditions.

[0010] On offshore sites, the pipes for transporting the fluids produced, especially on the seabed, are increasingly deep, reaching depths where the seawater is at temperatures below 15° C., below 10° C., or even close or equal to 4° C.

[0011] Similarly, on sites located in certain geographical zones, the air or the surface water may be cold, typically below 15° C., or below 10° C. Now, at such temperatures, the fluids produced undergo substantial cooling during their transportation. This cooling may be further amplified in the case of stoppage or a slowdown in production, in which cases the contact time between the fluids produced and the cold walls of the pipe increases.

[0012] When the temperature of the fluids produced drops, the industry concerned with extracting these fluids is commonly confronted with the formation of clathrates, also known as hydrate crystals, gas hydrates or quite simply hydrates. The risk for the industry concerned with extracting these fluids and especially concerned with petroleum, gas and condensate extraction is proportionately greater the lower the temperature of the production fluids and the higher the pressure of these fluids.

[0013] These problems of formation and/or agglomeration of hydrates may also be encountered in drilling muds or in completion fluids, during a drilling operation or a completion operation.

[0014] These clathrates are solid crystals (similar to ice crystals) formed by water molecules, also referred to as the "receiver", around one or more gas molecules, also referred to as the "guests", such as methane, ethane, propane, butane, carbon dioxide or hydrogen sulfide.

[0015] The formation and growth of hydrate crystals, induced by a lowering of the temperature of the production fluids, which emerge hot from the geological reservoir which contains them and which enter a cold zone, may cause clogging or blocking of the production pipes, the hydrocarbon (petroleum, condensate or gas) transportation pipes, or gate valves, flap valves and other elements liable to become totally or at least partially blocked. These cloggings/blockages may lead to losses of production of petroleum, condensates and/or gas, entailing appreciable or even very substantial economic losses. The reason for this is that the consequence of these cloggings and/or blockages will be a decrease in the production flow rate, or even stoppage of the production unit. In the event of a blockage, the consequence of searching for the zone of the blockage and removal of said blockage will be a loss of time and of profit for this unit. These cloggings and/or blockages may also lead to malfunction in safety elements (for example safety gate valves).

[0016] To reduce, delay or inhibit the formation and/or agglomeration of hydrates, various solutions have already been proposed or envisaged. Among these, mention may be made especially of a first solution which consists in dehydrating the crude oil or the gas upstream of the zone of the pipe where the temperature promotes the formation of these hydrates. This solution is, however, difficult or even impossible to implement under satisfactory economic conditions.

[0017] A second approach, which is also very expensive, consists in maintaining the temperature of the pipe at a temperature above the temperature of formation and/or agglomeration of hydrates, at a given pressure.

[0018] A third approach, which is frequently used, consists in adding a thermodynamic anti-hydrate, for example methanol or glycol, to the fluids produced containing the water/guest gas mixture to shift the equilibrium temperature for the formation of hydrates. In order to obtain acceptable efficacy, about 30% by weight of alcohol, relative to the amount of water, is generally introduced. However, the toxicity of methanol and the large amount of alcohol used are increasingly leading industrialists to adopt a fourth approach.

[0019] This fourth solution consists in adding an additive in low dosage, known as a low dosage hydrate inhibitor (LDHI) into the fluids produced comprising the water/guest gas mixture. This additive is also known as an anti-hydrate and is introduced at a low dosage, generally between 1% and 4% by weight, relative to the weight of water, it being understood that larger or smaller amounts are, of course, possible. Two types of anti-hydrate additives are currently known: anti-agglomerants and kinetic anti-hydrates.

[0020] The formation of hydrates depends mainly on the temperature and the pressure, and also on the composition of the guest gas(es). To be able to compare the performance of additives, the notion of subcooling value is used. The subcooling (SC) value is thus defined as the difference between the temperature of the fluids produced (or exploitation temperature T) and the thermodynamic equilibrium temperature of formation of the hydrate crystals (Teq) for a given pressure and a given composition of the hydrate-forming gases and of the aqueous phase, according to the following equation: SC=T−Teq.

[0021] When the subcooling value is less than or equal to 0° C., there is a risk of formation of gas hydrate.

[0022] Kinetic anti-hydrates act on the seeding and growth of the hydrate crystals. They retard the formation of hydrates by several hours, or even several days.

[0023] However, this type of hydrate inhibitor acts with difficulty at subcooling (SC) values below −10° C. for a given pressure. In other words, the time for appearance of crystals under these conditions is short enough for them to appear and to increase the pressure loss in the petroleum and gas production fluid transportation pipes.

[0024] Conversely, anti-agglomerants do not inhibit the formation of hydrate crystals, but disperse them in the form of fine particles, known as a slurry, which consequently prevents their agglomeration. The hydrates thus dispersed give rise to less or even no clogging or blocking, as mentioned previously, thus limiting the loss of hydrocarbon production.

[0025] In contrast with kinetic anti-hydrates, anti-agglomerants make it possible to avoid the problems of blocking and/or clogging as mentioned previously at subcooling (SC) values of the order of −15° C. to −20° C. for a given pressure, but are less efficient or even lose their efficiency at even lower subcooling values.

[0026] For example, US 2012/0161070 proposes anti-agglomerant chemical compositions. However, the tests performed are limited to a subcooling value of −17° C. Furthermore, the synthesis of these surfactants requires four reaction steps, if the steps for obtaining the fatty amine from renewable starting materials consisting of fatty acid are also counted. Limiting the number of synthetic steps is important for limiting the cost, the losses of yield, the waste and the quality problems.

[0027] US 2012/0157351 also proposes anti-agglomerant chemical compositions. However, the tests performed are limited to a subcooling value of −17° C. and the other chemical compositions proposed are not efficient for dispersing hydrates with a subcooling value of −20° C.

[0028] Given the exploitation medium (oceans, seas), it is increasingly common for anti-agglomerants also to have to have low ecotoxicity, satisfactory biodegradability and low bioaccumulation. According to the recommendations of the CEFAS (Centre for Environment, Fisheries and Aquaculture Science) in accordance with the OSPAR (Oslo-Paris Commission), in order for an additive to be green, i.e. environmentally compatible, it needs to meet two of the following three conditions:

[0029] 1) have an ecotoxicity (LC50 (lethal effects) and EC50 (toxic effects)) of greater than 10 $mg \cdot L^{-1}$;

[0030] 2) have a biodegradability (OCDE 306) in marine medium of greater than 60%; and

[0031] 3) have a bioaccumulation (Log Pow) (OCDE 117) of less than or equal to 3 or its molar mass greater than 700 $g \cdot mol^{-1}$.

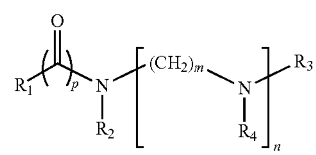
[0032] Other countries also impose two of these three conditions for additives used in petroleum and gas production, for instance corrosion inhibitors, kinetic anti-hydrates, anti-agglomerants, mineral deposit inhibitors, de-emulsifiers, deoilers, antifoam additives, paraffin inhibitors and dispersants, asphaltene inhibitors and dispersants, and hydrogen sulfide scavengers.

[0033] A real need consequently remains to develop an anti-agglomerant which is easy to manufacture in a low number of synthetic steps and readily industrializable, while at the same time complying with the recommendations of CEFAS or, at the very least, at least one (1), preferably at least two (2), more preferably three (3) of the environmental conditions mentioned above, and which is efficient for a subcooling value of less than or equal to −20° C., i.e. for a temperature difference between the extraction temperature, or exploitation temperature, and the thermodynamic equilibrium temperature at which hydrate crystals form, of less than or equal to −20° C.

[0034] The Proprietor has now discovered, surprisingly, that the use of one or more carboxylic amino acids of particular structure makes it possible to satisfy the objectives defined above.

[0035] A first subject of the present invention is thus the use of one or more compounds of formula (I), and salts thereof:

(I)



[0036] in which:

[0037] R_1 represents a linear or branched, saturated or unsaturated C_6 to C_{30} alkyl chain, said chain also possibly being interrupted with one or more hydrocarbon-based rings,

[0038] R_2 represents a hydrogen atom or a group —(CHR_a—CHR_b)—$COOR_5$, with R_a and R_b, which may be identical or different, representing, independently of each other, a hydrogen atom or a methyl group,

[0039] R_3 represents a hydrogen atom or a group —(CHR_a—CHR_b)—$COOR_6$, with R_a and R_b, which may be identical or different, representing, independently of each other, a hydrogen atom or a methyl group,

[0040] R_4 represents a hydrogen atom or a group —(CHR_a—CHR_b)—$COOR_7$, with R_a and R_b, which may be identical or different, representing, independently of each other, a hydrogen atom or a methyl group,

[0041] R_5, R_6 and R_7, which may be identical or different, represent, independently of each other, a hydrogen atom or a linear or branched, saturated or unsaturated C_1 to C_{12} alkyl chain,

[0042] it being understood that at least one of the radicals R_2, R_3 or R_4 comprises a carboxylic acid function (—COOH),

[0043] m represents an integer ranging from 1 to 6, and

[0044] n represents an integer ranging from 0 to 10, and

[0045] p is equal to 0 or 1 and preferably p is equal to 0,

[0046] for limiting, or even preventing, the formation and/or agglomeration of gas hydrates.

[0047] The use of the compound of formula (I) prevents or limits the agglomeration of gas hydrates and remains efficient for subcooling values of less than or equal to −20° C. It makes it possible especially to work at lower temperatures than the current temperatures while at the same time increasing the fluid hydrocarbon extraction yield, and to facilitate the completion or drilling at low temperatures and high pressures while limiting the impact on the environment.

[0048] The use of the compound of formula (I) also makes it possible to limit the concomitant use of corrosion inhibitor.

[0049] A subject of the present invention is also a process for limiting or even preventing the formation and/or agglomeration of gas hydrates, comprising a step of adding one or more compounds of formula (I) as defined above to a production fluid comprising an aqueous phase and one or more gases.

[0050] In the text hereinbelow, unless otherwise indicated, the limits of a range of values are included in that range, especially in the expressions "between" and "ranging from . . . to . . . ".

[0051] Other subjects, characteristics, aspects and advantages of the invention will become even more clearly apparent on reading the description and examples which follow.

[0052] The present invention also relates to the use of one or more compounds of formula (I), as defined previously, for limiting or even preventing the formation and/or agglomeration of gas hydrates.

[0053] Preferably, m is an integer ranging from 2 to 4, and more preferentially, m is equal to 2 or 3.

[0054] Preferably, n is an integer ranging from 0 to 4, and more preferentially, n is equal too, 1 or 2.

[0055] Preferably, all the radicals R_a and R_b are identical or different, and more preferentially, all the radicals R_a are identical and all the radicals R_b are identical. Better still, all the radicals R_a and R_b are identical and, entirely preferably, all the radicals R_a and R_b each represent a hydrogen atom.

[0056] According to a first preferred embodiment of the invention, p is equal to 0, R_2 represents a group —$(CH_2)_2$—$COOR_5$, R_3 represents a group —$(CH_2)_2$—$COOR_6$ and R_4 represents a group $(CH_2)_2$—$COOR_7$, with R_5, R_6 and R_7, which may be identical or different, representing, independently of each other, a hydrogen atom or a linear or branched, saturated or unsaturated C_1 to C_{12} alkyl chain, at least one of the radicals R_5, R_6 and R_7 representing a hydrogen atom.

[0057] More particularly, R_5, R_6 and R_7 are identical and each represent a hydrogen atom.

[0058] According to a second advantageous embodiment of the invention,

[0059] p is equal to 0, n is equal to 0,

[0060] R_1 represents a linear or branched, saturated or unsaturated C_8 to C_{18}, preferably C_{10} to C_{18} and more preferentially C_{12} to C_{18} alkyl chain,

[0061] R_2 represents a hydrogen atom,

[0062] R_3 represents a group —$(CHR_a$—$CHR_b)$—$COOR_6$, with R_a and R_b, which may be identical or different, representing, independently of each other, a hydrogen atom or a methyl group, R_a and R_b preferably being identical and each representing a hydrogen atom, and R_6 representing a hydrogen atom.

[0063] According to a third advantageous embodiment of the invention, p is equal to 0, n is equal to 0, R_1 represents a linear or branched, saturated or unsaturated C_8 to C_{18}, preferably C_{10} to C_{18} and more preferentially C_{12} to C_{18} alkyl chain,

[0064] R_2 represents a group —$(CHR_a$—$CHR_b)$—$COOR_5$, with R_a and R_b, which may be identical or different, representing, independently of each other, a hydrogen atom or a methyl group, R_a and R_b preferably being identical and each representing a hydrogen atom, and R_5 representing a hydrogen atom,

[0065] R_3 represents a group —$(CHR_a$—$CHR_b)$—$COOR_6$, with R_a and R_b, which may be identical or different, representing, independently of each other, a hydrogen atom or a methyl group, R_a and R_b preferably being identical and each representing a hydrogen atom, and R_6 representing a hydrogen atom.

[0066] According to one embodiment, when p is equal to 1, then R_2 represents a hydrogen atom and, preferably, n is other than zero (0).

[0067] According to a fourth advantageous embodiment of the invention, R_1 represents an alkyl chain, as defined above, i.e. a linear or branched, saturated or unsaturated 06 to 030 alkyl chain, interrupted with one or more —C(═O)—NH divalent groups, the divalent group preferably possibly not being in the end position of the alkyl chain. Preferably, the alkyl chain is interrupted with a —C(═O)—NH— divalent group.

[0068] The salts of the compounds of formula (I) that may be used according to the present invention may especially be carboxylate anions and/or cations on the nitrogen atom(s).

[0069] The counterions of these salts may be, for example and in a nonlimiting manner, alkali metal (for example sodium or potassium) ions, alkaline-earth metal (for example calcium or magnesium) ions, ammoniums, phosphoniums, halides (for example chloride, bromide or iodide), sulfate, hydrogen sulfate, mesylate, carboxylates, hydrogen carbonates, carbonates, phosphonates or phosphates.

[0070] The compounds of formula (I) that may be used in the context of the present invention are known and commercially available. Preferably, the compound of formula (I) may especially be N-cocoyl-β-aminopropanoic, N-cocoyl-β-aminodipropanoic, and mixtures thereof, N-tallow-β-aminopropanoic, N-tallow-β-aminodipropanoic, and mixtures thereof.

[0071] These compounds have the advantage of being readily synthesizable via procedures known to those skilled in the art, i.e. of being able to be obtained via a synthesis involving few steps.

[0072] The compound of formula (I) is used in an amount preferably ranging from 0.1% to 10% by weight, more preferentially from 0.3% to 8% by weight and better still from 0.4% to 4% by weight, relative to the total weight of the aqueous phase in a production fluid.

[0073] The content of aqueous phase may be measured on a sample of production fluid after decantation, according to the techniques known to those skilled in the art.

[0074] Preferably, the use according to the present invention limits or even prevents the formation and/or agglomeration of gas hydrates during the production of hydrocarbons, or during a drilling operation or during a completion operation.

[0075] More preferentially, the use according to the present invention limits or even prevents the formation and or agglomeration of gas hydrates in a process for extracting petroleum, condensates or gases, during drilling, the completion operation or during production.

[0076] The limitation or reduction, or even the prevention or blocking, of the formation of hydrates may be evaluated by means of the test described in the examples below.

[0077] Process for Limiting or Even Preventing the Formation and/or Agglomeration of Gas Hydrates

[0078] A subject of the present invention is also a process for limiting or even preventing the formation and/or agglomeration of gas hydrates, comprising a step of adding one or more compounds of formula (I) as defined above to a production fluid comprising an aqueous phase and one or more gases.

[0079] The total content of the aqueous phase present in the production fluid is generally between 10% and 90% by weight, relative to the total weight of the production fluid, i.e. relative to the total weight of the fluids.

[0080] The total content of aqueous phase defined above corresponds to the total proportion of aqueous phase initially present in the production fluid, i.e. in the initial mixture (aqueous phase and the other crude extraction liquids such as hydrocarbons, condensates, etc.).

[0081] The aqueous phase of the production fluid also comprises one or more dissolved gases that are capable of forming with water gas hydrates at a given temperature and pressure.

[0082] Some of the gases present in the aqueous phase of the production fluid are "guest" gases, as defined previously, and generally comprise methane, ethane, propane, butane, carbon dioxide, hydrogen sulfide, and mixtures thereof.

[0083] The compound of formula (I) is added in an amount preferably ranging from 0.1% to 10% by weight, more preferentially from 0.3% to 8% by weight and better still from 0.4% to 4% by weight, relative to the total weight of aqueous phase in the production fluid.

[0084] According to an advantageous embodiment, the compound of formula (I) is predissolved in a liquid chosen from water and organic solvents, and mixtures thereof.

[0085] Among the organic solvents that may be used, nonlimiting examples that may especially be mentioned include methanol, ethanol, isopropanol, n-butanol, isobutanol, 2-ethylhexanol, glycerol, ethylene glycol (or monoethylene glycol), 1,2-propylene glycol, 1,3-propylene glycol, hexylene glycol, butylglycol, ethylene glycol dibutyl ether, methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, N-methylpyrrolidone, cyclohexanone, xylenes, toluene, 1-octanol and 2-octanol, and mixtures of two or more thereof in all proportions.

[0086] According to another embodiment, one or more additives, which are well known to those skilled in the art, may be added. Such additives may be chosen, for example, in a nonlimiting manner, from anticorrosion agents, anti-paraffins, mineral deposition inhibitors, anti-asphaltenes, de-emulsifiers, surfactants and the like, and mixtures thereof, as described, for example, in U.S. Pat. No. 7,381,689 and WO 2014/0105764, including cationic surfactants, for instance quaternary alkyltrimethylammonium salts, quaternary alkyldimethylbenzylammonium salts, quaternary dialkyldimethylammonium salts, alkylimidazolinium salts, alkylamines and salts thereof, alkylamido(poly)amines and salts thereof, in which "alkyl-" denotes a hydrocarbon-based fatty chain (typically 8 to 30 carbon atoms).

[0087] When the compound of formula (I) is predissolved, it is advantageously present in an amount of greater than or equal to 10% by weight, more preferentially ranging from 15% to 75% by weight and better still ranging from 20% to 60% by weight, relative to the total weight of the solution.

[0088] The composition may be introduced into the production fluid continuously, discontinuously, regularly or irregularly, or temporarily, in one or more portions. The composition is generally introduced upstream of the zone at risk of the presence of hydrates, whether it be at the surface, at the well head or at the well bottom.

[0089] According to an advantageous embodiment, the fluid treated with the compound of formula (I) is a drilling mud or a completion fluid.

[0090] According to this embodiment, the composition is introduced into the drilling mud or into the completion fluid before or during the injection of the drilling mud or of the completion fluid.

[0091] The use according to the present invention especially has the advantage of using a compound of formula (I) that is relatively easy to synthesize. The compounds used in the context of the present invention also often have anticorrosion activity. As other advantages afforded by the present invention, mention may also be made of the fact that the anti-hydrates used satisfy at least one (1), preferably at least two (2) or even all three (3) environmental conditions mentioned previously, and especially a biodegradability of greater than 60% (OCDE 306), an ecotoxicity (LC50 or EC50) of greater than or equal to 10 mg·L-1, and also a bioaccumulation (log Pow) of less than or equal to 3 according to OCDE 117. In addition, the compounds used in the context of the present invention are efficient for a subcooling value of at least −20° C., better still of at least −22° C., or even below.

[0092] The invention will be understood more clearly in light of the examples that follow, which are given purely for illustrative purposes and which are not intended to limit the scope of the invention, defined by the attached claims.

EXAMPLES

[0093] In the examples that follow, all the amounts are indicated as weight percentages relative to the total weight of the composition, unless otherwise indicated.

Example 1: Anti-Agglomeration Test

[0094] The Compositions

[0095] The comparative compositions (A1 and A2) and the composition according to the invention (B1) were prepared from the ingredients whose contents are indicated as percentage of active material in the table below.

	Composition A1 (comparative)	Composition A2 (comparative)	Composition B1 (invention)
Amphoram ® CP1-MEG (1)	—	—	50
Noramium ® M2C (2)	50	—	—

-continued

	Composition A1 (comparative)	Composition A2 (comparative)	Composition B1 (invention)
Noramium ® M2SH [3]	—	50	—
Butyl glycol	50	50	50

[1] Amphoram ® CP1 (comprising N-cocoylamine, N-cocoyl-β-aminopropanoic and N-cocoyl-β-aminodipropanoic) as a mixture with monoethylene glycol (MEG) sold by CECA S.A.
[2] dicocoyldimethylammonium chloride, sold by CECA S.A.
[3] di-tallow-hydrogenodimethylammonium chloride, sold by CECA S.A.

[0096] The Protocol

[0097] The efficiencies of compositions A1, A2 and B1 as anti-agglomerants were determined on a model fluid representing a production fluid containing tetrahydrofuran (THF). THF hydrates form at atmospheric pressure and are regularly used for detecting the efficiency of compounds that are candidates as gas hydrate anti-agglomerants.

[0098] The model fluid comprises:

- **[0099]** 50% by weight of aqueous phase consisting of a mixture of demineralized water and tetrahydrofuran (THF) in a 1:1 ratio, and
- **[0100]** 50% by weight of isooctane.

[0101] The thermodynamic equilibrium temperature for hydrate formation of this model fluid is 2° C. at atmospheric pressure. In other words, the THF hydrates form at temperatures of less than or equal to 2° C.

[0102] The anti-agglomerant efficiency of the anti-hydrate compositions was measured at various subcooling values (−12° C. and −22° C.) and for various dosages. The dosage corresponds to the amount of anti-hydrate composition introduced into the aqueous phase of the production fluid.

[0103] The subcooling value represents the temperature difference between the exploitation, or imposed, temperature and the thermodynamic equilibrium temperature for hydrate formation of the production fluid. In other words, for a subcooling value of −12° C., the imposed temperature must be −10° C. Similarly, for a subcooling value of −22° C., the temperature must be −20° C.

[0104] The experimental device, described especially by M. L. Zanota (M. L. Zanota et al., Energy & Fuel, 2005, 19(2), (2005), 584-590), is composed of a motor which imposes an oscillating motion on a rack. The rack contains 12 borosilicate glass tubes 17 mm in diameter and 60 mm tall.

[0105] Each tube is closed and contains the mixture described above and also a 316L stainless-steel ball 0.8 cm in diameter. The ball allows the mixture to be stirred, allows the agglomeration of the hydrate crystals to be observed visually and constitutes a crystallization initiator.

[0106] The rack is immersed in a thermostatic bath, comprising a water/ethylene glycol mixture (1/1), the temperature of which varies between −30° C. and 30° C. by means of a Huber brand variostat.

[0107] The various samples are subjected to cooling and heating cycles governed by the programmable variostat. The temperature descent rates are defined and programmed. The variostat is equipped with two temperature probes, an internal one and an external one, connected to a computer allowing the temperature to be monitored and recorded by means of the Spy watch 1.1 software.

Dosage: 1% by Weight

[0108] The tubes were divided into four groups of three:

- **[0109]** Group 1 (control): aqueous mixture without additive
- **[0110]** Group 2 (comparative): aqueous mixture+1% by weight of composition A1, relative to the total weight of the aqueous phase,
- **[0111]** Group 3 (comparative): aqueous mixture+1% by weight of composition A2, relative to the total weight of the aqueous phase,
- **[0112]** Group 4 (invention): aqueous mixture+1% by weight of composition B1, relative to the total weight of the aqueous phase.

Dosage: 3% by Weight

[0113] The tubes were divided into four groups of three:

- **[0114]** Group 5 (control): aqueous mixture without additive
- **[0115]** Group 6 (comparative): aqueous mixture+3% by weight of composition A1 relative to the total weight of the aqueous phase
- **[0116]** Group 7 (comparative): aqueous mixture+3% by weight of composition A2 relative to the total weight of the aqueous phase
- **[0117]** Group 8 (invention): aqueous mixture+3% by weight of composition B1 relative to the total weight of the aqueous phase.

[0118] The tubes thus prepared are placed in the thermostatic bath at a temperature of 20° C. with stirring. The temperature is then lowered to −10° C., which corresponds to a subcooling value of −12° C. At this temperature, oscillation is maintained for 20 hours (the movement of the balls in the tubes is observed visually) before being stopped. After two hours of stoppage at −10° C., stirring is restarted, and the movement of the balls in the tubes is again observed.

[0119] The temperature is then lowered to −20° C. (again at a rate of −1° C. per minute), which corresponds to a subcooling value of −22° C. At this temperature of −20° C., oscillation is maintained for 20 hours before being stopped. After two hours of stoppage at −20° C., stirring is restarted, and the movement of the balls in the tubes is observed visually.

[0120] The efficiency of each of the compositions A1, A2 and B1 was then evaluated visually by observing the movement of the balls in the tubes. If the balls circulate, the test product is efficient. Conversely, if the balls remain blocked, or if hydrate crystals are stuck to the wall of the tube, the test product is not an efficient anti-agglomerant.

Results

[0121] The results for each of the groups described above are expressed in the table below:

TABLE 1

1% dosage				
	Number of balls blocked after 20 hours of stirring		Number of balls blocked after 2 hours of stoppage	
Subcooling value	−12° C.	−22° C.	−12° C.	−22° C.
Group 1 (control)	3/3	3/3	3/3	3/3
Group 2 (composition A1)	2/3	3/3	3/3	3/3

TABLE 1-continued

1% dosage				
	Number of balls blocked after 20 hours of stirring		Number of balls blocked after 2 hours of stoppage	
Subcooling value	−12° C.	−22° C.	−12° C.	−22° C.
Group 3 (composition A2)	2/3	3/3	3/3	3/3
Group 4(composition B1)	0/3	0/3	0/3	0/3

TABLE 2

3% dosage				
	Number of balls blocked after 20 hours of stirring		Number of balls blocked after 2 hours of stoppage	
Subcooling value	−12° C.	−22° C.	−12° C.	−22° C.
Group 5 (control)	3/3	3/3	3/3	3/3
Group 6 (composition A1)	1/3	3/3	2/3	3/3
Group 7 (composition A2)	0/3	3/3	1/3	3/3
Group 8 (composition B1)	0/3	0/3	0/3	0/3

[0122] The results of the above tables show that the compound of formula (I) leads to better anti-agglomeration properties than the compounds present in the comparative compositions (A1 and A2), irrespective of the dosage. Specifically, at a subcooling value of −12° C., after stoppage of the oscillation, and thus without stirring, the balls are free in the presence of the compound of the invention (groups 4 and 8), whereas they are blocked for the other comparative and control groups. Consequently, the hydrates formed are dispersed (in slurry form) in the presence of the compound of the invention, whereas they remain agglomerated in the presence of the comparative compounds.

Example 2: Ecotoxicity Tests

[0123] According to OCDE test 306 (marine medium), the composition of the invention (B1), comprising a compound of formula (I), has a biodegradability of 70%, i.e. greater than 60%. It is thus classified as "readily biodegradable". Its Log Pow measured according to OCDE 117 by HPLC is 2.93<3. Its Algal ecotoxicity is 2 $mg \cdot L^{-1}$.

[0124] The ecotoxicity data for composition B1 are collated in the table below.

Eco-toxicity data	Eco-toxicity (algae)	Eco-toxicity (fish)	Biodegrad-ability in marine medium (OCDE 306)	Bioaccumu-lation (Low Pow)
Composition B1	2 ($mg \cdot L^{-1}$)	3.9 ($mg \cdot L^{-1}$)	70%	2.93

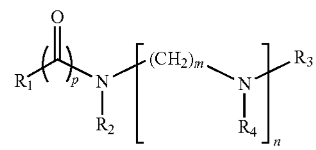
[0125] Composition B1 satisfies two of the conditions mentioned previously. Its biodegradability in marine medium is greater than 60% and its bioaccumulation is less than 3.

[0126] The use of composition B1 as defined previously is thus compatible with the environment. Conversely, Noramium® M2C and Noramium® M2SH are bioaccumulable and are not biodegradable. Their use is thus incompatible with the environmental standards in force.

1-11: (canceled)

12. A process for limiting or preventing the formation and/or agglomeration of gas hydrates, comprising combining (1) a production fluid comprising an aqueous phase and one or more gasses and (2) at least one compound represented by formula (I) or a salt thereof:

(I)



wherein

R_1 represents a linear or branched, saturated or unsaturated C_6 to C_{30} alkyl chain, wherein the alkyl chain is optionally interrupted with one or more hydrocarbon-based rings,

R_2 represents a hydrogen atom or a group —(CHR_a—CHR_b)—$COOR_5$, wherein R_a and R_b, which may be identical or different, represent, independently of each other, a hydrogen atom or a methyl group,

R_3 represents a hydrogen atom or a group —(CHR_a—CHR_b)—$COOR_6$, wherein R_a and R_b, which may be identical or different, represent, independently of each other, a hydrogen atom or a methyl group,

R_4 represents a hydrogen atom or a group —(CHR_a—CHR_b)—$COOR_7$, wherein R_a and R_b, which may be identical or different, represent, independently of each other, a hydrogen atom or a methyl group,

R_5, R_6 and R_7, which may be identical or different, represent, independently of each other, a hydrogen atom or a linear or branched, saturated or unsaturated C_1 to C_{12} alkyl chain,

wherein at least one of the radicals R_2, R_3 or R_4 comprises a carboxylic acid function (—COOH),

m represents an integer ranging from 1 to 6,

n represents an integer ranging from 0 to 10, and

p is 0 or 1.

13. The process of claim **12**, wherein

p is 0,

R_2 represents a group —$(CH_2)_2$—$COOR_5$,

R_3 represents a group —$(CH_2)_2$—$COOR_6$, and

R_4 represents a group —$(CH_2)_2$—$COOR_7$, wherein R_5, R_6 and R_7, which may be identical or different, represent, independently of each other, a hydrogen atom or a linear or branched, saturated or unsaturated C_1 to C_{12} alkyl chain, wherein at least one of the radicals R_5, R_6 and R_7 represents a hydrogen atom.

14. The process of claim **12**, wherein R_5, R_6 and R_7 each represent a hydrogen atom.

15. The process of claim **12**, wherein n is an integer ranging from 0 to 4.

16. The process of claim **12**, wherein

p is 0,

n is 0,

R_1 represents a linear or branched, saturated or unsaturated C_8 to C_{18} alkyl chain,

R_2 represents a hydrogen atom, and

R_3 represents a group —(CHR_a—CHR_b)—$COOR_6$, wherein R_a and R_b, which may be identical or different, represent, independently of each other, a hydrogen atom or a methyl group, and wherein R_6 represents a hydrogen atom.

17. The process of claim **12**, wherein

p is equal to 0 and

n is equal to 0,

R_1 represents a linear or branched, saturated or unsaturated C_8 to C_{18} alkyl chain,

R_2 represents a group —(CHR_a—CHR_b)—$COOR_5$, wherein R_a and R_b, which may be identical or different, represent, independently of each other, a hydrogen atom or a methyl group, and wherein R_5 represents a hydrogen atom, and

R_3 represents a group —(CHR_a—CHR_b)—$COOR_6$, wherein R_a and R_b, which may be identical or different, represent, independently of each other, a hydrogen atom or a methyl group, and wherein R_6 represents a hydrogen atom.

18. The process of claim **12**, wherein the formation and/or agglomeration of the gas hydrates is limited or prevented in a process for extracting petroleum, condensates or gas, during drilling, the completion operation or during production.

19. The process of claim **12**, wherein the compound represented by formula (I) is predissolved in a liquid chosen from water and organic solvents, and mixtures thereof.

20. The process of claim **19**, wherein the organic solvents are chosen from methanol, ethanol, isopropanol, n-butanol, isobutanol, 2-ethylhexanol, glycerol, ethylene glycol (or monoethylene glycol), 1,2-propylene glycol, 1,3-propylene glycol, hexylene glycol, butylglycol, ethylene glycol dibutyl ether, methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, N-methylpyrrolidone, cyclohexanone, xylenes, toluene, 1-octanol and 2-octanol, and mixtures of two or more thereof in all proportions.

21. The process of claim **19**, wherein the amount of the compound represented by formula (I) dissolved in the liquid is greater than or equal to 10%, relative to the total weight of the resulting solution.

22. The process of claim **12**, wherein the compound represented by formula (I) is combined with the production fluid in an amount ranging from 0.1% to 10% by weight, relative to the total weight of the aqueous phase of the production fluid.

23. The process of claim **12**, wherein the compound represented by formula (I) is combined with the production fluid in an amount ranging from 0.3% to 8% by weight, relative to the total weight of the aqueous phase of the production fluid.

24. The process of claim **12**, wherein the compound represented by formula (I) is combined with the production fluid in an amount ranging from 0.4% to 4% by weight, relative to the total weight of the aqueous phase of the production fluid.

25. The process of claim **12**, wherein the compound represented by formula (I) is in the form of a salt.

26. The process of claim **12**, wherein the proportion of the aqueous phase in the production fluid is from 10% to 90%, relative to the total weight of the production fluid.

27. The process of claim **12**, wherein the production fluid comprises at least one gas selected from the group consisting of methane, ethane, propane, butane, carbon dioxide, hydrogen sulfide, and mixtures thereof.

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