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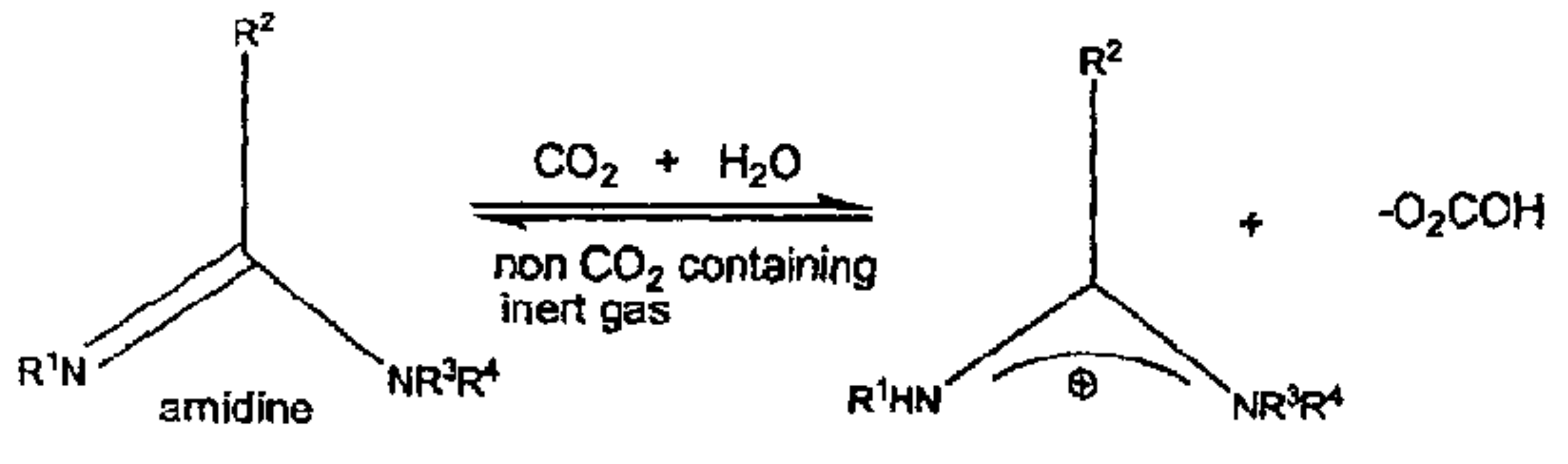
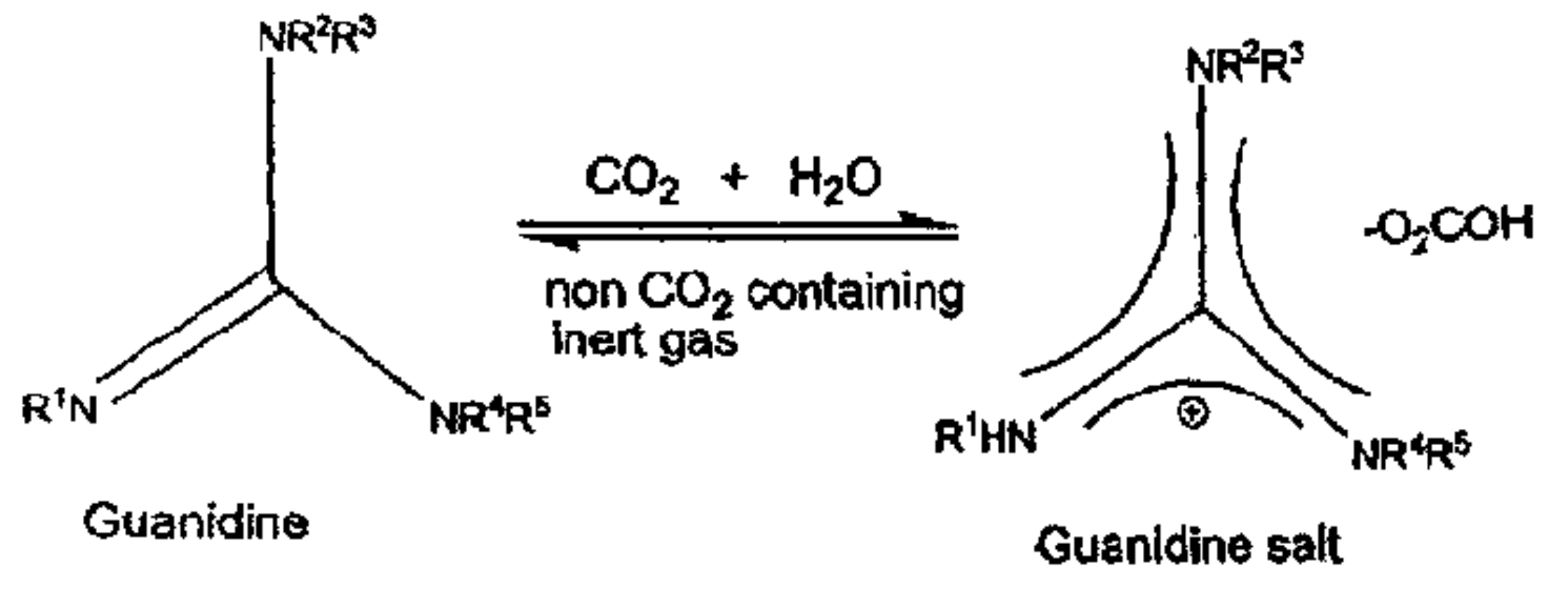
(54) **Titre :** SURFACTANTS REVERSIBLES, ET METHODES D'UTILISATION
(54) **Title:** REVERSIBLY SWITCHABLE SURFACTANTS AND METHODS OF USE THEREOF



(I)



(II)

$$R^1{-}NH_2 \underset{N_2}{\overset{CO_2}{\rightleftharpoons}} 1/2\,[R^1NH_3][R^1HNCO_2] \qquad \text{(III)}$$

$$R^1{-}NHR^2 \underset{N_2}{\overset{CO_2}{\rightleftharpoons}} 1/2\,[R^1NH_2R^2][R^1R^2NCO_2] \qquad \text{(IV)}$$

(57) **Abrégé/Abstract:**

A surfactant that reversibly converts to a non-surfactant upon contact with a gas containing substantially no carbon dioxide is described. The non-surfactant converts to the surfactant in the presence of carbon dioxide and water. The described compounds have at least one hydrophobic moiety, and either an amidine or guanidine moiety that converts to an amidinium or guanidinium bicarbonate salt, respectively, in the presence of water and carbon dioxide. Some embodiments require increased pressure to convert, others convert at 1 atmosphere.

ABSTRACT

A surfactant that reversibly converts to a non-surfactant upon contact with a gas containing substantially no carbon dioxide is described. The non-surfactant converts to the surfactant in the presence of carbon dioxide and water. The described compounds have at least one hydrophobic moiety, and either an amidine or guanidine moiety that converts to an amidinium or guanidinium bicarbonate salt, respectively, in the presence of water and carbon dioxide. Some embodiments require increased pressure to convert, others convert at 1 atmosphere.

Reversibly Switchable Surfactants and Methods of Use Thereof

FIELD OF THE INVENTION

The field of the invention is surfactants, and specifically surfactants that can be reversibly converted to a non-surfactant form.

BACKGROUND OF THE INVENTION

In some chemical and industrial processes it is desirable to create a stable emulsion of two immiscible liquids (e.g., water and oil). For example, in the field of oil drilling it is useful to force water into an underground space. In order to maximize the amount of oil recovered by this technique, surfactants are used and a stable emulsion is obtained. A surfactant is a molecule that has two portions: one portion is water-soluble (hydrophilic, lipophobic) while the other portion is oil-soluble (hydrophobic, lipophilic). Due to this property of dual solubility, surfactants are able to stabilize emulsions because they bridge the interface between the oil and the water.

Once placed in an oil and water mixture, a surfactant orients itself so that its water-soluble portion is surrounded by water molecules and its oil-soluble portion is surrounded by oil molecules. The mixture is therefore more likely to remain as an emulsion in the presence of a surfactant than it is to separate into its two distinct layers. Thus traditional surfactants are used to stabilize emulsions by preventing them from separating into distinct layers. Stable emulsions are desired in some industrial processes: however, once an emulsion is produced, it is often difficult to break it down and recover the immiscible liquids.

Surfactants are key to many industrial processes in manufacturing and in the energy industry. The careful design of surfactant molecules can greatly facilitate separation processes and thereby decrease the environmental impact of these processes. However, surfactants themselves may cause environmental damage when released to the environment. Even within industrial processes traditional surfactants may cause, rather than solve, separation problems when they stabilize unbreakable emulsions.

Emulsions that are stabilized by traditional surfactants require steps to break the emulsion down and capture the two distinct layers. In some cases, the process that is used to break down the emulsion irreversibly alters the traditional surfactant chemically and makes it ineffective as a surfactant for a second cycle in the process. Where the traditional surfactant is not altered in the emulsion break down process, the waste aqueous solution must be disposed of in a manner that prevents contamination of the environment by the surfactant. An example of the environmental damage that can be caused by surfactants is the reduction of surface tension in natural bodies of water. Even a small amount of surfactant that is released into natural waters will alter the surface tension of the water such that water bugs and mosquitoes are unable to walk upon it. The result is a lack of insects as food for fish and aquatic life, which can significantly alter the food chain.

Such disadvantages may be eliminated by the design and implementation of degradable surfactants. Degradable surfactants have been developed which are designed to degrade after release into the environment, for example, after prolonged exposure to sunlight. This degradation is slow and does not address the environmental contamination that occurs from the time of release to the time of the degradation.

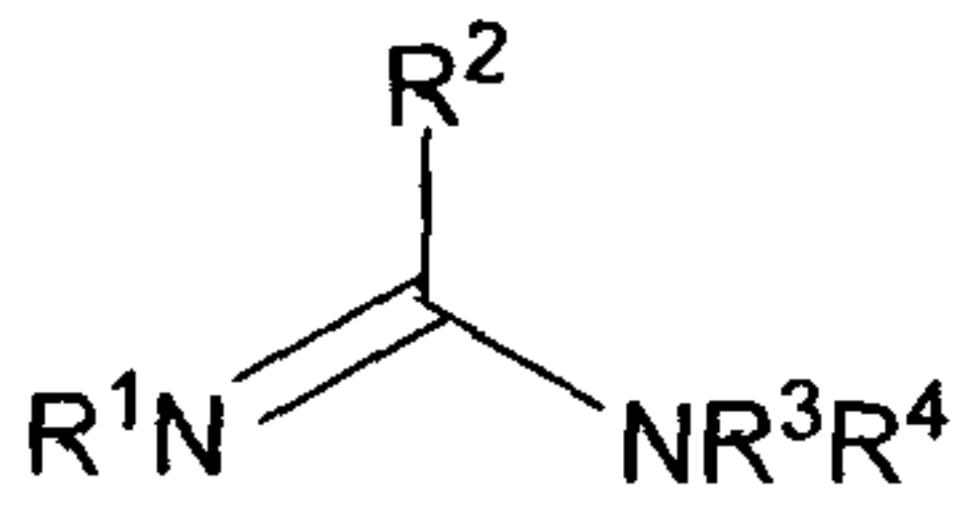
It is desirable to have compounds that act as a surfactant in one form, but can be chemically altered, by a trigger, into another form which does not have surfactant properties. An emulsion containing such a surfactant can be broken into its component layers by applying the appropriate trigger to turn off the surfactant. Some known controllable surfactants have cleavable portions. Thus, the trigger causes the surfactant to irreversibly fall apart into two or more fragments, where none of the fragments fulfill the role of the original molecule. The term "cleavable" is used to indicate such a molecule that is irreversibly changed into two or more fragments. These cleavable surfactants usually cleave slowly over time, and the triggers to cleave them are typically heat or acid. Cleavable surfactants are not suited to reuse or recycling since the cleaving reaction is irreversible.

Other controllable surfactants are "switchable surfactants". The term "switchable" is used to indicate a molecule that is *reversibly* changed when a trigger is applied. The switchable surfactant molecule's structure is thus changed to another structure with greatly reduced or even negligible surface activity. In order for the surfactant to be truly switchable, the non-surfactant form of the molecule must be convertible into the surface-active form by the application of another trigger or removal of the first trigger. Examples of known switchable surfactants are those switched on (forming the surfactant form) and off (forming the non-surfactant form) by triggers such as acid/base cycles, oxidation/reduction cycles, and photochemistry. The applications of these switchable surfactants are limited in some cases because of side reactions caused by the triggering agents. In the case of switchable surfactants that are used to stabilize emulsions, a photochemical switch is inefficient since the emulsions are usually cloudy and/or impermeable to light. Although a cloudy solution can be exposed to light, the photochemical reaction will be slow since the reaction will only occur where the light has effectively penetrated the solution. A further limitation of the known switchable surfactants is that a stoichiometric amount of acid/base or oxidizer/reducer is required which means a stoichiometric amount of toxic waste is produced and must be cleaned up before the waste can be safely released into the environment.

There is a need to have a surfactant that can effectively be reversibly converted between on and off forms using a non-toxic trigger. Such a surfactant would stabilize an emulsion when "on" and allow an emulsion to separate into its two phases when "off". Such a surfactant would be suited for recapture, and reuse.

SUMMARY OF THE INVENTION

In a first aspect, the invention provides a compound which reversibly converts to a salt upon contact with carbon dioxide in the presence of water, the compound having the general formula (I):



(I)

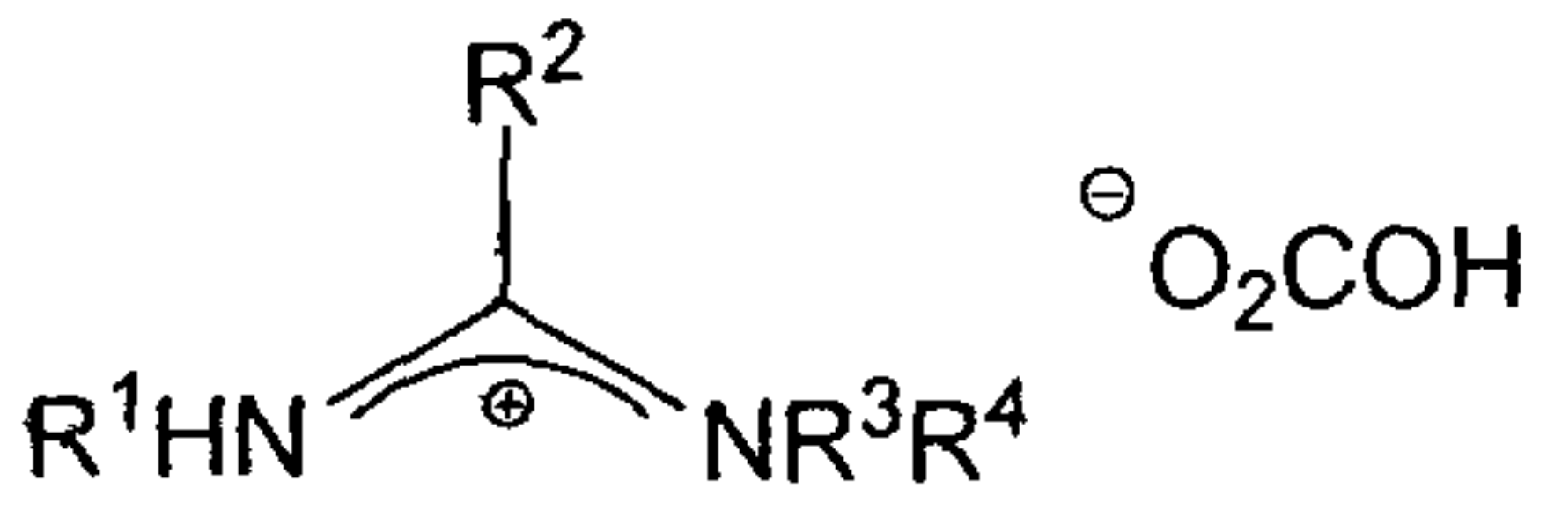
where at least one of R^1 R^2, R^3, and R^4 is a higher aliphatic/siloxyl moiety;

and the rest of R^1, R^2, R^3, and R^4 are selected from the group consisting of a C_1 to C_4 alkyl group, an Si_1 to Si_4 silyl group, and a C_nSi_m alkylsilyl group where n and m are numbers from 0 to 4 and n + m=4,

where the higher aliphatic/siloxyl moiety is a hydrocarbon and/or siloxyl moiety containing from C_{11} to C_{25} which is substituted or unsubstituted, and may optionally contain one or more $\{Si(CH_3)_2\text{-}O\}$ unit, an ether or ester linkage or both.

The compound may be a demulsifier in certain embodiments.

In a second aspect, the invention provides a surfactant which reversibly converts to a non-surfactant upon contact with a non-toxic gas that contains substantially no carbon dioxide, the surfactant having the general formula (IIa)



$$[R^1HN{\cdots}C(R^2){\cdots}NR^3R^4]^{\oplus}\ {}^{\ominus}O_2COH$$

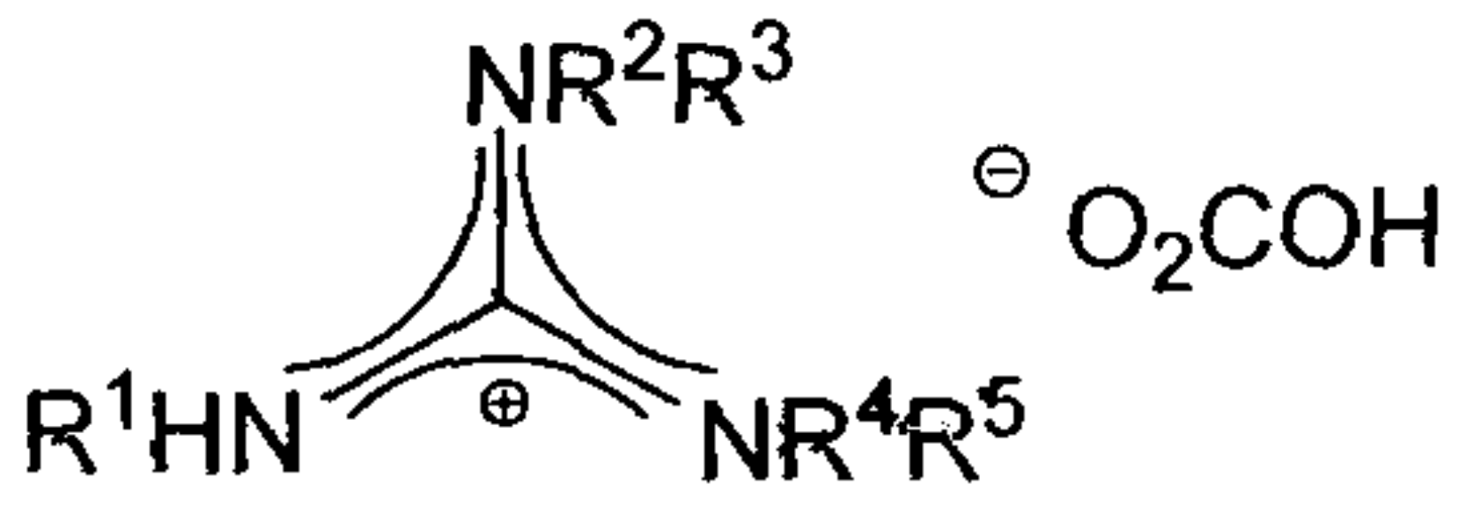
(IIa)

where at least one of R^1, R^2, R^3, and R^4 is a higher aliphatic/siloxyl moiety;

and the rest of R^1, R^2, R^3, and R^4 are selected from the group consisting of a C_1 to C_4 alkyl group, an Si_1 to Si_4 silyl group, and a C_nSi_m alkylsilyl group where n and m are numbers from 0 to 4 and n + m=4,

where the higher aliphatic/siloxyl moiety is a hydrocarbon and/or siloxyl moiety containing from C_{11} to C_{25} which is substituted or unsubstituted, and may optionally contain one or more $\{Si(CH_3)_2{-}O\}$ unit, an ether or ester linkage or both.

In a third aspect, the invention provides a surfactant which reversibly converts to a non-surfactant upon contact with a non-toxic gas that contains substantially no carbon dioxide, the surfactant having the general formula (IVa)



$$[R^1HN{\cdots}C(NR^2R^3){\cdots}NR^4R^5]^{\oplus}\ {}^{\ominus}O_2COH$$

(IVa)

where at least one of R^1, R^2, R^3, R^4, and R^5 is a higher aliphatic/siloxyl moiety;

and the rest of R^1, R^2, R^3, R^4, and R^5 are selected from the group consisting of a C_1 to C_4 alkyl group, an Si_1 to Si_4 silyl group, and a C_nSi_m alkylsilyl group where n and m are numbers from 0 to 4 and n + m=4,

where the higher aliphatic/siloxyl moiety is a hydrocarbon and/or siloxyl moiety containing from C_{11} to C_{25} which is substituted or unsubstituted, and may optionally contain one or more $\{Si(CH_3)_2\text{-}O\}$ unit, an ether or ester linkage or both.

In a fourth aspect, the invention provides a method for stabilizing an emulsion of two immiscible liquids comprising: combining the immiscible liquids to form a mixture; adding a compound of the first aspect to one of the liquids or to the mixture; exposing the mixture to carbon dioxide in the presence of water to convert the compound to a salt; and mixing the immiscible liquids vigorously to form a stable emulsion.

In a fifth aspect, the invention provides a method for stabilizing an emulsion of two immiscible liquids comprising: combining the immiscible liquids to form a mixture; adding to one of the liquids or to the mixture a surfactant of the second or third aspects or the neutral form of said surfactant; where the neutral form of said surfactant has been added in the prior step, exposing the mixture to carbon dioxide in the presence of water to convert said neutral form to the corresponding said surfactant; and mixing the immiscible liquids vigorously to form a stable emulsion.

In a sixth aspect, the invention provides, a method for separating two immiscible liquids from an emulsion which contains a surfactant of the second or third aspects, comprising: exposing the emulsion to a non-toxic gas that contains substantially no carbon dioxide to liberate carbon dioxide and convert the surfactant to a non-surfactant; wherein subsequent separation of the two immiscible liquids occurs.

The non-toxic gas that contains substantially no carbon dioxide may be selected from the group consisting of nitrogen, argon, and air that has had its carbon dioxide component substantially removed.

In a seventh aspect, the invention provides a method for separating two immiscible liquids from an emulsion which contains a surfactant of the second or third aspects, comprising: heating the emulsion to liberate carbon dioxide and convert the surfactant to a non-surfactant; wherein subsequent separation of the two immiscible liquids occurs.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1A depicts four schemes in which APSS molecule structures are shown in their non-surfactant (left) and surfactant (right) forms. The first scheme shows the conversion between amidine and amidinium bicarbonate according to the invention. The second scheme shows the conversion between guanidine and guanidinium bicarbonate according to the invention. The third scheme shows the conversion between primary long-chain amine and carbamate salt in which both anion and cation contain a long hydrophobic chain, according to the invention. The fourth scheme shows the conversion between secondary long-chain amine and carbamate salt in which both anion and cation contain a long hydrophobic chain.

Figure 1B depicts a scheme in which HPSS molecule structures are shown in their non-surfactant (left) and surfactant (right) forms.

Figure 1C shows the syntheses of APSS molecules N'-hexadecyl-N,N-dimethylacetamidine **1a** and N'-hexadecyl-N,N-dimethylacetamidinium bicarbonate **2a.**.

Figure 2 shows a plot of conductivity of a DMSO solution of **1a** at 23 °C as a function of time during three cycles of treatment with CO_2 followed by treatment with argon.

Figure 3 shows a plot of conductivity of aqueous solutions of **2a** as a function of concentration, wherein the break in the line indicates the critical micelle concentration.

Figure 4 shows examples of amidines of the invention.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, "aliphatic" refers to hydrocarbon moieties that are straight chain, branched or cyclic, may be alkyl, alkenyl or alkynyl, and may be substituted or unsubstituted. "Short chain aliphatic" refers to C_1 to C_4 aliphatic. "Long chain aliphatic" refers to C_5 to C_{25} aliphatic."

As used herein, "heteroatom" refers to non-carbon atoms, such as, for example, O, S, and N.

As used herein, "amidine" refers to a molecule with a structure $R^1N=C(R^2)-NR^3R^4$, where R^1 through R^4 are aliphatic or siloxyl or aliphatic/siloxyl as discussed below. The bicarbonate salt of such molecule is termed the "amidinium bicarbonate". It should be noted that amidine as used herein also includes the structure $R^1N{=}CH{-}NR^3R^4$ (i.e., R^2 is replaced by H), where R^1 and R^3, R^4 are as discussed below. As used herein, "guanidine" refers to a molecule with a structure $R^1N{=}C(NR^2R^3)(NR^4R^5)$ where R^1 through R^5 are aliphatic or siloxyl or aliphatic/siloxyl as discussed below. The bicarbonate salt of such molecule is termed the "guanidinium bicarbonate".

As used herein, "air that has had its carbon dioxide component substantially removed" means that the air has been depleted of carbon dioxide such that the remaining amount is insufficient to turn on a surfactant of the invention.

The invention provides a switchable surfactant that can be reversibly and readily switched between surfactant ("on") and non-surfactant ("off") forms by applying a non-hazardous trigger. A non-surfactant means a compound with little or no surface activity. The invention also provides a method for separating two immiscible liquids using a reversibly switchable surfactant. The invention further provides a method for maintaining an emulsion using a reversibly switchable surfactant. The surfactant may then be turned off and the immiscible liquids separated.

Referring to Figure 1A, four schemes are provided for atmospheric pressure switchable surfactants (APSS) according to the invention. Referring to Figure 1B, a scheme is provided for a high pressure-switchable surfactants (HPSS) according to the invention. Figure 1C shows the syntheses of APSS molecules N'-hexadecyl-N,N-dimethylacetamidine **1a** and N'-hexadecyl-N,N-dimethylacetamidinium bicarbonate **2a**.

Both APSS and HPSS of the invention use CO_2 in the presence of water as the trigger for switching on the surface activity, but differ in the pressure of CO_2 required and in the method for switching off the surface activity. The APSS molecules are able to react with CO_2 at 1 atm or less to produce the surfactant form. They are switched off by flushing the system with a non-toxic gas that is substantially free of CO_2 to remove the CO_2 from the system. Preferred gases that are substantially free of CO_2 include, for example, N_2 or air with the carbon dioxide removed, and argon. HPSS molecules require a greater pressure of CO_2 in order to become surfactants and are switched off by a reduction in CO_2 pressure to about 1 atm. HPSS embodiments may be more time efficient.

As shown in Figure 1A, APSS molecules include amidines, guanidines and primary and secondary amines, each with higher aliphatic/siloxyl portion(s) as discussed below. Such amidines or guanidines are preferably peralkylated. The term "peralkylated" means that the amidine or guanidine contains no N-H bonds. This lack of

N-H groups is to avoid irreversible reactions with carbon dioxide. As discussed below, preferred compounds of the invention do not contain reactive moieties such as, for example, halo groups and unsaturated bonds.

Compounds of the invention have at least one higher aliphatic (C_5-C_{25}) and/or siloxyl group that is soluble in the non-aqueous phase and a polar group which in the surfactant form is soluble in the aqueous phase. A siloxyl group contains $\{Si(CH_3)_2\text{-}O\}$ units. It should be understood that a compound of the invention may have a higher aliphatic/siloxyl group which is a combination of hydrocarbon and siloxyl units. The purpose of this group is to provide good solubility in the non-aqueous or hydrophobic phase. Accordingly, a compound having a long chain group including an ether moiety is also encompassed by the invention, as this "higher aliphatic/siloxyl group" still provides solubility in the non-aqueous or hydrophobic phase. In preferred embodiments, the higher aliphatic/siloxyl group is higher alkyl. This is because alkenyl and alkynyl groups may be undesirably reactive. The higher aliphatic/siloxyl group may be substituted with one or more moieties such as, for example, aryl, $Si(alkyl)_3$, phenyl, heteroaryl where the heteroatom is an oxygen, and alkoxy. Reactive substituents such as halo, amine, and -$N(alkyl)_2$ are not preferred, though, for example, a tertiary amino group is less reactive and could be a substituent in some embodiments. Hydrophilic substituents on the higher aliphatic/siloxyl group, such as, for example, OH, SH and COOH are also not preferred.

It is preferred that the compound of the invention have one higher aliphatic/siloxyl group, although it is expected that having two or three higher aliphatic/siloxyl moieties would still enable the compound to function in the intended way. In embodiments of amidines of the invention where there are two higher aliphatic/siloxyl groups, preferably they are R^1 and R^2, or R^2 and R^3, or R^1 and R^4, or R^3 and R^4. That is, hydrophobic portions of the molecule are sequestered together, and apart from hydrophilic portions of the molecule. Embodiments with three higher aliphatic/siloxyl groups preferably have the higher alkyl groups in the R^2, R^3 and R^4 positions. Similarly, sequestration of higher aliphatic/siloxyl groups applies to guanidine compounds of the invention.

The remaining R groups of the compounds of the invention that are not higher aliphatic/siloxyl are lower aliphatic/silyl groups, and are preferably small, non-polar and non-reactive. Examples of such groups include lower alkyl (C_1 to C_4) groups. Preferred examples of the lower aliphatic/silyl groups are CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$, $Si(CH_3)_3$, and phenyl; a methyl group is particularly preferred.

Syntheses of two amidine compounds of the invention, and demonstration of their properties are described and discussed in the working examples below. A similar guanidine compound was also synthesized, wherein R^1 was hexadecyl and the remaining R groups were methyl. However, during its separation, this compound formed an emulsion with organic solvent and water so work on it has not continued.

In certain embodiments, the invention provides a cleavable switchable surfactant including a sensitive functional group that can be cleaved by exposure of the surfactant to acid, base, ozone, or light.

In certain preferred embodiments of the APSS molecules, at least one aliphatic/siloxyl group includes a functionality such as an ester moiety, which allows the surfactant to be readily cleaved when in the environment. It should be understood that the non-carbonyl oxygen of the ester moiety should not be adjacent to nitrogen of the amidine or guanidine, to minimize undesirable reactivity. However, the ester moiety should not be spaced too far from the amidine or guanidine such that after the cleavage the amidine or guanidine is still able to act as a surfactant. Rather, the ester moiety should be spaced 1-3 carbons from the nitrogen.

Figure 1B shows an HPSS molecule (R^1-NR^2R^3), where R1 is higher aliphatic/siloxyl as defined above for APSS molecules. As a tertiary amine, the depicted HPSS molecule is somewhat less basic than the APSS molecules. This implies that an HPSS molecule requires higher CO_2 pressures to react and form the salt form (surfactant). Typical HPSS molecules are nitrogen-containing bases with basicities that are below those of the APSS molecules, but that are still sufficient to stabilize bicarbonate salts at elevated pressure. For example, alkyldimethylamines where the alkyl group is a long hydrophobic chain, are expected to have sufficient basicity. An HPSS tertiary amine has been synthesized where R^1 is dodecyl and R^2 and R^3 are both methyl, and is to be tested. It should be understood that the invention further encompasses amidine or guanidine compounds that have low basicities and react with CO_2 in the presence of water under high pressure (i.e., are HPSS compounds).

Although the requirement for high pressure in generation of an HPSS surfactant can be viewed as a disadvantage, the ability to switch off such a molecule rapidly by reduction of the CO_2 pressure may conversely be viewed as an advantage. For these reasons, the HPSS molecules may be particularly suited to EOR (or WAG) applications (discussed below), where elevated CO_2 pressure is used.

The invention provides non-surfactant compounds that react with CO_2 in the presence of water to generate bicarbonate or carbamate salts which are useful surfactants. One portion of the cation of the bicarbonate salt and both portions of the carbamate salt have a hydrophobic moiety; therefore due to the presence of both a charged portion and a hydrophobic portion, the salts have surface activity. Compounds of the invention may be added to the aqueous layer or the non-aqueous layer prior to mixing, or to the emulsion after mixing.

Carbon dioxide may be provided from any convenient source, for example, a vessel of compressed $CO_2(g)$ or as a product of a non-interfering chemical reaction. The surfactant can be converted to non-surfactant (or switched off) by exposing the mixture to an non-toxic gas that does not contain carbon dioxide. The non-toxic gas which does not contain carbon dioxide may be provided from any convenient source, for example, a vessel of compressed non-toxic gas (e.g. $N_2(g)$, air which has had its $CO_2(g)$ removed, Ar(g)) or as a product of a non-interfering chemical reaction. Conveniently, such exposure is achieved by bubbling the gas through the mixture. However, it is important to recognize that heating the mixture is an alternative method of driving off the CO_2, and this method of converting the surfactant to non-surfactant is also encompassed by the invention. In certain situations, especially if speed is desired, both bubbling and heat can be employed.

Reuse and recycling of surfactants of the invention are convenient, with attendant economic benefits. As depicted in Figure 2, the time required to switch between the surfactant and non-surfactant forms according to the invention is short. In certain applications, it may be advantageous to turn off the surfactant and then turn it back on again. For example, the surfactant could be turned on to stabilize an emulsion, and turned off to allow for separating and decanting of the hydrophobic and/or hydrophilic layers. In its non-surfactant form, the switchable surfactant will partition into the non-aqueous phase. Once the non-aqueous phase has been decanted, the surfactant can be isolated by adding fresh aqueous solution and converting the non-surfactant to its surfactant form. The newly formed surfactant will then partition into the aqueous phase. Thus the surfactant can be reused. In some embodiments it may be desirable to isolate the surfactant in its switched on form. This salt form would separate from aqueous solutions when turned off, allowing for easy recovery and reuse of the surfactant.

The invention provides a convenient system to control the presence or absence of a surfactant in a mixture such as an emulsion. Thus, it is useful in many industrial applications. In the oil and gas industry, where mixtures of crude oil or gas and water must be extracted from subterranean cavities, emulsions can first be stabilized with a surfactant of the invention. Subsequently, the emulsion can be conveniently and readily broken by bubbling the emulsion with an appropriate gas to turn off the surfactant. The use of switchable surfactants in enhanced oil recovery (EOR) could allow for simpler recovery of the emulsified oil at the production point. Oil field operations are used to dealing with CO_2 as a reagent, and some EOR processes (e.g. the water-alternating-gas or "WAG" process) use water, high pressure CO_2, and surfactants together (Schramm, L. L., Ed. Foams: Fundamentals and Applications in the Oil Industry; American Chemical Society: Washington, D.C., 1994 and Borchardt, J. K. In Kirk-Othmer Encyclopedia of Chemical Technology; 4th ed.; Kroschwitz, J. I., Howe-Grant, M., Eds.; Wiley: New York, 1996; Vol. 18, p 405). Emulsions in the product oil impede separation, a problem which could be eliminated by a reversibly switchable surfactant.

Reversibly switchable surfactants of the invention are well suited for controlling CO_2 hydrate formation in oil field and petroleum transport applications. Also, switchable surfactants are employable for deoiling and demulsification applications. For example, a high HLB reversibly switchable surfactant could be used to break water out of produced oil, and then switched off to avoid downstream problems (toxicity, biodegradability, and emulsification) with the recovered water. For such an application, a surfactant that does not switch on again upon exposure to air is preferred. An HPSS surfactant may be particularly suitable.

A switchable surfactant of the invention is employable in the inverse emulsion polymerization of water soluble polymers. This would allow manufacture of very high molecular weight polymers that could subsequently be recovered from the inverse emulsion and dried to produce a product (dry-form high MW or branched polymers) that could not be achieved in a solution polymerization process because of the tendency for such products to form gels. Low HLB (hydrophile/lipophile balance) switchable surfactants are preferred in this application, and the surfactant should not act as a chain-transfer agent.

The switchable surfactant system according to the invention can facilitate water/solid separations in mining. In mineral recovery, switchable surfactants may be suitable as flotation reagents which are mineral-specific agents that adsorb to the mineral particles to render them hydrophobic and therefore likely to float upon aeration. Flotation reagents designed on the basis of switchable surfactants could be recycled. Switchable surfactants of the invention can be useful in water/solvent separations in biphasic chemical reactions. An example is homogeneously-catalyzed catalysis in organic/aqueous mixtures. Initially, with the surfactant "switched on", a water-soluble homogeneous catalyst dissolved in water could be used to catalyze the hydrogenation or hydroformylation of organic substrates such as olefins in an immiscible organic phase. With appropriate agitation or shear to create an emulsion, the reaction should be fairly rapid. After the reaction is complete, the surfactant is switched off to break the emulsion, and then the two phases are separated. The surfactant, being at this point a nonpolar organic molecule, will be retained in the organic phase but can be readily precipitated from that solution by being switched back on again. The surfactant can then be recovered by filtration so that it can be reused and will not contaminate the product or waste streams.

Applications that may benefit from reversibly switchable surfactants include polymerization (see Example 10). Switchable surfactants of the invention can find use as transient antifoams in distillation columns, replacing traditional cationic surfactants.

Another application for reversibly switchable surfactants is protection and deprotection of nanoparticles. Nanoparticles and other materials are frequently temporarily protected during synthetic procedures by traditional surfactants. They could be more readily deprotected and cleaned if reversibly switchable surfactants were used. The switchable surfactants and methods of use thereof according to the invention can lessen environmental impact of industrial processes, both by saving energy normally expended during separations and by improving the purity of wastewater emitted from production facilities. The presence of a switchable surfactant in waste effluent could lead to significantly less environmental damage since effluent can be readily decontaminated by treatment with the appropriate trigger prior to its release into the environment.

WORKING EXAMPLES

Example 1. Synthesis of amidine compounds N'-hexadecyl-N,N-dimethylacetamidine (**1a**) **and** N'-dodecyl-N,N-dimethylacetamidine (**1b**).

N'-alkyl-N,N-dimethylacetamidines **1a** (N'-hexadecyl-N,N-dimethylacetamidine) and **1b** (N'-dodecyl-N,N-dimethylacetamidine) were synthesized by heating an equimolar amount of the appropriate long chain primary amine with dimethylacetamide dimethyl acetal for 10 - 20 min at 60 °C without solvent. Methanol, a byproduct, was removed by evaporation under high vacuum. The yield of the N'-alkyl-N,N-dimethylacetamidines was quantitative and was determined gravimetrically. The purity was 90% and was determined by ^{1}H NMR spectroscopy. The major impurity was N-alkyl-O-methylacetacetimidate (N-hexadecyl-O-methylacetacetimidate **3a,** and N-dodecyl-O-methylacetacetimidate,**3b**) as identified by ^{1}H NMR and gas chromatography/mass spectroscopy. Either the crude mixture of **1a** and **3a** or the crude mixture of **1b** and **3b** could be used as a reversibly switchable surfactant without further purification. However, a higher purity sample of the amidine **1a** or **1b** may be obtained by converting it to **2a** and **2b**, respectively, as described in the following Examples and reconverting it to **1a** or **1b** by suspending it in tetrahydrofuran and bubbling argon for 30 min at room temperature, and removing the tetrahydrofuran under reduced pressure.

N'-hexadecyl-N,N-dimethylacetamidine (**1a**): N'-hexadecyl-N,N-dimethylacetamidine: ^{1}H NMR (CDCl$_3$): 0.88 (t, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH$_2$CH$_3$), 1.28 (m, 26H, C$_{13}$H$_{26}$), 1.49 (quintet, $^{3}J_{HH}$ = 7.6, NCH$_2$CH$_2$C$_{14}$H$_{29}$), 1.87 (s, 3H, CCH$_3$), 2.87 (s, 6H, N(CH$_3$)$_2$), 3.17 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H, NCH$_2$). ^{1}H NMR (DMSO-d$_6$) 0.85 (t, $^{3}J_{HH}$ = 6.4Hz, 3H, CH$_2$CH$_3$), 1.24 (m, 26H, C$_{13}$H$_{26}$), 1.40 (quintet, $^{3}J_{HH}$ =6.8, NCH$_2$CH$_2$C$_{14}$H$_{29}$), 1.79 (s, 3H, CCH$_3$), 2.76 (s, 6H, N(CH$_3$)$_2$), 3.04 (t, $^{3}J_{HH}$ =6.8Hz, 2H, NCH$_2$). ^{1}H NMR (MeOD-d$_4$) 0.92 (t, $^{3}J_{HH}$ = 6.6Hz, 3H, CH$_2$CH$_3$), 1.32(m, 29H, C$_{13}$H$_{26}$, CCH$_3$), 1.51 (quintet, $^{3}J_{HH}$ =6.0, NCH$_2$CH$_2$C$_{14}$H$_{29}$), 2.98(s, 6H, N(CH$_3$)$_2$), 3.25 (t, $^{3}J_{HH}$ =6.4 Hz, 2H, NCH$_2$). ^{13}C NMR (CDCl$_3$): 12.4 , 14.1, 22.7, 27.6, 29.4,29.7,31.5, 31.9, 32.4, 38.0, 158.8. IR (neat): 721(w), 1008(m), 1187(w), 1343(m), 1464(m), 1629(s, ν(C=N)), 2825(s), 2923(s).

N'-dodecyl-N,N-dimethylacetamidine (**1b**): ^{1}H NMR (CDCl$_3$): 0.89 (t, $^{3}J_{HH}$ = 8.8 Hz, 3H, CH$_3$C$_{11}$H$_{22}$), 1.29 (m, 18H, CH$_3$C$_9$H$_{18}$CH$_2$CH$_2$N), 1.51 (quintet, $^{3}J_{HH}$ = 9.2Hz, 2H, CH$_3$C$_9$H$_{18}$CH$_2$CH$_2$N), 1.89 (s, 3H, CCH$_3$), 2.88 (s, 6H, N(CH$_3$)$_2$), 3.18 (t, $^{3}J_{HH}$ = 10Hz, 2H, C$_{11}$H$_{22}$CH$_2$N). ^{1}H NMR (DMSO-d$_6$) 0.86 (t, $^{3}J_{HH}$ = 8.8Hz, 3H, CH$_2$CH$_3$), 1.24 (m, 18H, C$_9$H$_{18}$), 1.40 (quintet, $^{3}J_{HH}$ =8.8, CH$_3$C$_9$H$_{18}$CH$_2$CH$_2$N), 1.79 (s, 3H, CCH$_3$), 2.76 (s, 6H, N(CH$_3$)$_2$), 3.04 (t, $^{3}J_{HH}$ = 8.8Hz, 2H, NCH$_2$). ^{1}H NMR (MeOD-d4) 0.92 (t, ^{3}JHH = 8.8Hz, 3H, CH2CH3), 1.31(m, 21H, C9H18,, CCH3), 1.49 (quintet, ^{3}JHH =8.8, CH$_3$C$_9$H$_{18}$CH$_2$CH$_2$N), 2.94(s, 6H, N(CH3)2), 3.22 (t, 3JHH =9.6Hz, 2H, NCH2). ^{13}C NMR (CDCl$_3$): 12.4, 14.1, 22.7, 27.6,29.4,29.7,31.9,32.4, 38.0, 50.2,158.8. IR (neat): 1010 (m), 1184 (m), 1343 (s), 1466 (m), 1630 (s, ν(C=N)).

Example 2. Synthesis and characterization of amidinium bicarbonates N'-hexadecyl-N,N-dimethylacetamidinium bicarbonate (**2a**) and N'-dodecyl-N,N-dimethylacetamidinium bicarbonate (**2b**)

Carbon dioxide gas was bubbled through a solution of the crude N'-alkyl-N,N-dimethylacetamidine in wet acetonitrile solution. The resulting white precipitate, the bicarbonate salt of the amidine, was obtained after filtration in a 98% yield.

N'-hexadecyl-N,N-dimethylacetamidinium bicarbonate (**2a**): ^{1}H NMR (MeOD-d_4) 0.92 (t, $^3J_{HH}$ = 6.6Hz, 3H, CH_2CH_3), 1.32(m, 29H, $C_{13}H_{26}$, CCH_3), 1.64 (quintet, $^3J_{HH}$ =6.6), 3.14(s, 3H, NCH_3), 3.27(s, 3H, NCH_3), 3.42 (t, $^3J_{HH}$ =7.2 Hz, 2H, NCH_2). IR (KBr): 837 (m, bicarbonate), 1257 (m), 1418 (m), 1644 (s, ν(C=N)). MS e/Z (High resolution): M+H$^+$ expected for $C_{20}H_{43}N_2$ 311.3426, observed 311.3414. MS e/Z (Electrospray anionic, low resolution): M expected for HCO_3^- 61.0, observed 60.6.

N'-dodecyl-N,N-dimethylacetamidinium bicarbonate (**2b**): ^{1}H NMR (MeOD-d4) 0.92 (t, ^{3}JHH = 6.4Hz, 3H, CH2C*H3*), 1.34(m, 29H, C13*H26,* CCH3), 1.64 (quintet, ^{3}JHH =6.8), 3.15(s, 3H, NC*H3*), 3.28(s, 3H, NC*H3*), 3.42 (t, ^{3}JHH =7 .2 Hz, 2H, NC*H2*) ^{13}C NMR (MeOD-d4) 13.0, 22.3, 26.2, 29.0, 29.2, 29.3, 29.7, 31.7, 44.5, 160.0, 164.6. IR (KBr): 833 (m, bicarbonate), 1007 (w), 1404 (m), 1651 (s, ν(C=N)). MS e/Z (low resolution): M expected for $C_{16}H_{35}N_2$ 255.5, observed 255.3. MS (ES anionic, low resolution): M expected for HCO_3^- 61.0, observed 61.2.

Example 3. Reversible conversion of amidine compounds N'-hexadecyl-N,N-dimethylacetamidine (**1a**) and N'-dodecyl-N,N-dimethylacetamidine (**1b**) **to surfactants**

To further confirm that amidines could be converted to amidinium bicarbonates by exposure to carbon dioxide in the presence of water, the following experiment was performed. Independently, two amidines, **1a** (see Figure 1C) and **1b**, were prepared and characterized. Each of **1a** and **1b** was placed in diethyl ether, the solution was bubbled with CO_2, and the resulting precipitate was isolated and characterized as amidinium bicarbonate salt (**2a, 2b**). Each of the bicarbonate salts was then reconverted into the amidine **1a, 1b** by bubbling argon through a solution of **2a, 2b** in toluene. The isolated reconverted **1a** and **1b** were characterized by ^{1}H NMR and IR spectroscopy (see Example 1).

The reversibility and repeatability of the conversion of **1a** to **2a** were confirmed by monitoring the conductivity using a JENWAY conductivity meter 4071 of a solution of **1a,**

2a in dimethylsulfoxide (DMSO) while carbon dioxide and then argon were bubbled through the solution for 3 cycles (see Figure 2).

Example 4. Thermogravimetric analysis of compound 2a

Thermogravimetric analysis (TGA) was used to determine the optimum temperature for driving off carbon dioxide from a solid sample of **2a**. A solid sample of **2a** showed TGA peaks at 62 °C (3% loss), 76 °C (further 12% loss) and 226 °C (almost complete loss). The first two peaks, which are partly merged, are consistent with water and CO_2 loss (expected 5% and 12% loss) respectively.

Example 5. Conductivity measurement of amidine compound 2a

The critical micelle concentration (CMC) for **2a** was determined from a plot of the conductivity of the compound in water as a function of concentration of compound **2a** which is Figure 3; the break in the line indicates a CMC of 0.23 mM.

The conductivity of compound **2a** (19.6 mM) in undried DMSO (5 mL) was measured using a JENWAY conductivity meter 4071. CO_2 gas was bubbled through the solution for 60 min at room temperature (23 °C), after which argon was bubbled through the solution for 65 min. The CO_2 and Ar treatments were each performed twice more as indicated in Figure 2.

Example 6. Solubilization of Nile Red by amidinium bicarbonate 2a

The following experiment was performed to study the use of a reversible switchable surfactant at atmospheric pressure to solubilize a hydrophobic dye, Nile Red. This experiment showed that compound **2a** was capable of acting as a surfactant and facilitated the dissolution in water of a dye that is not otherwise soluble in water. Following the solubilization, compound **2a** was converted to compound **1a** and the dye was observed to be insoluble in the water.

Distilled water (3.5 mL) was added to a glass vial at atmospheric pressure in open air. Nile Red (in excess) was added to the vial in solid form. The dark coloured Nile Red dye did not dissolve but remained in suspension in the clear colourless water. The vial containing the suspension was capped and vigorously shaken on a sonicating machine for 3 minutes, after which the contents appeared as a faint pink transparent suspension with dark flakes on the bottom and surface of the water. Compound **2a** (20 mg) was added and the vial containing the suspension was capped and shaken by hand for 30 seconds. The contents then appeared as a dark purple transparent solution with a small amount of undissolved Nile Red on the bottom and surface of the solution. The solution was allowed to stand overnight. The following morning, the dark purple solution remained unchanged in appearance. The solubilization of the Nile Red demonstrated the surfactant properties of compound **2a**.

The vial of purple solution was suspended in a water bath which was maintained at 75 °C and a stream of argon gas was bubbled through the hot solution for 3 hours. At the end of the 3 hours, the vial contents appeared as a clear colourless solution with dark coloured material floating on the top and lying on the bottom of the vial. Thus, compound **2a** was converted to compound **1a** under the influence of the heat and the argon stream. Since compound **1a** is a non-surfactant, the Nile Red precipitated out of solution and the water no longer appeared coloured.

EXAMPLE 7. Shake testing of the ability of amidinium bicarbonate 2a to stabilize a hexadecane/water emulsion

Whether or not the new compounds **2a** and **2b** are capable of stabilizing an emulsion was evaluated by automated shaking of mixtures of hexadecane and water containing **1a** (90 mg). Although an emulsion formed, it had clearly separated into two somewhat cloudy layers within 5 minutes after the cessation of shaking. However, if the mixture was treated with CO_2 before the shaking (i.e., **1a** was converted to **2a**), the emulsion was much more stable.

Specifically, hexadecane (4 mL), water (2 mL), and **1a** (90 mg) were combined in a septum-capped vial under CO_2. CO_2 gas was bubbled through the solution for 1 h. The flask was then shaken in a Retsch™ MM2 mixer mill (Retsch, Haan, Germany) at a speed setting of 100 for 10 min. The vial was then placed on a bench and photographed after various time intervals. After the photograph at 24 hours, the sample was flushed with argon at 65°C for 2 h.

Shake tests were also performed under argon instead of CO_2, using an otherwise identical method.

Although an emulsion formed prior to CO_2 treatment, it had clearly separated into two somewhat cloudy layers within 5 minutes after the cessation of shaking. However, when the solution was treated with CO_2 before the shaking, the emulsion was much more stable. It showed no evidence of separation for 3 h, at which point a thin layer of cloudy (but not frothy) liquid began to appear at the bottom of the flask. After 24 h, the thin cloudy layer had grown to 18% of the volume of the sample, while the emulsion still occupied 82% of the volume. Bubbling argon through the emulsion at 65°C resulted in an entirely clear separation of the hexadecane and water layers after 2 h; both layers were transparent, not cloudy.

EXAMPLE 8. Shake testing of the ability of amidinium bicarbonate 2a to stabilize a crude oil/water emulsion

Similar experiments to Example 7 were performed with crude oil. Crude oil (4 mL), when shaken for 10 minutes with water (2 mL) but without any additive, was able to form a fairly stable emulsion by itself. The same mixture of oil and water but additionally with surfactant compound **2a** also formed a fairly stable emulsion. However, the oil and water mixture under argon with non-surfactant **1a** added formed an unstable emulsion which separated into two layers within 30 minutes. The detailed procedure, including controls, follows.

i) Crude oil (4 mL), water (2 mL), and **1a** (90 mg) were combined in a septum-capped vial under CO_2. CO_2 gas was bubbled through the solution for 1 h, converting **1a** to **2a**. The flask was then shaken in a Retsch MM2 mixer mill at a speed setting of 100 for 10 min. The vial was then placed on a bench and photographed after various time intervals. The mixture formed a stable emulsion that showed no sedimentation for 2 h.

ii) Crude oil (4 mL), water (2 mL), and **1a** (90 mg) were combined in a septum-capped vial under Ar. Ar gas was bubbled through the solution for 1 h. The flask was then shaken in a Retsch MM2 mixer mill at a speed setting of 100 for 10 min. The vial was then placed on a bench and photographed after various time intervals. After 30 min, the emulsion had separated.

iii) Crude oil (4 mL) and water (2 mL) with no amidine were combined in a septum-capped vial under Ar. Ar gas was bubbled through the solution for 1 h. The flask was then shaken in a Retsch MM2 mixer mill at a speed setting of 100 for 10 min. The vial was then placed on a bench and photographed after various time intervals. The mixture formed a stable emulsion which showed no sedimentation for 6 h.

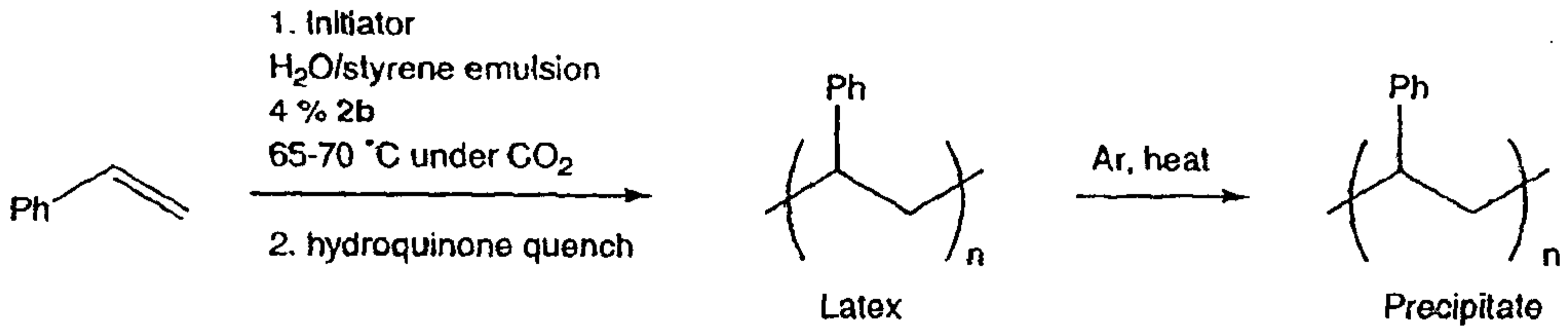
Example 9. Critical micelle concentration determination of amidinium bicarbonate 2a

The conductivity of various concentrations of **2a** in purified water (purified using a Millipore Simplicity™ water purification system capable of exceeding ASTM Type 1 quality standards) were measured using a JENWAY conductivity meter 4071 (Jenway, Barloworld Scientific Ltd, Essex, England), as shown in Figure 3. The CMC was taken to be the concentration at the breakpoint of the plot of conductivity versus concentration (Schultz, P.C.; Clausse, D.; *J. Chem. Ed.* **2003**, *80*, 1053).

Example 10. Emulsion polymerization of styrene in the presence of amidinium bicarbonate 2b

Emulsion polymerization using **2b** as a surfactant was successfully achieved. The thermally-initiated polymerization was performed in a styrene-in-water emulsion stabilized by **2b** under CO_2 for 5 h at 65-70 °C per the equation below. Specifically, CO_2 was bubbled through a stirred mixture of styrene (2 mL), water (8 mL) and **2b** (400 mg) for 30 min at room temperature. 2', 2'-azobis(2-methylpropinamidine) dihydrochloride (187 mg) was added. The mixture was heated to maintain a temperature between 65-70 °C and the bubbling of CO_2 was continued. After 5 h, several drops of hydroquinone solution (2% in water) were added to stop the reaction.

The particle size distribution was measured; the number-weighted mean diameter was 2.79 μm, the surface-weighted mean diameter was 7.90 μm, and the weight-weighted mean diameter was 17.0 μm. Switching compound **2b** to **1b** was effected by bubbling argon through the system at 65 °C, followed by cooling to room temperature, and allowing the latex (suitable for collection as the desired end product) to settle. The latex particles were identified as polystyrene by NMR spectroscopy. Without the argon treatment at 65 °C, the latex did not settle within an observation time period of 3 days.



The scope of the claims should not be limited by the preferred embodiments set forth in the examples, but should be given the broadest interpretation consistent with the description as a whole.

We claim:

1. A composition comprising:

(a) water or an aqueous solution;

(b) a switchable surfactant compound that comprises:

a hydrophobic portion, and

a nitrogen-containing salt portion comprising a protonated amidine moiety, a protonated guanidine moiety, or a protonated amine moiety, wherein said nitrogen-containing salt portion reversibly converts to a non-salt form upon contact with a source of heat and/or a non-toxic gas that is substantially free of carbon dioxide;

(c) a water immiscible liquid that is in a stable emulsion with said water or aqueous solution and forms an unstable emulsion or other two-phase mixture with said water or aqueous solution when the switchable surfactant compound is converted to the non-salt form, or

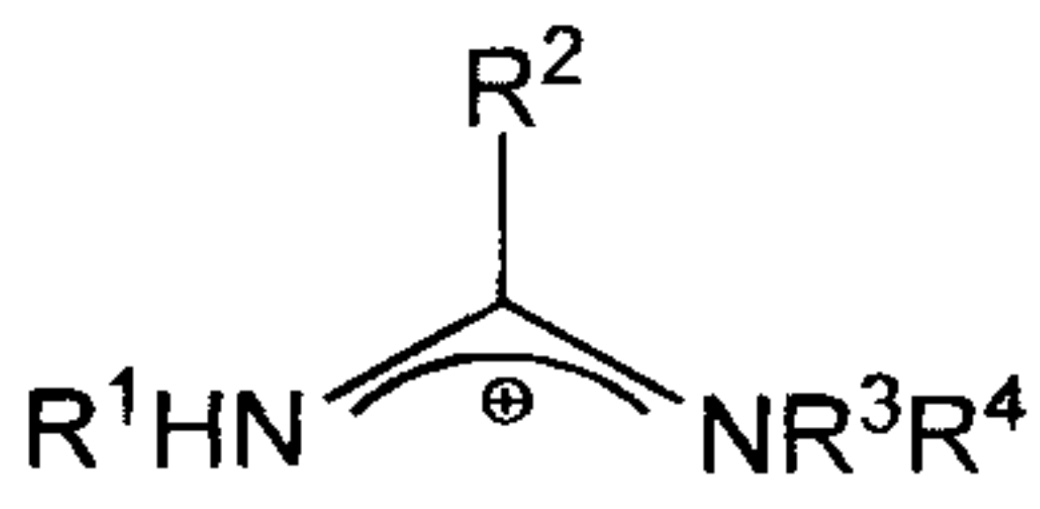
a water insoluble solid that is in a stable suspension with said water or aqueous solution and forms an unstable suspension or other two-phase mixture with said water or aqueous solution when the switchable surfactant compound is converted to the non-salt form; and

(d) dissolved CO_2.

2. The composition of claim 1, wherein component (c) is a water immiscible liquid that is in a stable emulsion with said water or aqueous solution and forms an unstable emulsion or other two-phase mixture with said water or aqueous solution when the switchable surfactant compound is converted to the non-salt form.

3. The composition of claim 1 or 2, wherein the nitrogen-containing salt portion comprises a protonated amidine moiety.

4. The composition of claim 3, wherein the protonated amidine moiety comprises the general formula (II):



(II)

wherein

at least one of R^1, R^2, R^3, and R^4 is a higher aliphatic/siloxyl moiety; and

the rest of R^1, R^2, R^3, and R^4 are selected from the group consisting of a C_1 to C_4 alkyl group, an S_1 to S_4 silyl group, and a C_nSi_m alkylsilyl group, where n and m are numbers from 0 to 4 and n + m = 4,

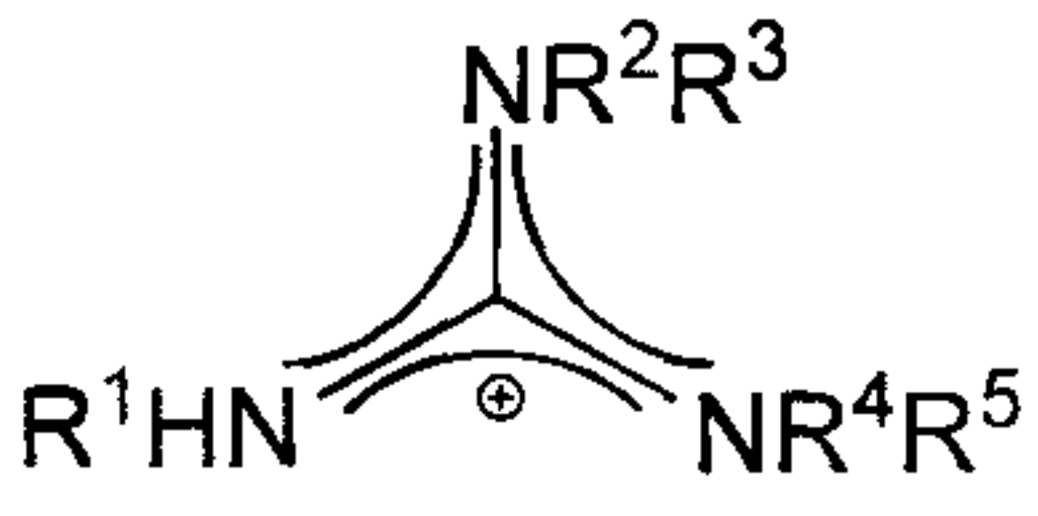
where the higher aliphatic/siloxyl moiety is a hydrocarbon and/or siloxyl moiety containing from C_5 to C_{25} which is substituted or unsubstituted, and may optionally contain one or more {$Si(CH_3)_2$-O} unit, an ether or ester linkage or both.

5. The composition of claim 4, wherein the higher aliphatic/siloxyl moiety is a hydrocarbon and/or siloxyl moiety containing from C_{11} to C_{25} which is substituted or unsubstituted, and may optionally contain one or more {$Si(CH_3)_2$-O} unit, an ether or ester linkage or both.

6. The composition of any one of claims 3 to 5, wherein the composition comprises N'-hexadecyl-N,N-dimethylacetamidinium bicarbonate or N'-dodecyl-N,N-dimethylacetamidinium bicarbonate.

7. The composition of claim 1 or 2, wherein the nitrogen-containing salt portion comprises a protonated guanidine moiety.

8. The composition of claim 7, wherein the protonated guanidine moiety comprises the general formula (IV):



(IV)

wherein

at least one of R^1, R^2, R^3, R^4, and R^5 is a higher aliphatic/siloxyl moiety; and the rest of R^1, R^2, R^3, R^4, and R^5 are selected from the group consisting of a C_1 to C_4 alkyl group, an S_1 to S_4 silyl group, and a C_nSi_m alkylsilyl group, where n and m are numbers from 0 to 4 and n + m = 4,

where the higher aliphatic/siloxyl moiety is a hydrocarbon and/or siloxyl moiety containing from C_5 to C_{25} which is substituted or unsubstituted, and may optionally contain one or more {$Si(CH_3)_2$-O} unit, an ether or ester linkage or both.

9. The composition of claim 8, wherein the higher aliphatic/siloxyl moiety is a hydrocarbon and/or siloxyl moiety containing from C_{11} to C_{25} which is substituted or unsubstituted, and may optionally contain one or more {$Si(CH_3)_2$-O} unit, an ether or ester linkage or both.

10. The composition of claim 1 or 2, wherein the nitrogen-containing salt portion comprises a protonated amine moiety.

11. The composition of claim 10, wherein the protonated amine moiety comprises the general formula (VI):

$$R^1\text{-}NHR^2R^{3\,+}$$

(VI)

wherein

at least one of R^1, R^2, and R^3 is a higher aliphatic/siloxyl moiety; and

the rest of R^1, R^2, and R^3 are selected from the group consisting of H, and lower aliphatic/silyl groups,

where the higher aliphatic/siloxyl moiety is a hydrocarbon and/or siloxyl moiety containing from C_5 to C_{25} which is substituted or unsubstituted, and may optionally contain one or more {$Si(CH_3)_2$-O} unit, an ether or ester linkage or both, and where the lower aliphatic/silyl group is a hydrocarbon and/or silyl moiety having a chain length of, or corresponding to, C_1 to C_4, which is substituted or unsubstituted.

12. The composition of claim 11, wherein the composition comprises a compound of formula (VIa):

$$[R^1\text{-}NH_2R^2]^+\ [R^1R^2NCO_2]^-$$

(VIa)

wherein

at least one of R^1 and R^2 is a higher aliphatic/siloxyl moiety as defined in claim 11, and

where only one of R^1 and R^2 is a higher aliphatic/siloxyl moiety, the other is selected from the group consisting of H, and lower aliphatic/silyl groups.

13. The composition of claim 11 or 12, wherein the higher aliphatic/siloxyl moiety is a hydrocarbon and/or siloxyl moiety containing from C_{11} to C_{25} which is substituted or unsubstituted, and may optionally contain one or more $\{Si(CH_3)_2\text{-}O\}$ unit, an ether or ester linkage or both.

14. The composition of claim 12 or 13, wherein the lower aliphatic/silyl groups are C_1-C_4 alkyl or $Si(CH_3)_3$.

15. The composition of claim 11, wherein the composition comprises a compound of formula (VIb):

$$[R^1\text{-}NHR^2R^3]^+ [O_2COH]^-$$

(VIb)

wherein

at least one of R^1, R^2, and R^3 is a higher aliphatic/siloxyl moiety as defined in claim 11; and

the rest of R^1, R^2, and R^3 are lower aliphatic/silyl groups.

16. The composition of claim 15, wherein the composition is maintained under an atmosphere of CO_2 at a pressure of greater than 1 atm.

17. The composition of claim 15 or 16, wherein the switchable surfactant compound reversibly converts to a non-salt form upon exposure to a pressure of carbon dioxide of 1 atm or less.

18. The composition of any one of claims 15 to 17, wherein the higher aliphatic/siloxyl moiety is a hydrocarbon and/or siloxyl moiety containing from C_{11} to C_{25} which is substituted or unsubstituted, and may optionally contain one or more $\{Si(CH_3)_2\text{-}O\}$ unit, an ether or ester linkage or both.

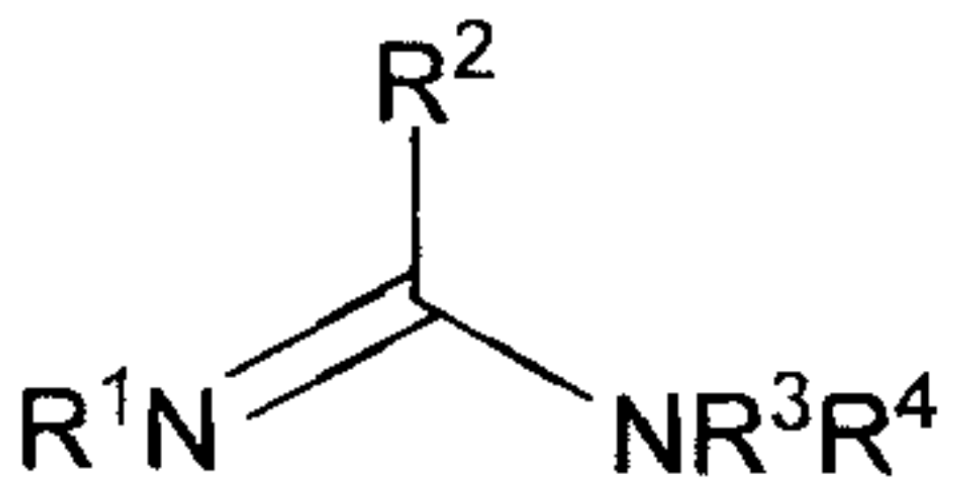
19. The composition of any one of claims 15 to 18, wherein the lower aliphatic/silyl groups are C_1-C_4 alkyl or $Si(CH_3)_3$.

20. The composition of any one of claims 1 to 19, wherein the non-toxic gas that is substantially free of carbon dioxide is nitrogen, air which has had its CO_2 (g) removed, or argon.

21. The composition of any one of claims 1 to 14, wherein the composition is maintained under an atmosphere of CO_2 at a pressure of 1 atm or less.

22. The composition of any one of claims 1 to 14, wherein the composition is maintained under an atmosphere of CO_2 at a pressure of greater than 1 atm.

23. A system for controlling presence and absence of a surfactant in a mixture comprising a compound which reversibly converts to a salt upon contact with carbon dioxide in the presence of water, the compound having the general formula (I):



(I)

wherein

at least one of R^1, R^2, R^3, and R^4 is a higher aliphatic/siloxyl moiety; and

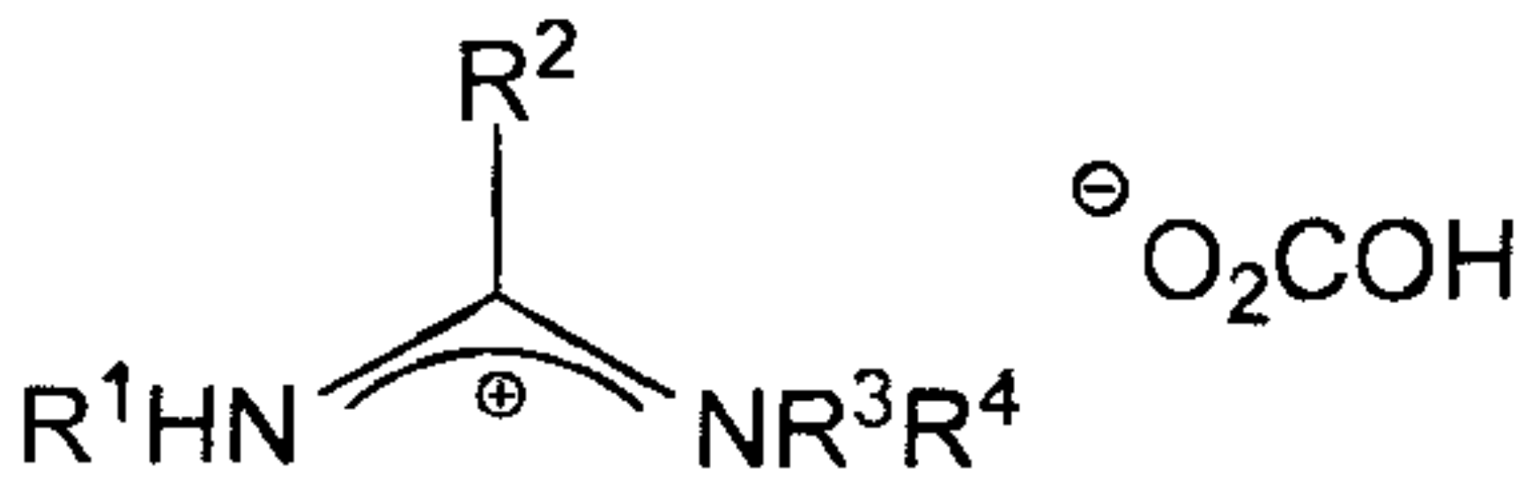
the rest of R^1, R^2, R^3, and R^4 are selected from the group consisting of a C_1 to C_4 alkyl group, an S_1 to S_4 silyl group, and a C_nSi_m alkylsilyl group, where n and m are numbers from 0 to 4 and n + m = 4,

where the higher aliphatic/siloxyl moiety is a hydrocarbon and/or siloxyl moiety containing from C_{11} to C_{25} which is substituted or unsubstituted, and may optionally contain one or more $\{Si(CH_3)_2\text{-}O\}$ unit, an ether or ester linkage or both,

wherein when the presence of surfactant is desired, the compound is exposed to carbon dioxide in the presence of water, resulting in protonation of the compound, and

wherein when the absence of surfactant is desired, any carbon dioxide in said mixture is at a level that is insufficient to convert the compound to or maintain the compound in surfactant form.

24. A system for controlling presence and absence of a surfactant in a mixture comprising a surfactant which reversibly converts to a non-surfactant upon contact with a source of heat and/or a non-toxic gas that is substantially free of carbon dioxide, wherein the surfactant is a compound having the general formula (IIa):



(IIa)

wherein

at least one of R^1, R^2, R^3, and R^4 is a higher aliphatic/siloxyl moiety; and

the rest of R^1, R^2, R^3, and R^4 are selected from the group consisting of a C_1 to C_4 alkyl group, an S_1 to S_4 silyl group, and a C_nSi_m alkylsilyl group, where n and m are numbers from 0 to 4 and n + m = 4,

where the higher aliphatic/siloxyl moiety is a hydrocarbon and/or siloxyl moiety containing from C_5 to C_{25} which is substituted or unsubstituted, and may optionally contain one or more $\{Si(CH_3)_2\text{-}O\}$ unit, an ether or ester linkage or both,

wherein when the presence of surfactant is desired, the mixture comprises carbon dioxide in the presence of water at a level sufficient to convert non-surfactant to surfactant and to maintain the surfactant, and

wherein when the absence of surfactant is desired, any carbon dioxide in the mixture is depleted so that the surfactant becomes deprotonated, resulting in said non-surfactant.

25. The system of claim 24, wherein when the presence of surfactant is desired, the mixture comprises carbon dioxide at a pressure of 1 atm or less.

26. The system of claim 24, wherein when the presence of surfactant is desired, the mixture comprises carbon dioxide at a pressure of greater than 1 atm.

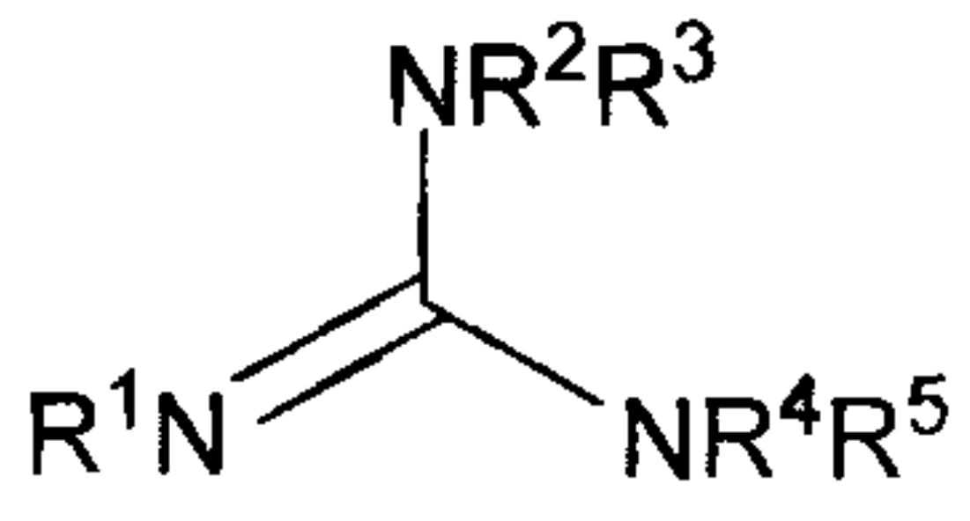
27. The system of claim 24, wherein the carbon dioxide is depleted by contacting the mixture with a source of heat and/or a non-toxic gas that is substantially free of carbon dioxide.

28. The system of claim 27, wherein the non-toxic gas that is substantially free of carbon dioxide is nitrogen, air which has had its CO_2 (g) removed, or argon.

29. The system of claim 23, wherein the compound of formula (I) is N'-hexadecyl-N,N-dimethylacetamidine or N'-dodecyl-N,N-dimethylacetamidine.

30. The system of claim 24, wherein the compound of formula (IIa) is N'-hexadecyl-N,N-dimethylacetamidinium bicarbonate or N'-dodecyl-N,N-dimethylacetamidinium bicarbonate.

31. A system for controlling presence and absence of a surfactant in a mixture comprising a compound which reversibly converts to a salt upon contact with carbon dioxide in the presence of water, the compound having the general formula (III):



(III)

wherein

at least one of R^1, R^2, R^3, R^4, and R^5 is a higher aliphatic/siloxyl moiety; and

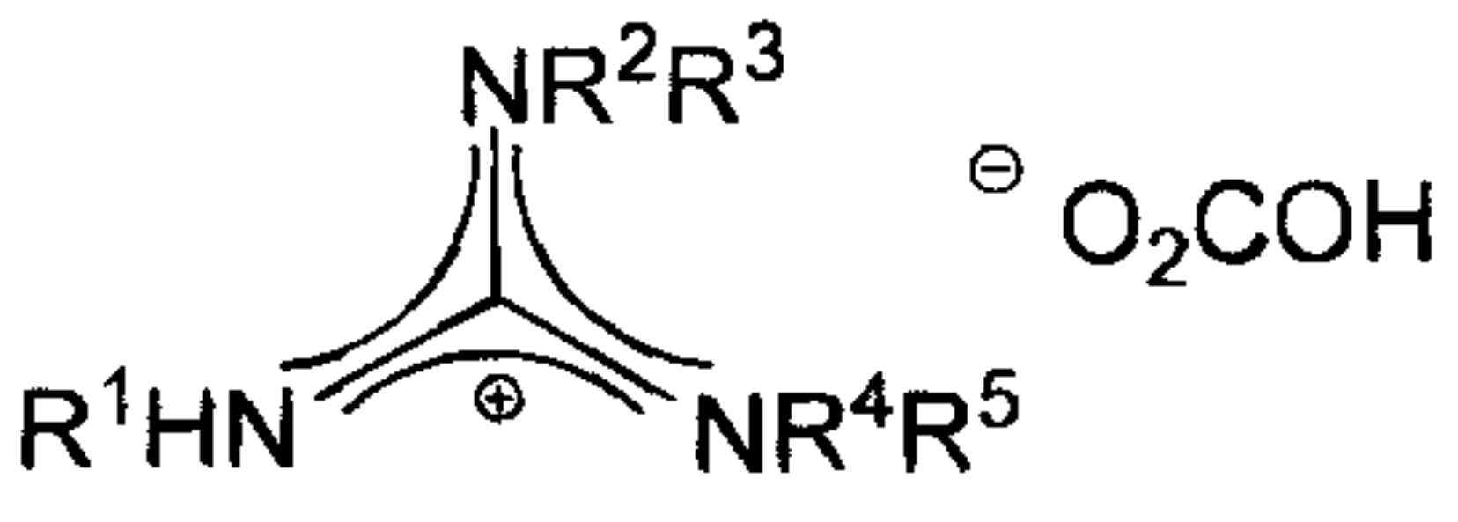
the rest of R^1, R^2, R^3, R^4, and R^5 are selected from the group consisting of a C_1 to C_4 alkyl group, an S_1 to S_4 silyl group, and a C_nSi_m alkylsilyl group, where n and m are numbers from 0 to 4 and n + m = 4,

where the higher aliphatic/siloxyl moiety is a hydrocarbon and/or siloxyl moiety containing from C_5 to C_{25} which is substituted or unsubstituted, and may optionally contain one or more $\{Si(CH_3)_2\text{-}O\}$ unit, an ether or ester linkage or both,

wherein when the presence of surfactant is desired, the compound is exposed to carbon dioxide in the presence of water, resulting in protonation of the compound, and

wherein when the absence of surfactant is desired, any carbon dioxide in said mixture is at a level that is insufficient to convert the compound to or maintain the compound in surfactant form.

32. A system for controlling presence and absence of a surfactant in a mixture comprising a surfactant which reversibly converts to a non-surfactant upon contact with a source of heat and/or a non-toxic gas that is substantially free of carbon dioxide, wherein the surfactant is a compound having the general formula (IVa):



(IVa)

wherein R^1, R^2, R^3, R^4, and R^5 are defined as in claim 31,

wherein when the presence of surfactant is desired, the mixture comprises carbon dioxide in the presence of water at a level sufficient to convert non-surfactant to surfactant and to maintain the surfactant, and

wherein when the absence of surfactant is desired, any carbon dioxide in the mixture is depleted so that the surfactant becomes deprotonated, resulting in said non-surfactant.

33. The system of claim 32, wherein when the presence of surfactant is desired, the mixture comprises carbon dioxide at a pressure of 1 atm or less.

34. The system of claim 32, wherein when the presence of surfactant is desired, the mixture comprises carbon dioxide at a pressure of greater than 1 atm.

35. The system of claim 32, wherein the carbon dioxide is depleted by contacting the mixture with a source of heat and/or a non-toxic gas that is substantially free of carbon dioxide.

36. The system of claim 35, wherein the non-toxic gas that is substantially free of carbon dioxide is nitrogen, air which has had its CO_2 (g) removed, or argon.

37. A system for controlling presence and absence of a surfactant in a mixture comprising a compound which reversibly converts to a salt upon contact with carbon dioxide in the presence of water, the compound having the general formula (V):

$$R^1\text{-}NR^2R^3$$

(V)

wherein

at least one of R^1, R^2, and R^3 is a higher aliphatic/siloxyl moiety; and

the rest of R^1, R^2, and R^3 are selected from the group consisting of H, and lower aliphatic/silyl groups,

where the higher aliphatic/siloxyl moiety is a hydrocarbon and/or siloxyl moiety containing from C_5 to C_{25} which is substituted or unsubstituted, and may optionally contain one or more $\{Si(CH_3)_2\text{-}O\}$ unit, an ether or ester linkage or both, and where the lower aliphatic/silyl group is a hydrocarbon and/or silyl moiety having a chain length of, or corresponding to, C_1 to C_4, which is substituted or unsubstituted,

wherein when the presence of surfactant is desired, the compound is exposed to carbon dioxide in the presence of water, resulting in protonation of the compound, and

wherein when the absence of surfactant is desired, any carbon dioxide in said mixture is at a level that is insufficient to convert the compound to or maintain the compound in surfactant form.

38. A system for controlling presence and absence of a surfactant in a mixture comprising a surfactant which reversibly converts to a non-surfactant upon contact with a source of heat and/or a non-toxic gas that is substantially free of carbon dioxide, wherein the surfactant is a compound having the general formula (VIa):

$$[R^1\text{-}NH_2R^2]^+ \, [R^1R^2NCO_2]^-$$

(VIa)

wherein

at least one of R^1 and R^2 is a higher aliphatic/siloxyl moiety as defined in claim 37, and

where only one of R^1 and R^2 is a higher aliphatic/siloxyl moiety, the other is selected from the group consisting of H, and lower aliphatic/silyl groups, and where the lower aliphatic/silyl group is a hydrocarbon and/or silyl moiety having a chain length of, or corresponding to, C_1 to C_4, which is substituted or unsubstituted,

wherein when the presence of surfactant is desired, the mixture comprises carbon dioxide in the presence of water at a level sufficient to convert non-surfactant to surfactant and to maintain the surfactant, and

wherein when the absence of surfactant is desired, the carbon dioxide in the mixture is depleted, resulting in conversion of surfactant to non-surfactant.

39. The system of claim 38, wherein when the presence of surfactant is desired, the mixture comprises carbon dioxide at a pressure of 1 atm or less.

40. The system of claim 38, wherein when the presence of surfactant is desired, the mixture comprises carbon dioxide at a pressure of greater than 1 atm.

41. The system of claim 38, wherein the carbon dioxide is depleted by contacting the mixture with a source of heat and/or a non-toxic gas that is substantially free of carbon dioxide.

42. The system of claim 41, wherein the non-toxic gas that is substantially free of carbon dioxide is nitrogen, air which has had its CO_2 (g) removed, or argon.

43. A system for controlling presence and absence of a surfactant in a mixture comprising a surfactant which reversibly converts to a non-surfactant upon contact with a source of heat and/or a non-toxic gas that is substantially free of carbon dioxide, wherein the surfactant is a compound having the general formula (VIb):

$$[R^1\text{-}NHR^2R^3]^+ \, [O_2COH]^-$$

(VIb)

wherein

at least one of R^1, R^2, and R^3 is a higher aliphatic/siloxyl moiety as defined in claim 37;

the rest of R^1, R^2, and R^3 are selected from the group consisting of lower aliphatic/silyl groups, where the lower aliphatic/silyl group is a hydrocarbon and/or silyl moiety having a chain length of, or corresponding to, C_1 to C_4, which is substituted or unsubstituted,

wherein when the presence of surfactant is desired, the mixture comprises carbon dioxide in the presence of water at a level sufficient to convert non-surfactant to surfactant and to maintain the surfactant, and

wherein when the absence of surfactant is desired, the carbon dioxide in the mixture is depleted, resulting in conversion of surfactant to non-surfactant.

44. The system of claim 43, wherein when the presence of surfactant is desired, the mixture comprises carbon dioxide at a pressure of greater than 1 atm.

45. The system of claim 43, wherein the carbon dioxide is depleted by reducing the pressure of carbon dioxide to 1 atm or less.

46. The system of any one of claims 37 to 45, wherein the lower aliphatic/silyl groups are C_1-C_4 alkyl or $Si(CH_3)_3$.

47. The system of claim 46, wherein the lower aliphatic/silyl groups are CH_3, CH_2CH_3, $CH(CH_3)_2$, or $C(CH_3)$.

48. Use of a compound of formula (I) as defined in claim 23 or 29 as a demulsifier.

49. Use of a compound of formula (III) as defined in claim 31 as a demulsifier.

50. Use of a compound of formula (V) as defined in claim 37 as a demulsifier.

51. Use of a compound of formula (IIa) as defined in claim 24 or 30 as a surfactant.

52. Use of a compound of formula (IVa) as defined in claim 32 as a surfactant.

53. Use of a compound of formula (VIa) as defined in claim 38 as a surfactant.

54. Use of a compound of formula (VIb) as defined in claim 43 as a surfactant.

55. A method for separating two immiscible liquids from an emulsion or a liquid and a solid from a suspension which emulsion or suspension contains a surfactant of formula (IIa) as defined in claim 24 or 30, comprising:

exposing the emulsion or suspension to heat and/or a non-toxic gas that is substantially free of carbon dioxide to liberate carbon dioxide and convert the surfactant to a non-surfactant;

wherein subsequent separation of said two immiscible liquids or said liquid and solid occurs.

56. A method for separating two immiscible liquids from an emulsion or a liquid and a solid from a suspension which emulsion or suspension contains a surfactant of formula (IVa) as defined in claim 32, comprising:

exposing the emulsion or suspension to heat and/or a non-toxic gas that is substantially free of carbon dioxide to liberate carbon dioxide and convert the surfactant to a non-surfactant;

wherein subsequent separation of said two immiscible liquids or said liquid and solid occurs.

57. A method for separating two immiscible liquids from an emulsion or a liquid and a solid from a suspension which emulsion or suspension contains a surfactant of formula (VIa) as defined in claim 38, comprising:

exposing the emulsion or suspension to heat and/or a non-toxic gas that is substantially free of carbon dioxide to liberate carbon dioxide and convert the surfactant to a non-surfactant;

wherein subsequent separation of said two immiscible liquids or said liquid and solid occurs.

58. The method of any one of claims 55 to 57, wherein the non-toxic gas that is substantially free of carbon dioxide is nitrogen, air which has had its CO_2 (g) removed, or argon.

59. A method for separating two immiscible liquids from an emulsion or a liquid and a solid from a suspension which emulsion or suspension contains a surfactant of formula (VIb) as defined in claim 43 and which is exposed to carbon dioxide at a pressure of greater than 1 atm, the method comprising:

reducing the pressure of carbon dioxide to 1 atm or less to convert the surfactant to a non-surfactant;

wherein subsequent separation of said two immiscible liquids or said liquid and solid occurs.

60. A method for stabilizing an emulsion of two immiscible liquids or a suspension of a liquid and a solid comprising:

combining said two immiscible liquids or said liquid and solid to form a mixture;

adding to one of the liquids or to the mixture a surfactant of formula (IIa) as defined in claim 24 or 30, or the neutral form of said surfactant;

where the neutral form of said surfactant has been added in the prior step, exposing the mixture to carbon dioxide in the presence of water so that the neutral form is converted to the corresponding said surfactant; and

agitating the mixture to form a stable emulsion or suspension.

61. A method for stabilizing an emulsion of two immiscible liquids or a suspension of a liquid and a solid comprising:

combining said two immiscible liquids or said liquid and solid to form a mixture;

adding to one of the liquids or to the mixture a surfactant of formula (IVa) as defined in claim 32, or the neutral form of said surfactant;

where the neutral form of said surfactant has been added in the prior step, exposing the mixture to carbon dioxide in the presence of water so that the neutral form is converted to the corresponding said surfactant; and

agitating the mixture to form a stable emulsion or suspension.

62. A method for stabilizing an emulsion of two immiscible liquids or a suspension of a liquid and a solid comprising:

combining said two immiscible liquids or said liquid and solid to form a mixture;

adding to one of the liquids or to the mixture a surfactant of formula (VIa) as defined in claim 38, or the neutral form of said surfactant;

where the neutral form of said surfactant has been added in the prior step, exposing the mixture to carbon dioxide in the presence of water so that the neutral form is converted to the corresponding said surfactant; and

agitating the mixture to form a stable emulsion or suspension.

63. The method of any one of claims 60 to 62, wherein the carbon dioxide is present at a pressure of 1 atm or less.

64. The method of any one of claims 60 to 62, wherein the carbon dioxide is present at a pressure of greater than 1 atm.

65. A method for stabilizing an emulsion of two immiscible liquids or a suspension of a liquid and a solid comprising:

combining said two immiscible liquids or said liquid and solid to form a mixture;

adding to one of the liquids or to the mixture a surfactant of formula (VIb) as defined in claim 43, or the neutral form of said surfactant;

where the neutral form of said surfactant has been added in the prior step, exposing the mixture to carbon dioxide at a pressure of greater than 1 atm in the presence of water so that the neutral form is converted to the corresponding said surfactant; and

agitating the mixture to form a stable emulsion or suspension.

66. A method of emulsion polymerization comprising the steps of:

combining a monomer, water, a surfactant of formula (IIa) as defined in claim 24 or 30, and a polymerization initiator in the presence of carbon dioxide;

agitating so that an emulsion is created;

exposing the emulsion to a non-toxic gas that is substantially free of carbon dioxide so that the surfactant is converted to a non-surfactant; and

isolating and collecting the polymer.

67. A method of emulsion polymerization comprising the steps of:

combining a monomer, water, a surfactant of formula (IVa) as defined in claim 32, and a polymerization initiator in the presence of carbon dioxide;

agitating so that an emulsion is created;

exposing the emulsion to a non-toxic gas that is substantially free of carbon dioxide so that the surfactant is converted to a non-surfactant; and

isolating and collecting the polymer.

68. A method of emulsion polymerization comprising the steps of:

combining a monomer, water, a surfactant of formula (VIa) as defined in claim 38, and a polymerization initiator in the presence of carbon dioxide;

agitating so that an emulsion is created;

exposing the emulsion to a non-toxic gas that is substantially free of carbon dioxide so that the surfactant is converted to a non-surfactant; and

isolating and collecting the polymer.

69. The method of any one of claims 66 to 68, wherein the carbon dioxide is present at a pressure of 1 atm or less.

70. The method of any one of claims 66 to 68, wherein the carbon dioxide is present at a pressure of greater than 1 atm.

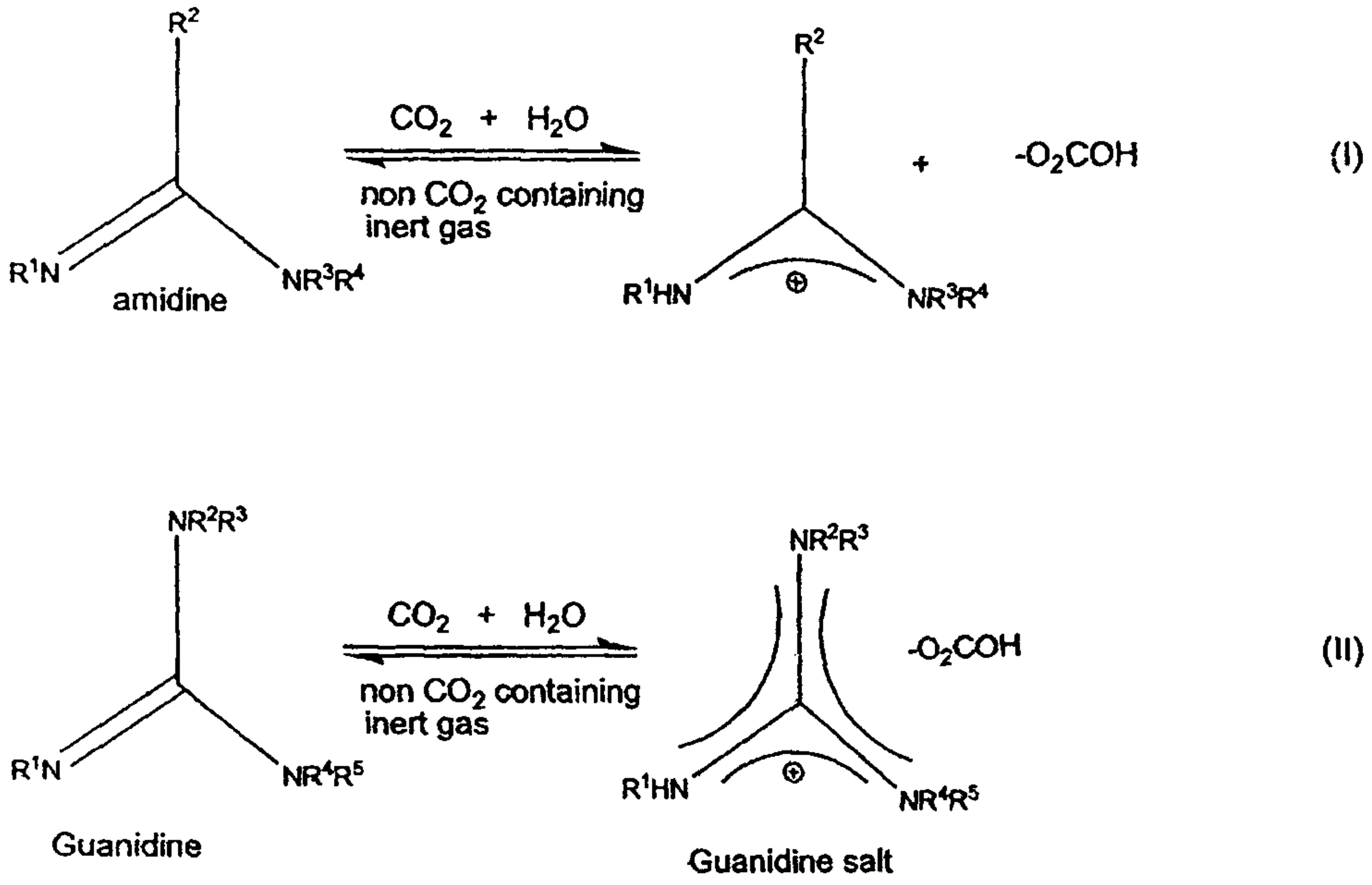
71. A method of emulsion polymerization comprising the steps of:

combining a monomer, water, a surfactant of formula (VIb) as defined in claim 43, and a polymerization initiator in the presence of carbon dioxide at a pressure of greater than 1 atm;

agitating so that an emulsion is created;

reducing the pressure of carbon dioxide to 1 atm or less so that the surfactant is converted to a non-surfactant; and

isolating and collecting the polymer.



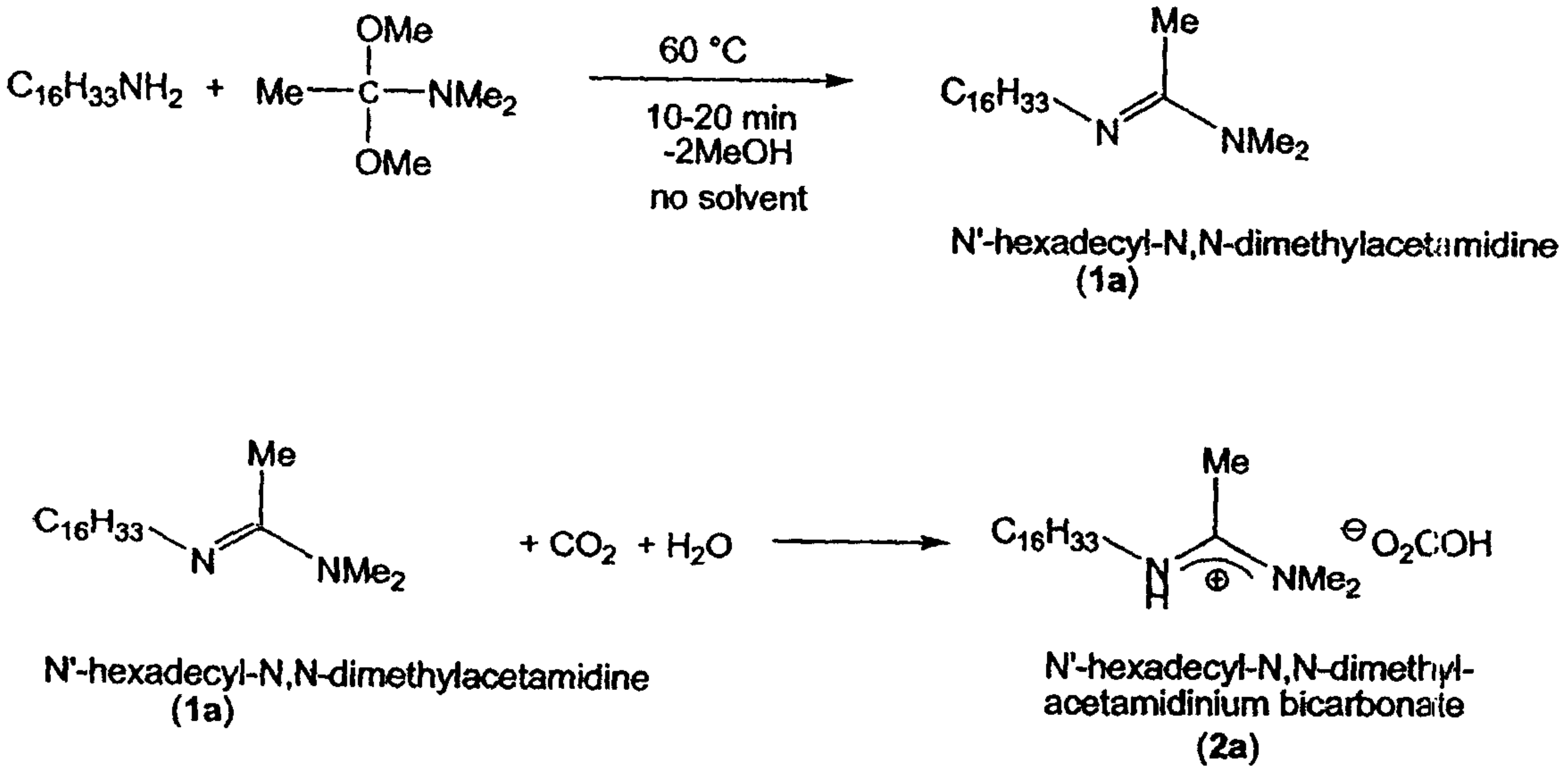
$$R^1\text{—}NH_2 \underset{N_2}{\overset{CO_2}{\rightleftharpoons}} 1/2\ [R^1NH_3][R^1HNCO_2] \qquad (III)$$

$$R^1\text{—}NHR^2 \underset{N_2}{\overset{CO_2}{\rightleftharpoons}} 1/2\ [R^1NH_2R^2][R^1R^2NCO_2] \qquad (IV)$$

Figure 1A

$$R^1\text{-}NR^2R^3 \xrightleftharpoons[\text{lower } P_{CO2}]{H_2O\text{, higher } P_{CO2}} [R^1\text{-}NHR^2R^3][O_2COH]$$

Figure 1B



N'-hexadecyl-N,N-dimethylacetamidine
(1a)

N'-hexadecyl-N,N-dimethylacetamidine
(1a)

N'-hexadecyl-N,N-dimethyl-acetamidinium bicarbonate
(2a)

Figure 1C

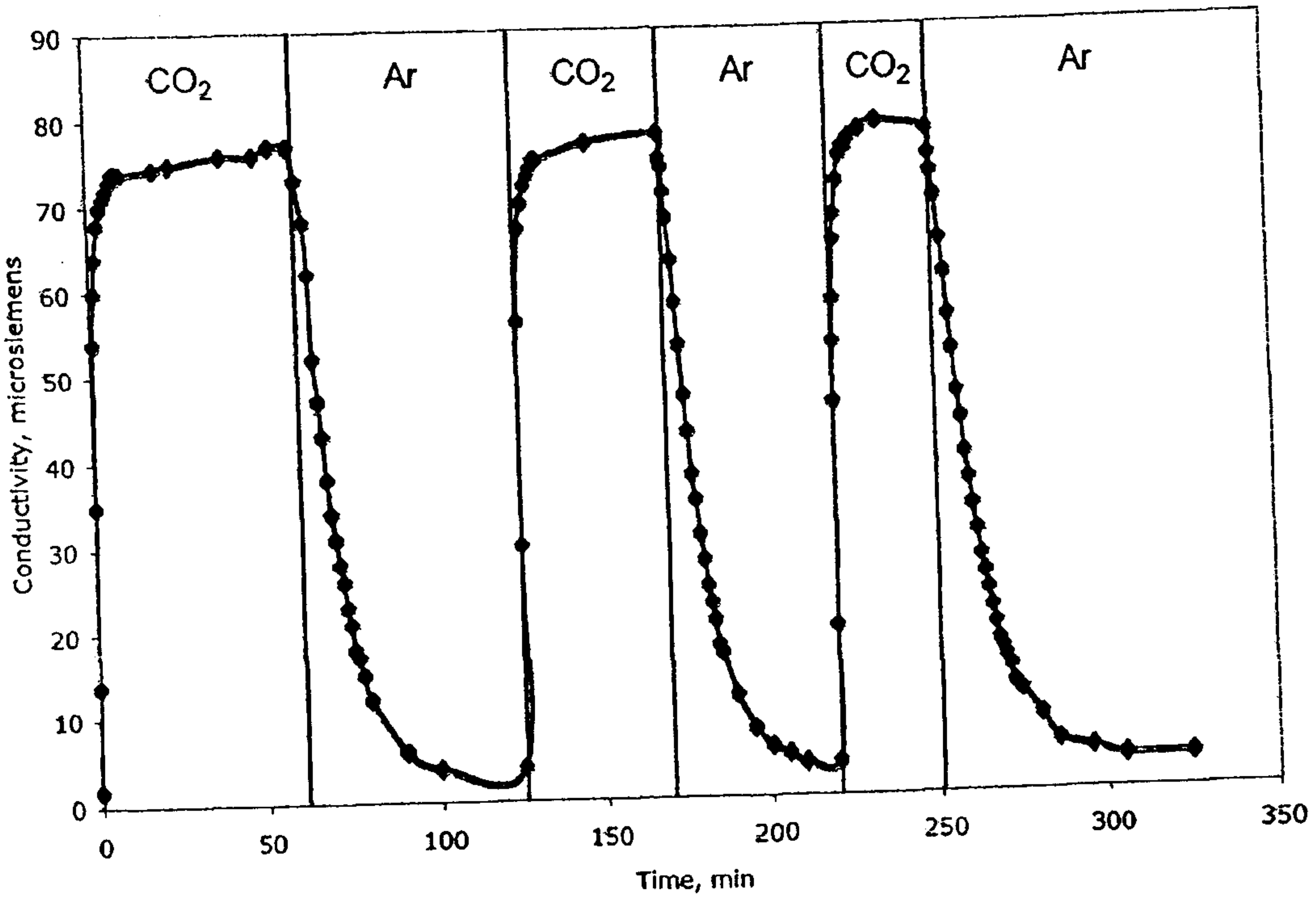

CO$_2$
Ar
CO$_2$
Ar
CO$_2$
Ar
90
80
70
60
50
40
30
20
10
0
Conductivity, microsiemens
0
50
100
150
200
250
300
350
Time, min

Figure 2

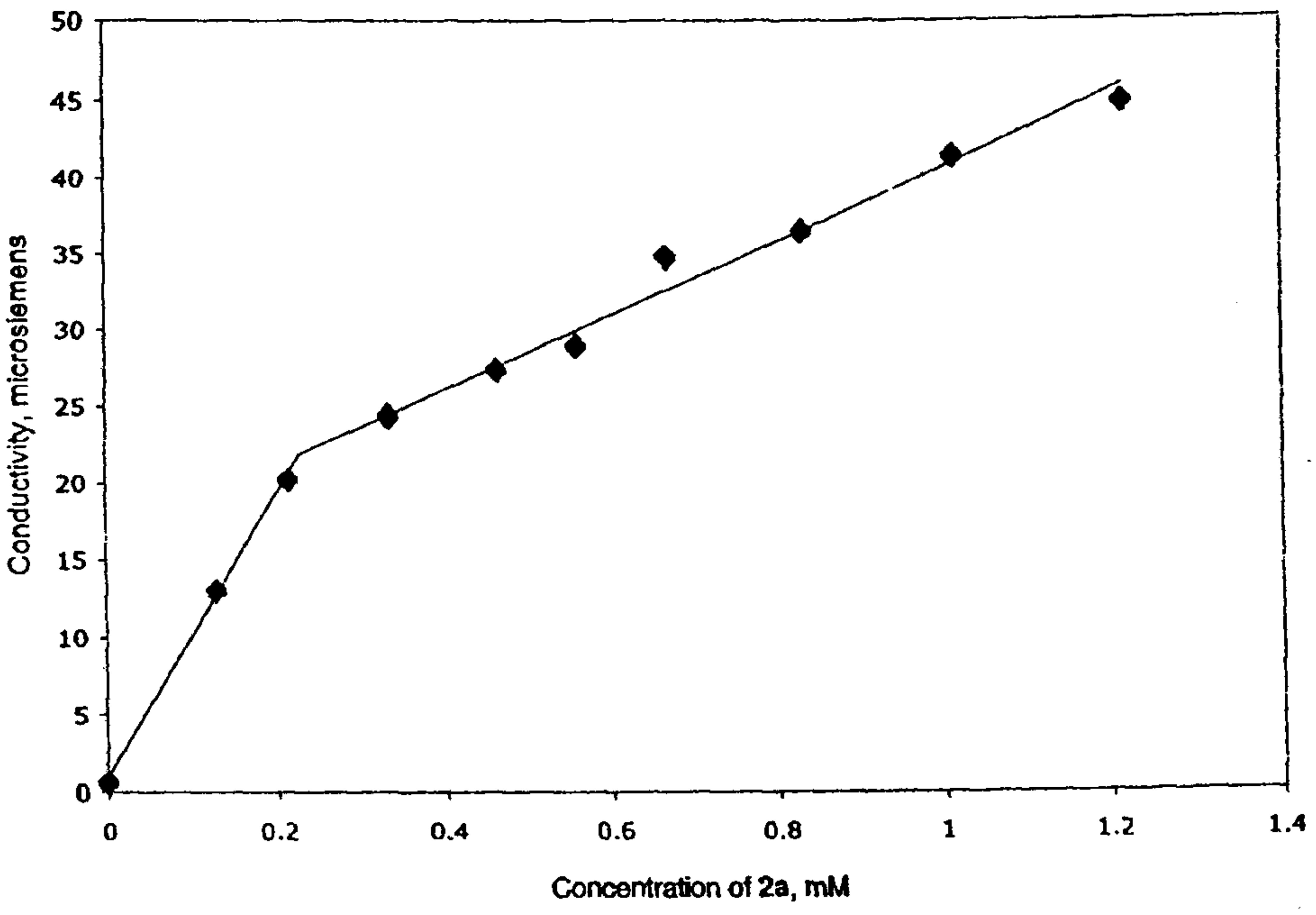

Conductivity, microsiemens
50
45
40
35
30
25
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
Concentration of 2a, mM

Figure 3

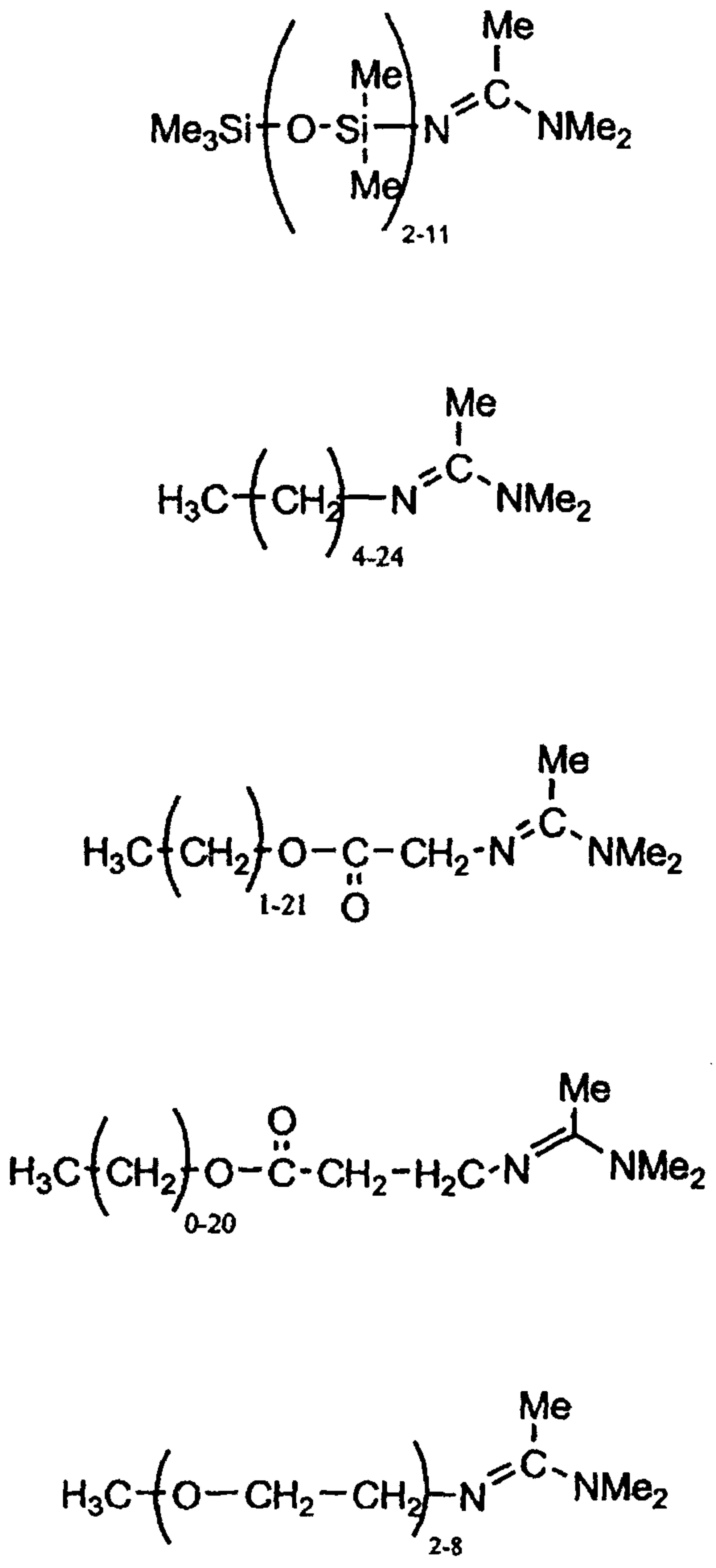
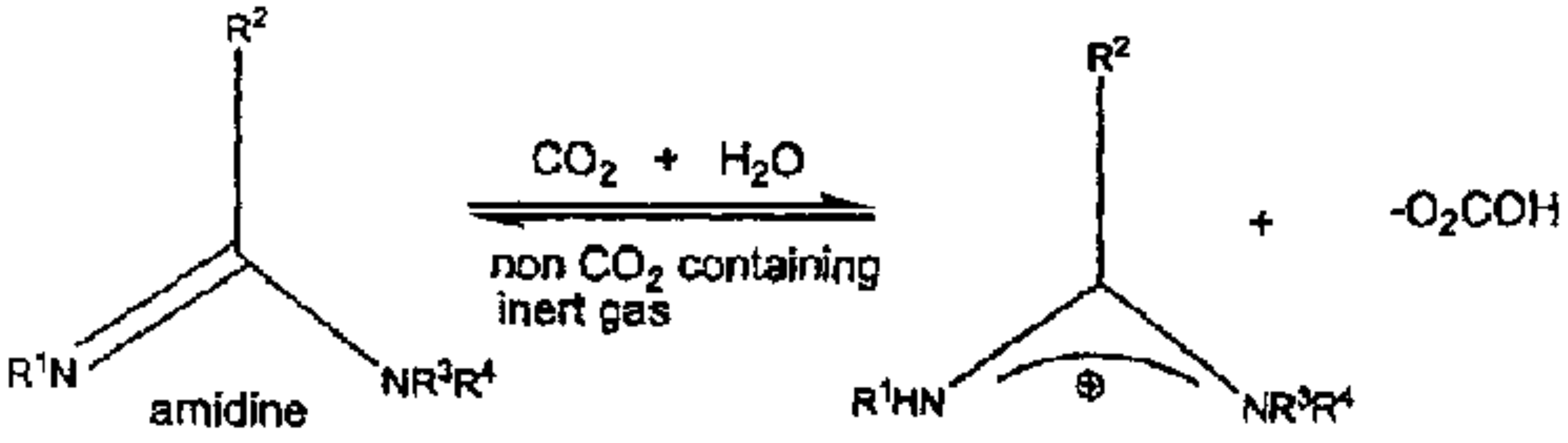
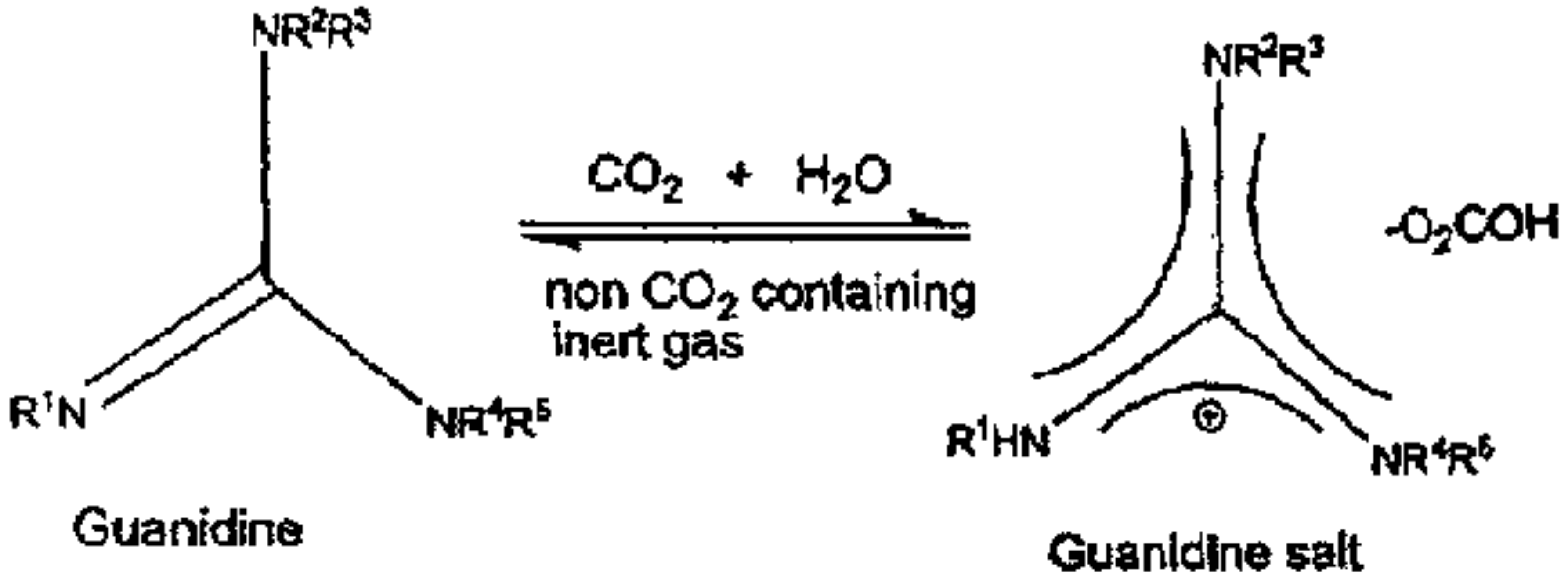

Me
Me
Me3Si
O-Si
N
C
NMe2
Me
2-11
Me
H3C
CH2
N
C
NMe2
4-24
Me
H3C
CH2
O
C
O
CH2
N
C
NMe2
1-21
O
Me
H3C
CH2
O
C
CH2
H2C
N
NMe2
0-20
Me
H3C
O
CH2
CH2
N
C
NMe2
2-8

Figure 4



(I)



(II)

$$R^1\text{—}NH_2 \underset{N_2}{\overset{CO_2}{\rightleftharpoons}} 1/2\,[R^1NH_3][R^1HNCO_2] \qquad \text{(III)}$$

$$R^1\text{—}NHR^2 \underset{N_2}{\overset{CO_2}{\rightleftharpoons}} 1/2\,[R^1NH_2R^2][R^1R^2NCO_2] \qquad \text{(IV)}$$