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Switchable Surfactants

Master of Science Thesis in the Master Degree Programme, Materials and Nanotechnology

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CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden, 2011

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Abstract

The switchable surfactants are molecules that can be reversibly converted between surface active and inactive forms by application of triggers. The switchable property of a surfactant could be favourable both in terms of environmental and economical aspects due to the possibility of recovering and reusing the compounds in different beneficial applications.

In the present work, in order to realize the N, N-di(propylamino) dodecylamine as a switchable surfactant, this surfactant was exposed to carbon dioxide to produce (mono) and (di) carbamate forms and afterwards the carbamates were exposed to nitrogen in order to revert them to the original amine form. The efficiency of (mono)carbamate synthesis process was improved to a complete hundred percent conversion. The (di)carbamate form was synthesized in varying pH environment and the best conversion was obtained at pH 12.

The critical micelles concentration (CMC) was studied to compare the surface activity of amine form and its corresponding carbamate forms. The results showed that the CMC values were similar to each other but slightly higher surface activity was determined for amine form.

Emulsion studies were performed for both amine form and its corresponding carbamate forms for investigating the efficiency of amine form in producing emulsions and its corresponding carbamate forms to see the effect on separation of emulsion. The emulsions consisting of carbamate forms had very short term stability whereas its amine forms had long term stability.

In order to investigate toxicity of amine and its corresponding carbamate forms, Microtox test and Algae Aquatic Toxicity test were conducted. Microtox test indicated that amine form can be considered toxic to marine organisms but its corresponding carbamate forms can be considered environmentally friendly. On the other hand, algae toxicity test estimations indicated higher toxicity for amine form and its (mono)carbamate form but lower for its (di)carbamate form.

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1 Introduction

Akzo Nobel Surface Chemistry (ANSC), headquartered in Stenungsund, manufactures speciality surfactants and polymers which are utilized in Consumer and Industrial applications. ANSC integrate wide range of applications and possess expertise in cationic, anionic, nonionic and amphoteric surfactants also synthetic and bio-polymer additives additionally to its existing products.

One important class of surfactants is the amine based cationic surfactant. Surface activity for the temporarily quarternized and amine based surfactants, depends on certain factors namely pH, salt, and free amino groups being altered to non-surface active groups by performing chemical reactions. Carbamate is the example of non-surface active derivatives of alkylamines that can be formed easily with CO₂. The compounds are obtained either in air during storage or with exposing CO₂ which is easier to achieve. Reversibility of carbamate to surface active amine is easily accomplished by N₂ as triggers and heating for expelling CO₂ from the carbamate.

The aim of this work is further development and optimization of N, N-di(propylamino) dodecylamine to be employed as a switchable surfactant and studying characterisation of N, N-di(propylamino) dodecylamine and its corresponding carbamate forms. Additional objective was to work on the physicochemical properties of amine and its corresponding carbamate forms. Emulsion studies have been performed for investigating the efficiency of amine form in producing emulsions and its corresponding carbamate forms to see the effect on the separation of emulsions. Lastly, toxicity tests have been performed in order to see the effect of amine and its carbamate forms to the aqueous environment.

The diploma work was conducted in collaboration with Akzo Nobel Surface Chemistry AB and department of Chemical and Biological Engineering, Chalmers University of Technology. The work has been performed at Akzo Nobel Surface Chemistry Synthesis Laboratory in Stenungsund, Sweden during September 2010 - March 2011.

2 Theory

2.1 Surfactants

The term surfactant is used as a reference to surface active agents. Surfactants are amphiphilic compounds, meaning that they consist of two different portions. One moiety is a polar or ionic group that attracts to polar solvents and another moiety is a non-polar group (hydrocarbon chain) attracting to non-polar solvents. Polar or ionic ‘head’ has strong interaction with water molecules and that is the reason why it is known as hydrophilic (or lipophobic). Whereas, hydrocarbon chain (non-polar group) ‘tail’ interacts with oil instead of water molecules, therefore, is called hydrophobic (or lipophilic). (Figure 1)

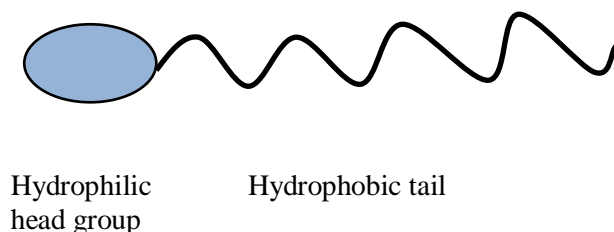


Figure 1 Schematic illustration of a surfactant.

The duality of a surfactant leads to its accumulation at interfaces between immiscible phases and the surfactant forms aggregates by self-assembly. ^[1] This phenomenon causes the surfactants to act as a bridge between two interfaces. On the whole, there are five different interfaces;

- Solid-vapour *surface*
- Solid-liquid
- Solid-solid
- Liquid-vapour *surface*
- Liquid-liquid

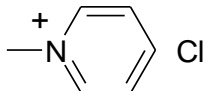
The presence of a surfactant reduces the surface or interfacial tension by lowering the free energy at the phase boundary and thus decreasing the work required to expand the interface. As the aggregation of a surfactant increases at the interface, the surface tension reduces accordingly.

Surfactants have been widely utilized both in everyday life and industrial applications including: pharmacy, food, detergency, agriculture, paints, paper, adhesives, petroleum industry and emulsifiers in chemical processing.

2.2 Types of Surfactants

The surfactants consist of two different parts, one is non-polar group (hydrophobic part) that may be branched or linear and can be comprised of one or two hydrocarbon chains. However, the surfactants are mainly classified according to the charge of their polar head group (hydrophilic part) as anionic, non-ionic, cationic, and zwitterionic. Some examples of main classes and their some main applications can be seen in Table 1.

Table 1 Examples of main classes of surfactants. [2]

Class	Head Group	Main applications
Anionic	$-\text{CO}_2^- \text{Na}^+$ $-\text{SO}_3^- \text{Na}^+$ $-\text{O}-\text{SO}_3^- \text{Na}^+$ $-\text{O}-\text{PO}_3^- \text{Na}^+$ $-(\text{OCH}_2\text{CH}_2)_n-\text{O}-\text{SO}_3^- \text{Na}^+$	Soaps Synthetic detergents Detergents, personal care products Corrosion inhibitors, emulsifiers Liquid detergents, toiletries, emulsifiers
Cationic	$-\text{N}(\text{CH}_3)_3^+ \text{Cl}^-$  $>\text{N}(\text{CH}_3)_2^+ \text{Cl}^-$	Bitumen emulsions Bactericides, antistatic agents Fabric and hair conditioners
Zwitterionic	$-\text{N}^+(\text{CH}_3)_2-\text{CH}_2-\text{CO}_2^-$ $-\text{N}^+(\text{CH}_3)-\text{CH}_2-\text{SO}_3^-$	Shampoos, cosmetics
Non-ionic	$-(\text{OCH}_2\text{CH}_2)_n\text{OH}$	Detergents, emulsifiers

Anionics are considered as by far the largest surfactant class and carboxylate, phosphate, sulphate and sulfonate are the most frequently used examples of the anionic polar groups. The second largest surfactant class is non-ionic surfactants and the most common polar group is either a polyether or a polyhydroxyl unit. The most of the cationic surfactants are characterized by a nitrogen atom that carries cationic charge and nitrogen-based products such as fatty amines are most general examples of them. Besides, cationic surfactants are categorized into two different groups; acidic and neutral. An example of acidic cationic surfactants salt is dodecylamine hydrochloride (Figure 2) which carries at least one proton on the positive nitrogen.

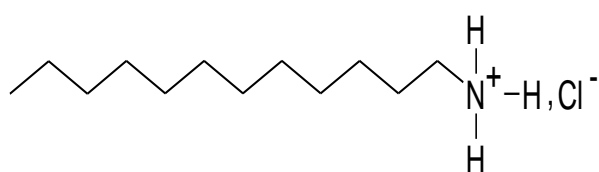


Figure 2 Dodecylamine hydrochloride

Neutral cationic surfactants (non-acidic and non-basic in water) are saturated with carbons linked to positive nitrogen atom. Cetyltrimetylammonium bromide (CTAB) with a nitrogen atom bonded to four carbons (Figure 3) is a common example of neutral cationic surfactants.

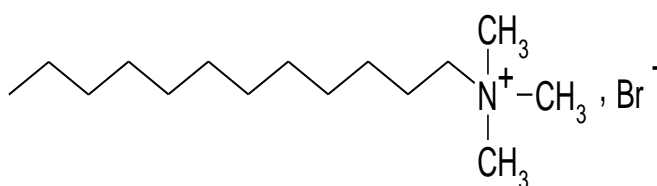
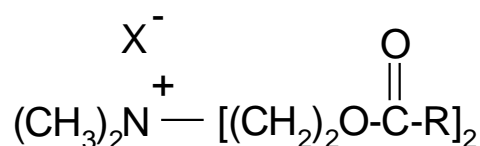


Figure 3 Cetyltrimetylammonium bromide (CTAB)

Zwitterionic surfactants that are the smallest surfactant class consist of two oppositely charged groups. *N*-alkyl derivatives of simple amino acids are commonly used as zwitterionic surfactants, such as betaine, amino propionic acid and glycine. ^[3]

2.3 Cleavable Surfactants

Cleavable surfactants are surface active compounds which characteristically have a weak bond deliberately built in-between the ‘‘head’’ and ‘‘tail’’ groups.^[4] The cleavable bond such as an ester bond (Figure 4) ensures the molecules cleave when trigger is applied that is why, the surface active form of the molecule is converted into the surface inactive form. However, cleavable surfactants are used for certain purposes such as improving the biodegradability^[5] but they have some disadvantages: (1) irreversible alteration between active and in-active form, (2) the slow occurrence of the cleavage step and (3) the use of environmentally harmful triggers such as an acid or base.^[6]



R = long hydrophobic chain
X = Cl, Br, or CH₃SO₄

Figure 4 Molecular structure of a conventional quaternary ammonium surfactant.

2.4 Switchable Surfactants

A molecule is switchable when it can be reversibly altered by activation of a trigger. The switchable surfactants are molecules whose structures are thus changed to another form and as a consequence surface activities can undergo completely reversible transition between active and inactive forms.^[7]

Traditional surfactants cannot be converted between active and inactive form and cleavable surfactants can only be irreversibly converted between active and inactive form. In contrast, switchable surfactants can be reversibly converted between active and inactive form upon application of a trigger or disposal of the present trigger. The trigger that is used to switch the molecule can vary depending on the area of application. These triggers can be CO₂^[7-9], air,

oxidation/reduction cycles ^[10], and photochemistry ^[11]. The cost and safety of triggers have to be taken into account when choosing the type of reagent.

The switchable surfactants may provide some beneficial applications in emulsion polymerization, in the oil industry, pharmaceutical manufacture, or other commercial chemical process. ^[7, 12]

One important application for switchable surfactants is in the oil industry. The presence or absence of a surfactant in the mixture plays a very critical role in oil drillings process, where water is used as a pump into an underground oil reservoir. By this way, water and crude oil mixture contact with each other. Surfactants consist of two portions, one of them hydrophilic (water-soluble, lipophobic) and the other is hydrophobic (oil-soluble, lipophilic). As they have dual solubility property, they are able to bridge the interface between the water and oil and thus stable emulsion is obtained. Afterwards, when trigger is taken away from the system or the system is purged by flushing gas to turn off the surfactant, emulsion may be appropriately broken and emulsion is separated to its two distinct layers. Due to reversibility of switchable surfactants active and inactive state, they can allow to maximize the recovery amount of emulsified oil when used in enhanced oil recovery (EOR) process. ^[7]

Switchable surfactants can be used to control CO₂ hydrate formation in oil and petroleum transport applications as well as in demulsification and deoiling applications. In order to separate water from produced oil, a high HLB reversibly switchable surfactant could be utilized and this recovered water provides to turn off the downstream problems (toxicity, biodegradability, and emulsification). When surfactant is exposed to air, it is desired not to switch on again as in such application. ^[9]

The other potential application for switchable surfactants is in emulsion polymerization of water soluble polymers which are prepared by polymerization of a monomer's inverse emulsion in a hydrophobic solvent. If the switchable surfactants are in the system, inverse emulsion mixture could be obtained and polymerization reaction can occur. Moreover, switchable surfactants can be used in an emulsion or microemulsion polymerization of water insoluble polymers. Flushing gas is exposed to the mixture in order for the surfactant to turn to " off " state as soon as polymerization is complete. Then organic solvent and polymer precipitates are separated by the " off " surfactant. In this manner, it is possible to

manufacture very high molecular weight polymers which are obtained after filtering and drying. However, in the absence of surfactants in solution polymerization process, producing high molecular weight polymers is difficult due to their tendency to form gels. As a consequence, with the presence of switchable surfactant it is possible to control the polymer particle size, and then switchable surfactant is switched “ off ” to be able to precipitate the polymer from solution. ^[7, 9]

Another potential application for switchable surfactants is the synthesis and stabilization of metallic nanoparticles which can be convertibly functionalized for directed assembly by using switchable surfactant which act as a particle stabilizing agent. Beside this, switchable surfactants can be used for protection and deprotection of nanoparticles. Normally, as traditional surfactants often temporarily protect the nanoparticles and other materials during synthetic procedure, switchable surfactants would allow them to more readily deprotected and cleaned. ^[9]

When nanoparticles, colloids, latexes, and other particulates are synthesized without a coating of surfactants, their particles tend to agglomerate into undesirably large particles and in this case, switchable surfactant may be used to protect the surface of them. ^[7]

Switchable surfactants may switch off once the paint or coating is applied to a surface in air. This may be another application of switchable surfactants in latex paints and other coating formulations.

Switchable surfactants may have applications to form switchable-polarity solvents (SPS). In such an extraction and precipitation process, switchable surfactants may be used to regulate the polarity of the solvent at different steps.

Switchable surfactant system may be useful for breaking a hydrophobic or hydrophilic substance out from a mixture which consists of water/aqueous solution and surfactant for hydrophobic substance or organic solvent and surfactant for hydrophilic substance. This system can be used to separate oil from porous rock, spilled oil from contaminated soil, desirable organic compounds from biological material (plant or animal), ink from paper, dirt from clothing and caffeine from coffee, metal salts from soil, salts or polyols (e.g., sugars)

from organic mixtures. As a consequence, ‘‘ off ‘‘ state of switchable surfactant may recover the extracted substance from solvent. ^[9]

Switchable surfactants may be employed in water/solvent separations in biphasic chemical reactions. Homogeneously-catalyzed reactions in organic/aqueous mixtures are given an example for their application. Firstly, as using the catalyze reactions, dissolve a water-soluble homogeneous catalyst with the surfactant ‘‘ on ‘‘ in water. Since the emulsion is created, the connection of two phases and mass transfer are augmented and thus the reaction occurs at a rapid rate. Then the reaction is complete and phases are separated when the emulsion is broken by surfactant ‘‘ off ‘‘. The surfactant will be kept in the organic phase because it is a nonpolar organic molecule in ‘‘ off ‘‘ form. If the surfactant is turned back ‘‘ on ‘‘ state, it may be precipitated from that solution. All in all, by using filtration techniques, the surfactant may be recovered, thus it may be reused and by this way waste streams are not polluted. ^[9]

The other potential application for switchable surfactants is employed for water/solid separation in mining. Switchable surfactant may be used as flotation reagents which adsorb to mineral particles to render them hydrophobic causing them to float. These flotation reagents are used as mineral specific reagents and, it is possible to remove them from minerals and recycled. ^[9]

Furthermore, switchable surfactants may be employed as transient antifoams in distillation columns, replacing traditional cationic surfactants, corrosion inhibitors. Also they can find application area in oil-sands separation processes, and in cleaning of equipment. ^[9]

2.5 Critical Micelles Concentration

The surfactants are amphiphilic molecules which consist of two different parts and they affect different solutes with their polarity characteristics. One part of the molecule is a polar group which is attracted to polar solvents, commonly water and the other part of the molecule is non-polar and is attracted to non-polar solvents, for instance air or oil. This duality of a surfactant leads to accumulation at interfaces between immiscible phases and self-assembly of surfactant aggregates is formed as micelles. ^[13]

The behaviour of surfactants in aqueous solution depends on their concentrations. Normally, surfactants behave as a dissolved substance when present in an aqueous solution at low concentrations. Nevertheless, adsorption is observed at the air-water interface leading to decreased surface tension due to reduction of surface free energy. When concentrations of surfactants further increases, adsorption also raises and at a certain concentration where all interfaces are saturated with surfactant unimers, aggregation is started and micelles are formed. The concentration, at which micelle formation is initiated, is defined as the critical micelle concentration, CMC. Furthermore, even if the concentration of the surfactant increases higher than CMC, all surfactants join into the micelles and the unimer concentration stays constant.^[14] (See Figure 5)

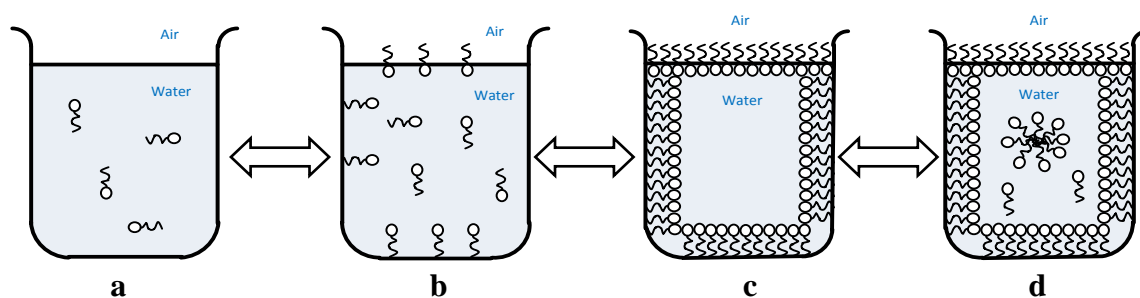


Figure 5: *a) A surfactant as dissolved substance b) Adsorption of surfactant at the air-water interface c) a monolayer of surfactants is formed at the interfaces d) formation of micelles*

Many physicochemical properties of a solution change at the CMC such as turbidity, conductivity and surface tension. Hereby, CMC can be determined by measurements of these properties. (Figure 6)

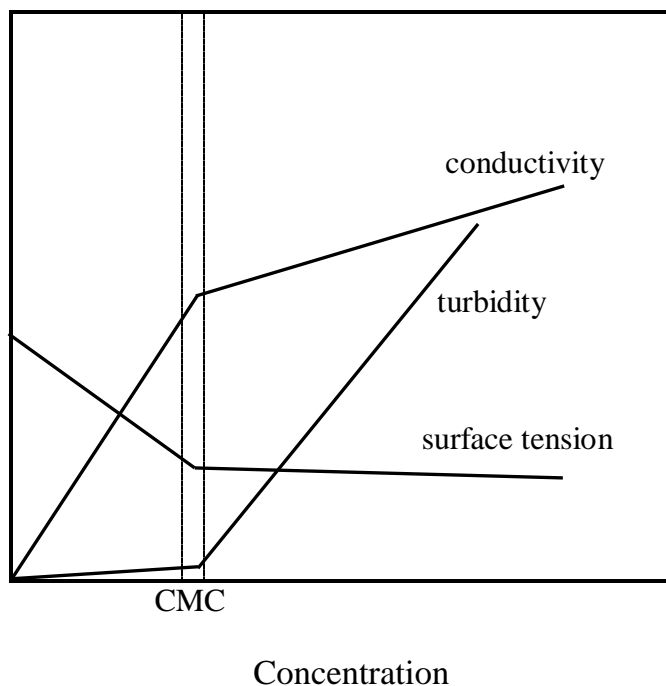


Figure 6 Critical micelle concentration (CMC)

CMC is affected by various factors, for example increasing the size of the ‘‘head’’ (polar or hydrophilic group) or reducing the size of the ‘‘tail’’ (non-polar or hydrophobic group) will result in an increased CMC. Furthermore, CMC will reduce when polar head group’s charge density is reduced by counterions or electrolyte addition to ionic surfactant. Besides these factors, temperature and pH also influence the CMC. The CMC of a surfactant is an important parameter as it is unique to each surfactant and influences the control of solubilisation and emulsification. ^[15]

2.6 Emulsions

The thermodynamically unstable, heterogeneous system, in which at least one immiscible liquid is dispersed in another with a wide range of small droplets, is defined as an emulsion. (Figure 7) The main types of emulsions appear as O/W (oil-in-water) in which oil droplets are dispersed in water and conversely W/O (water-in-oil) in which water droplets are dispersed in oil. ^[16] The oil is normally referred to as the organic liquid phase. The emulsion is formed by relatively large droplet sizes (1-10 μ m). As emulsions are unstable, they cannot form spontaneously. In order to make an emulsion, high-share mixers, colloid mills,

homogenizer, and sonic and ultrasonic dispersers are used whereas steric, particle and electrostatic approaches are used to stabilize the emulsion.^[16-17] In contrast to emulsions, microemulsions are thermodynamically stable mixtures. They have relatively larger droplet sizes (3-20nm) and they are transparent and highly dynamic.

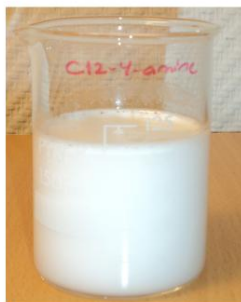


Figure 7 Dodecylamine/water emulsion.

2.7 Biodegradation and Aquatic Toxicity

As mentioned previously, surfactants have been widely utilized both in household and industrial applications. This leads to the consumption of a great amount of synthetic surfactants which eventually interact with aquatic environments, hereby, microorganisms, animals and plants may be influenced with these surfactants. Therefore, designing new surfactants, aquatic toxicity, biodegradation, and bioaccumulation ability of surfactants should be taken into account.

Biodegradation that is a process, carried out by bacteria, relies on concentration, pH and temperature factors. There are two important criteria known when considering biodegradation: primary and ultimate degradation. While, primary degradation of surfactants is characterized by loss of surface active property in a certain time interval, the ultimate degradation is performed with conversion of surfactant molecules into carbon dioxide, water and oxides of the other elements by a series of enzymatic reactions. Moreover, many structural changes of a surfactant affect biodegradation. For example, (1) biodegradation rate decreases with increasing substitution level of an aliphatic amine, (2) biodegradability of primary diamines surfactants increases with the introduction of three or more methylene

groups between two terminal amino groups, (3) tertiary amines surfactants with CH_3 , $\text{CH}_2\text{CH}_2\text{OH}$ or CH_2COOH substitutions are more biodegradable, while tertiary amines surfactants C_4 to C_{18} biodegrade very slowly. Also, surfactant solubility in water and labile bonds are another important characteristic features to affect the rate of biodegradation.

Aquatic toxicity that is determined on fish, daphnia or algae, is given for fish as LC_{50} which is abbreviation of lethal concentration or for daphnia and algae as EC_{50} which is abbreviation of effective concentration. In order to be considered as toxic, values should be below 1 mg/l after 96h testing on fish and algae and 48h on daphnia. The value that is above 10 mg/l, is a preferable for environmentally benign surfactants.^[18]

Figure 8 illustrates the environmental ranking of surfactant that is based on values of the biodegradation test and aquatic toxicity. The dashed area of the diagram are “approved areas” for biodegradation and aquatic toxicity.

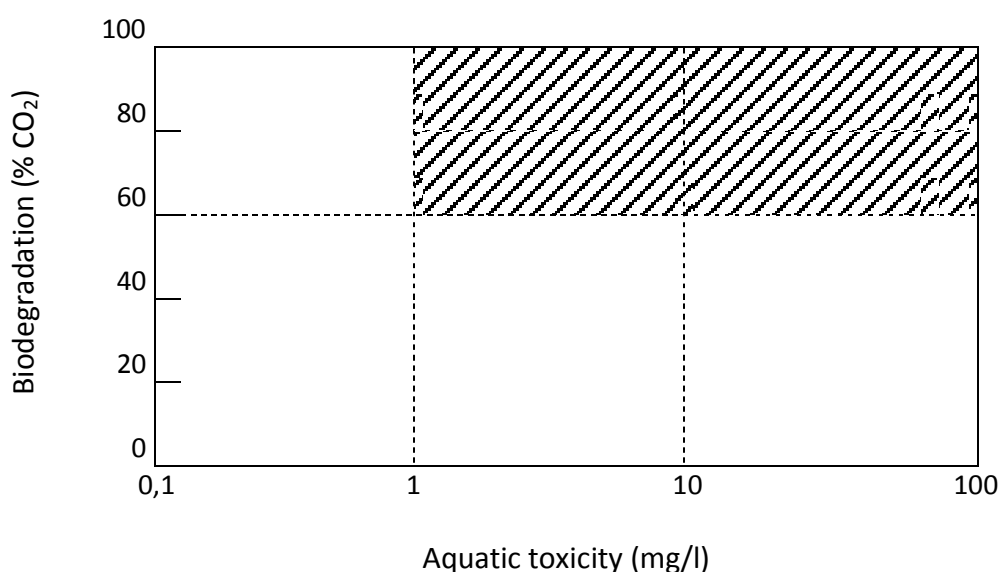


Figure 8 Environmental ranking of surfactants.

3 Experimental

3.1 Materials

C12-Y-amine (95%) was distilled from Triameen Y12D {0.31% C12-amine (N-Dodecylamine), 7.49% C12-propylene-diamine (N-(propylamino) dodecylamine), 91.6% C12-Y-amine (N,N-di(propylamino) dodecylamine)}, which was obtained from Akzo Nobel Surface Chemistry AB. The distillation products were analysed with gas chromatography (GC) on a Varian 3400, with a silica capillary column; 12m, 0.2mm id, 0.33µm film thickness.

CO₂ gas was purchased from AGA in order to enhance the Carbamate forms.

For the synthesis of (di)carbamate from C12-Y-amine, the environment was maintained at a constant pH using NaOH which was bought from Merck.

Nitrogen gas was supplied from Akzo Nobel Surface Chemistry AB for the enhancement of reverse reactions.

The carbamate products were analysed with nuclear magnetic resonance (NMR) on a Varian VXR-400.

For the emulsion studies, Xylene and Dodecane were purchased from Merck.

Surface tension and CMC were measured according to Du Noüy ring method with KSV Tensiometer Sigma 70.

Toxicity was measured with Microtox and Algae Aquatic Toxicity method. The luminous marine bacteria (*Vibrio Fisheri*) were used in Microtox test.

3.2 Synthesis and purification of C12-Y-amine

The N, N-di(3-aminopropyl) dodecylamine (C12-Y-amine) synthesis and purification were conducted as established and described by our group previously.^[19] In short, the C12-Y-amine is synthesized by a Michael addition of two moles of acrylonitrile to one mole of a Dodecylamine at 110 °C for 12h to form an N,N-di-cyanoethyl-dodecylamine intermediate, which is subsequently hydrogenated at 140 °C to produce N, N-di(3-aminopropyl) dodecylamine (C12-Y-amine).^[19]

The C12-Y-amine was distilled at 223 °C and 0 mbar from Triameen Y12D with the yield of 148.83g. The purity was identified by gas chromatography and ¹H NMR spectroscopy to be 95%.

¹H-NMR (CD₃OD): δ 0.8 (t, 3H), δ 1.2 (m, 18H), δ 1.4 (q, 2H), δ 1.55 (q, 4H), δ 2.36 (t, 2H), δ 2.39 (t, 4H), δ 2.58 (t, 4H).

3.3 Synthesis of Carbamate

3.3.1 Synthesis of C12-Y-amine (mono)carbamate

C12-Y-amine (5.0 g, 0.0167 mole) was dissolved in 45 g de-ionized water in a 3-neck flask at 50 °C for 15 minutes. The solution was transparent and clear. After C12-Y-amine had completely dissolved in water, CO₂ gas exposure was initiated through the mixture to 2 bar at 50 °C for 3.5h and the magnetic stirrer was applied at maximum rate.

CO₂ gas was introduced into the system by holding the gas needle slightly above the surface of the solution in order to prevent foam formation and to achieve homogenous distribution of the CO₂ into the solution. Yellow-brown solution was observed after 2h of carbon dioxide exposure and (mono)carbamate formation was obtained at 3.5h and the conversion was identified by NMR to be 100%.

3.3.2 Synthesis of C12-Y-amine (di)carbamate

C12-Y-amine (2.5 g, 0.0083 mole) was dissolved in 19 g de-ionized water and 5 ml 5M NaOH in a 5-neck flask at 50°C for 15 minutes. The solution was transparent and clear. Right after C12-Y-amine had completely dissolved in water, CO₂ gas exposure was initiated through the mixture to 2 bar at 50°C for 140 minutes. 5M NaOH (13.23ml) was added to the system during the reaction to achieve a constant pH of 12. Magnetic stirrer was applied at maximum rate.

CO₂ gas was introduced into the system by holding the gas needle slightly above the surface of the solution in order to prevent foam formation and to achieve homogenous distribution of the CO₂ into the solution. Yellow-white solution was observed after 2h of carbon dioxide exposure. After 140 minutes, a gel mixture was obtained and the (di)carbamate formation was measured by NMR to be 61%.

3.4 Emulsion Studies

In order to observe the emulsifier behaviour of surfactant before and after carbon dioxide exposure, standard emulsification method from Akzo Nobel Surface Chemistry AB was performed. Surfactant (0.25 g) and oil (4.75 g) were added in de-ionised water (95 g) in 100 ml graduated cylinder. The oils were xylene, dodecane and surfactants were C12-Y-amine before carbon dioxide exposure, C12-Y-amine (mono)carbamate and C12-Y-amine (di)carbamate after carbon dioxide exposure. The system was shaken by hand several times and by Ultra Turrax T25 mixer mill at a speed setting of 8000 for 1 min to create an emulsion. Stability of emulsions were observed by vision and evaluated by the percentage of emulsion versus total volume. The results are shown in Table 2.

3.5 CMC

In order to measure the surface tension and determine the CMC values of aqueous solution of C12-Y-amine and its two different carbamate forms, Du Noüy ring method was performed on KSV Tensiometer Sigma 70 at room temperature.

For the CMC measurement of C12-Y-amine, 0.05wt% aqueous solution was prepared in an Erlenmeyer flask and for the CMC measurements of two different carbamates formed after exposure to carbon dioxide, 0.5wt% aqueous solutions were prepared in an Erlenmeyer flask. The result can be seen in diagram 4.

3.6 Toxicity Test with Microtox

C12-Y-amine (0.52 g) was dissolved in up to 500g de-ionized water in a flask. Part of the solution (50 ml) was taken and HCl (3.5 ml 0.1M) was added in order to adjust the pH to 7.3 . Aqueous solutions (0.5wt %) were prepared for each carbamate form and the pH of carbamate aqueous solutions were adjusted to 7.3 with HCl.

The solutions were transferred to a solution containing luminous marine bacteria (*Vibrio Fisheri*). When emitted light decreased to 50%, which was designated as effective concentration (EC₅₀), the concentration was measured and processed by a computer program. EC₅₀ was calculated at two different time intervals (5 and 15 min). The results are shown in Table 3.

3.7 Algae Toxicity Test

In order to performed the algae toxicity test was collaborated with department of Regulatory and Applied Life Sciences, Akzo Nobel, in the Netherlands. The test was conducted according to Algae Toxicity Test OECD 201 procedure. The results are indicated in Table 4.

3.8 Reverse Reactions

3.8.1 Synthesis of C12-Y-amine from C12-Y-amine (mono)carbamate

C12-Y-amine (mono)carbamate (3 g, 0.0087 mole) was dissolved in up to 30g de-ionized water in a 3-neck flask at 95°C for 15 minutes. The solution was observed to be brown. After C12-Y-amine (mono)carbamate had completely dissolved in water, nitrogen gas exposure was initiated through the mixture at 95°C for 4h and the magnetic stirrer was applied at maximum rate.

Nitrogen gas was introduced into the system by holding the gas needle slightly above the surface of the solution in order to prevent foam formation and to achieve homogenous distribution of the nitrogen gas into the solution. Yellow-brown solution was observed after 2h of nitrogen gas exposure and 93% (mono)carbamate switched back to C12-Y-amine form at 4h and this conversion was analysed by ¹H NMR spectroscopy and yellowish solution was obtained.

3.8.2 Synthesis of C12-Y-amine from C12-Y-amine (di)carbamate

C12-Y-amine (di)carbamate (3 g, 0.0078 mole) was dissolved in up to 30g de-ionized water in a 3-neck flask at 95°C for 2 minutes. The solution was transparent and clear. After C12-Y-amine (di)carbamate had completely dissolved in water, nitrogen gas exposure was initiated through the mixture at 95°C for 6h and the magnetic stirrer was applied at maximum rate.

Nitrogen gas was introduced into the system by holding the gas needle slightly above the surface of the solution in order to prevent foam formation and to achieve homogenous distribution of the nitrogen gas into the solution. Yellowish solution was obtained after 6h of nitrogen gas exposure and 77.4% (di)carbamate switched back to C12-Y-amine form and the conversion was analysed by NMR.

4 Results and Discussion

4.1 Synthesis and purification of N, N-di(3-aminopropyl) dodecylamine (C12-Y-amine)

C12-Y-amine surfactant, N, N-di(3-aminopropyl) dodecylamine, was synthesized by a Michael addition of two moles of acrylonitrile to one mole of a Dodecylamine in order to form an N, N-di-cyanoethyl-dodecylamine intermediate, which is afterwards hydrogenated to produce N, N-di(3-aminopropyl) dodecylamine (Figure 9) that was previously reported by Hans Oskarsson and co-workers ^[19]

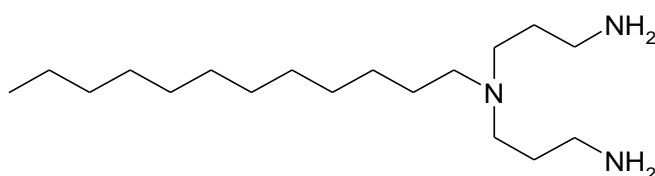


Figure 9 N, N-di(3-aminopropyl) dodecylamine (C12-Y-amine)

C12-Y-amine surfactant, N, N-di(3-aminopropyl) dodecylamine was produced in two steps as indicated in figure 10 and 11.

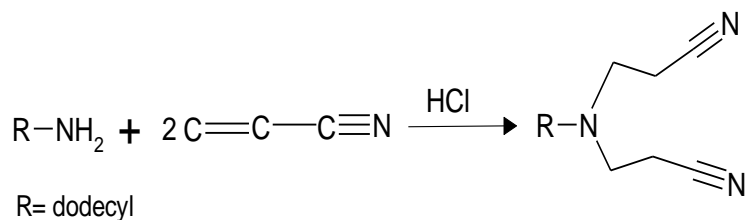


Figure 10 Synthesis of N, N-di(cyanoethyl) dodecylamine

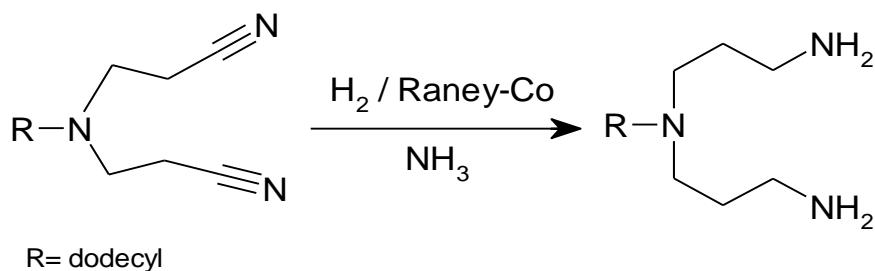


Figure 11 Synthesis of *N, N*-di(3-aminopropyl) dodecylamine

Vacuum distillation was performed in order to accomplish pure product of the *N, N*-di(3-aminopropyl) dodecylamine (C12-Y-amine). The purity was identified as 95 area% by gas chromatography with a fused silica capillary column and ^1H NMR spectroscopy (Figure 12).

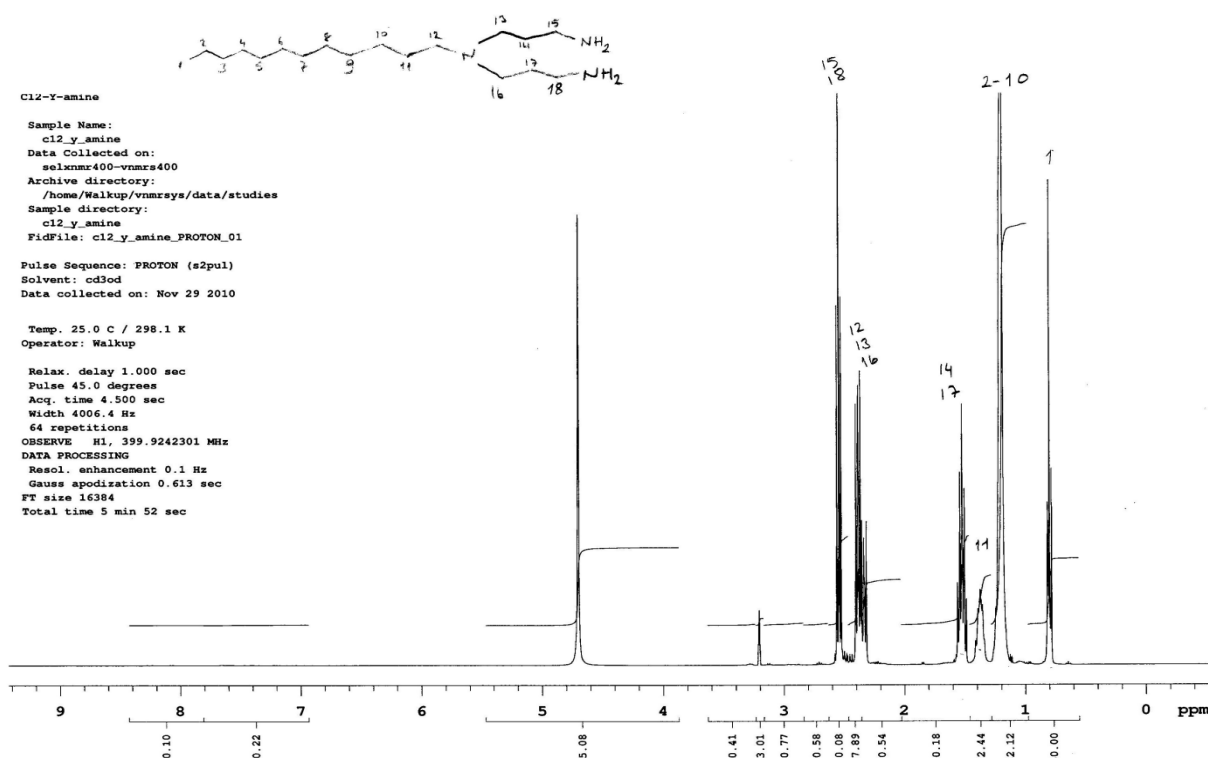


Figure 12 ^1H NMR spectrum of C12-Y-amine (CD_3OD)

4.2 Synthesis of C12-Y-amine (mono)carbamate

The C12-Y-amine was successfully achieved to form C12-Y-amine (mono)carbamate salt with CO₂ gas exposure in the presence of H₂O and by liberating hydrogen ions. (Figure13). C12-Y-amine (mono)carbamate salt includes two groups at the end, one of them positively charged and the other is negatively charged.

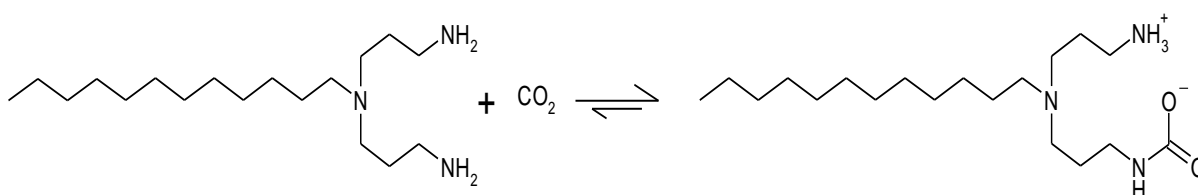


Figure 13 Synthesis of C12-Y-amine (mono)carbamate

The conversion of C12-Y-amine to its (mono)carbamate form was proven by NMR to be 100%. The ¹H-NMR spectrum was obtained and chemical shift for the amine after CO₂ exposure is illustrated in spectrum (Figure 14). Before CO₂ treatment, the spectrum of amine shows a signal around 2.5-2.6ppm which is corresponding of the hydrogen atoms on the carbons which are the closest atom to each terminal primary amine of C12-Y-amine but after CO₂ treatment, a new signal in the ¹H NMR spectrum which appears around 3.0-3.1ppm which is indicative of formation of the hydrogen atoms on the carbons which are closest atom to each terminal primary amine of C12-Y-amine. This chemical shifting on the spectrum clarifies formation of the intermolecular ion pair comprising of one free protonated amine and one amine in carbamate form. Moreover, carbamate conversion was determined by comparison of signals before and after shifting.

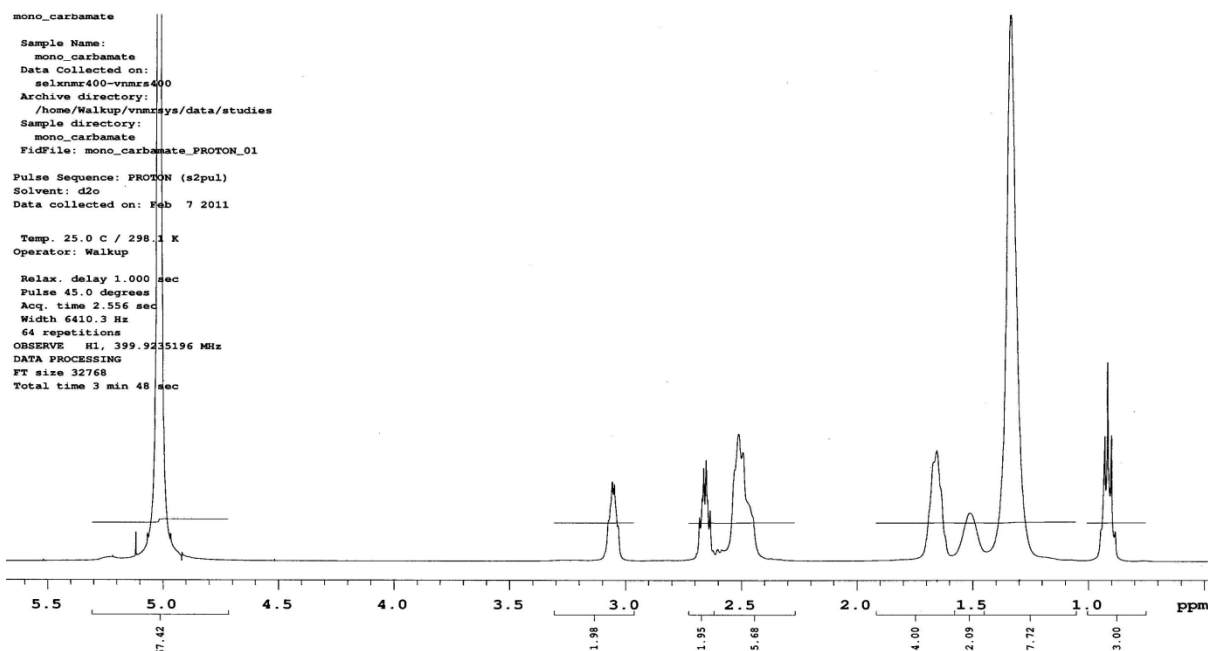


Figure 14 ^1H NMR spectrum of C12-Y-amine (mono)carbamate salt (D_2O)

4.3 Synthesis of C12-Y-amine (di)carbamate

The reactions of C12-Y-amine (di)carbamate were performed with CO_2 gas exposure in the presence of H_2O and with addition of NaOH which was used to keep pH constant during the reaction (Figure 15). C12-Y-amine (di)carbamate includes two groups at the end, both are negatively charged.

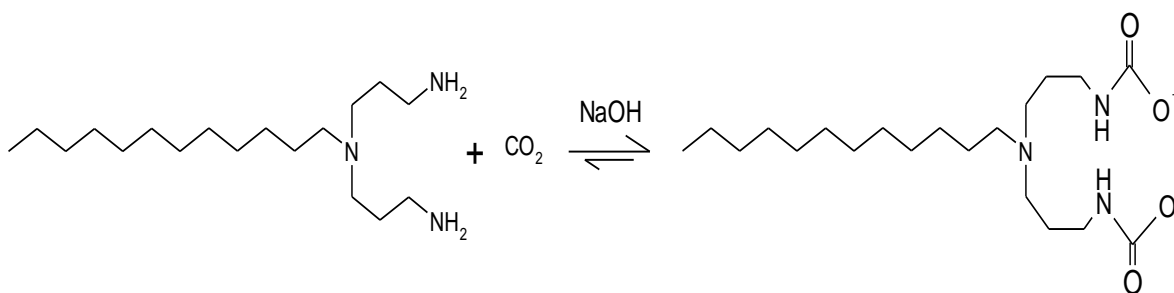


Figure 15 Synthesis of C12-Y-amine (di)carbamate

The conversion of C12-Y-amine to its (di)carbamate form was identified by NMR spectrometer. The ^1H NMR spectrum of C12-Y-amine (di)carbamate showed the appearance

of a new signal around 3.0-3.1ppm which was the chemical shift of a carbamate anion (Figure 16) as explained in (mono)carbamate formation experiment. The comparison of before and after shifting gave the ratio of (di)carbamate formation.

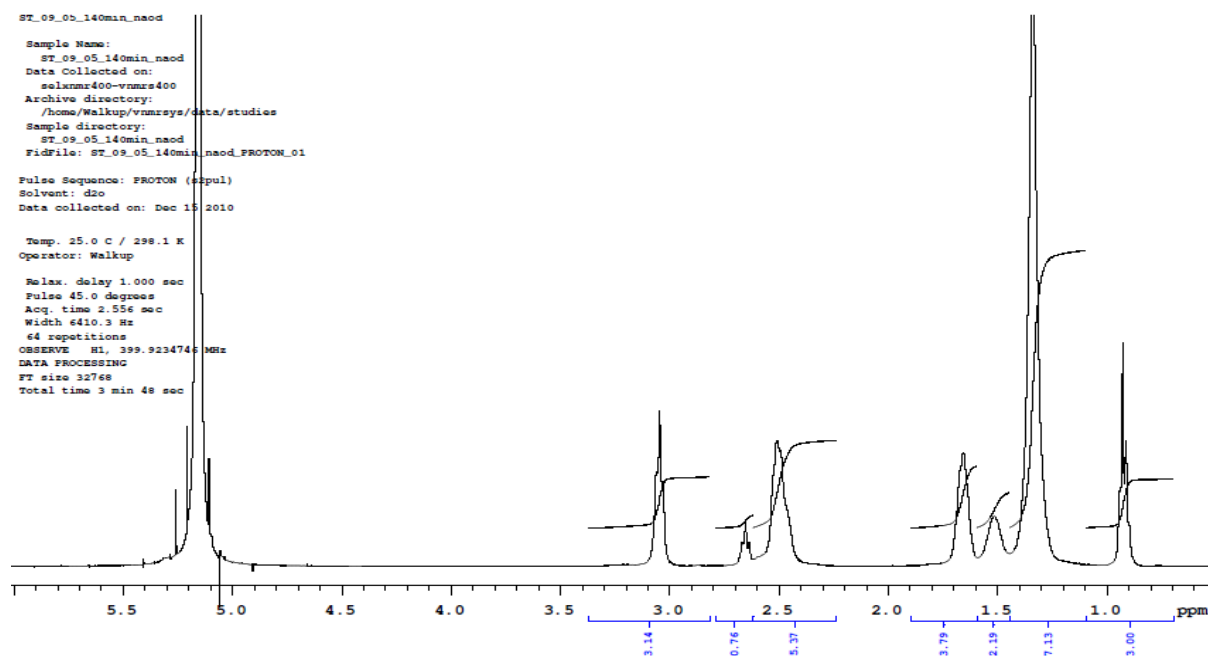


Figure 16 ^1H NMR spectrum of C12-Y-amine (di)carbamate salt (D_2O)

In order to achieve high efficiency of C12-Y-amine (di)carbamate form, different fixed pH values of 8, 9, 10, 11, 12, 13 were tested respectively. The (di)carbamate conversion at different fixed pH was identified by NMR and the highest conversion of (di)carbamate form was achieved at pH of 12 to be 61%. The effect of pH on a formation of (di)carbamate is illustrated in diagram 1.

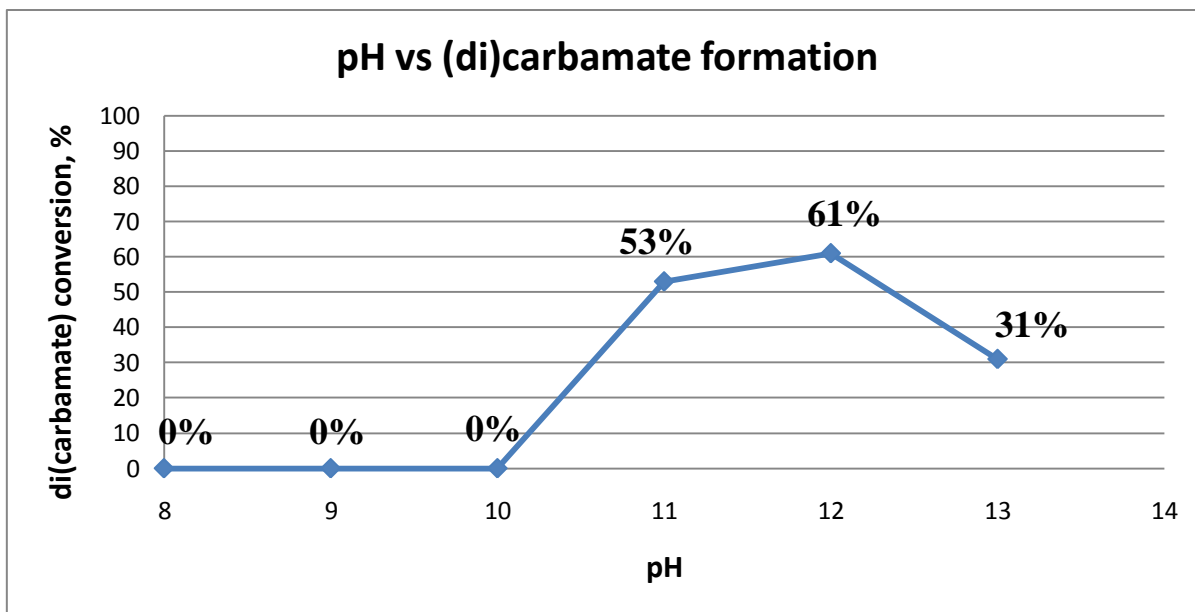


Diagram 1 Effect of pH on C12-Y-amine (di)carbamate formation.

As indicated in the diagram 1, C12-Y-amine (di)carbamate formation was not observed at pH of 8, 9 and 10 but according to ^1H NMR spectra C12-Y-amine (mono)carbamate formation was identified at these pH values. While (di)carbamate conversion increases pH of 11, 12, conversion of (di)carbamate decreases at pH of 13. The more increase in pH results in higher conversion of (di)carbamate up to a certain extent.

4.4 Emulsion Studies

In order to observe the emulsification effect of C12-Y-amine surfactant and its carbamate forms (C12-Y-amine (mono) and (di) carbamate) after carbon dioxide exposure, standard emulsification method from Akzo Nobel Surface Chemistry AB was performed. Dodecane and xylene were chosen as oil, they are aliphatic and aromatic, respectively. The ratio of water-oil-surfactant was used as 95wt%-4.75wt%-0.25wt%, which was shaken for several times by Ultra Turrax T25 mixer mill at a speed setting of 8000 for 1 minute to create an emulsion. Stability of emulsions was observed by vision and evaluated by the percentage of emulsion versus total volume. (Table 2)

Table 2 Emulsification results of C12-Y-amine and its carbamate forms.

Type of Oil	Surfactants	Shaken Time (min)	Emulsion Results
Dodecane	C12-Y-amine	5	Good Emulsion
	C12-Y-amine (mono)carbamate	1	Good Emulsion
	C12-Y-amine (di)carbamate	1	Good Emulsion
Xylene	C12-Y-amine	5	Good Emulsion
	C12-Y-amine (mono)carbamate	2	Good Emulsion
	C12-Y-amine (di)carbamate	5	Good Emulsion

In dodecane case, C12-Y-amine before CO₂ treatment and its carbamate forms after CO₂ treatment gave 100% emulsion but emulsion formation of carbamate forms were more rapid than their neutral form. The formation of dodecane/water emulsion was depicted in diagram 2a.

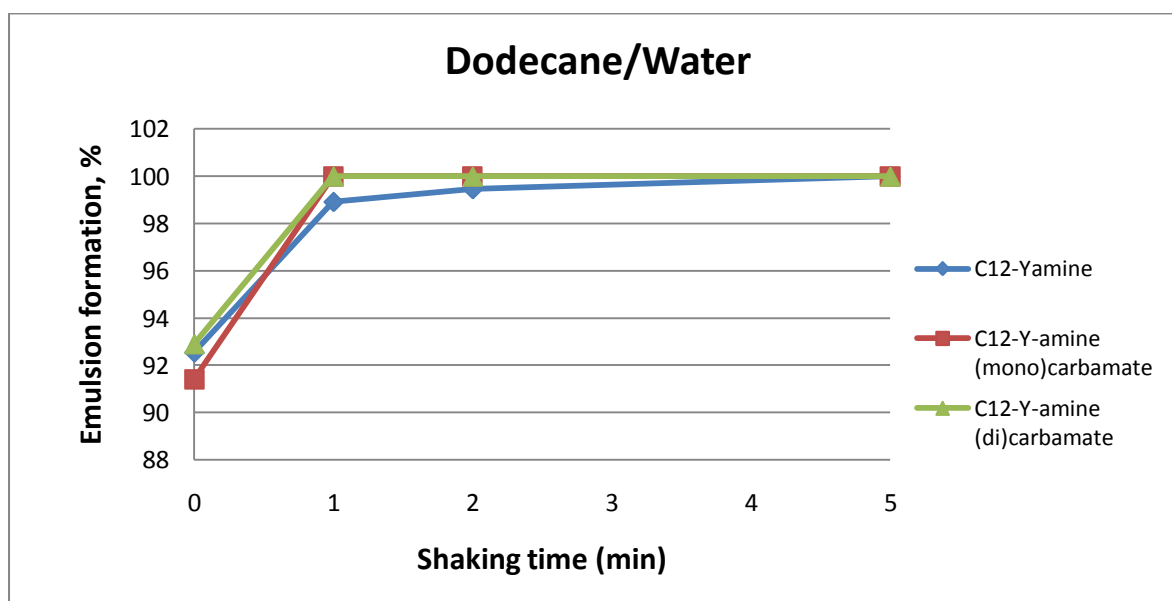


Diagram 2a Formation of Dodecane/Water emulsion.

However, in xylene case, some differences were observed on the carbamate forms especially on the C12-Y-amine (di)carbamate form which gave good emulsion (96,6 %) after shaken 5 min but did not reach to 100% of emulsion even after shaken 15min. These emulsion formations can be seen in diagrams 2b.

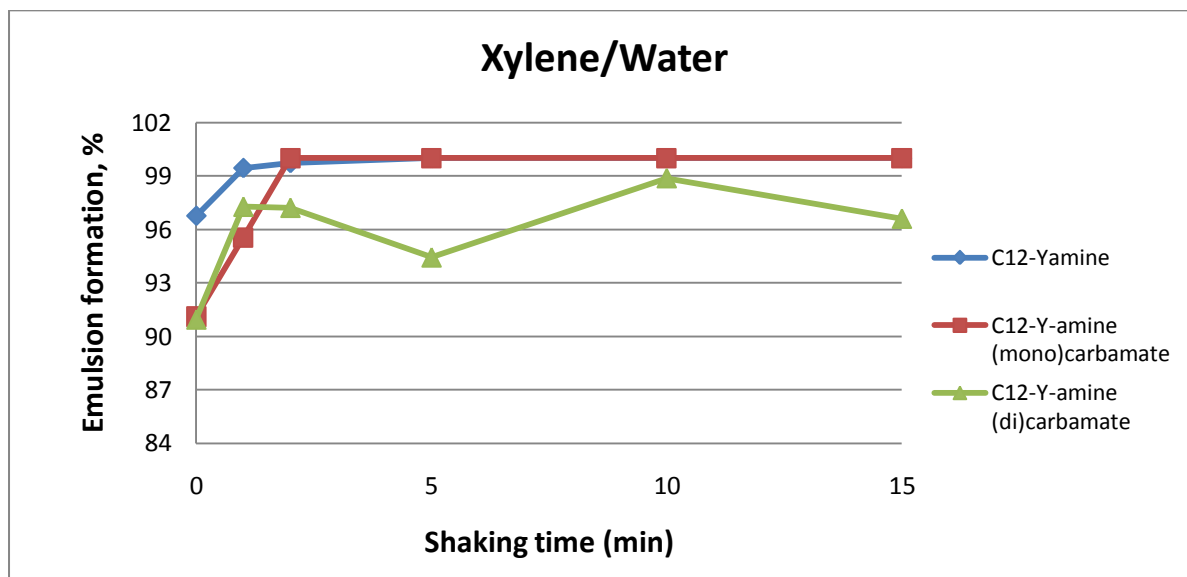


Diagram 2b Formation of Xylene/Water emulsion.

Phase separation is a critical criterion to indicate stability of emulsions. Phase separations of dodecane/water emulsions are indicated in the diagram 3a. It can be noticed that although in carbamate forms of C12-Y-amine emulsion system were achieved more than 90% phase separated at 3h, C12-Y-amine emulsion system presented as a stable emulsion even at 17h. Separations at 72h were 96,7%, 93,5% for the (mono) and (di)carbamate emulsion system respectively whereas in C12-Y-amine emulsion system phase separation began to be observed after 17h and reached 11,5% separation at 72h. As it can be concluded, the carbamate forms of C12-Y-amine can be considered as weaker emulsifier than C12-Y-amine form. This can be the consequence of lower surface activity of carbamate forms with respect to C12-Y-amine.

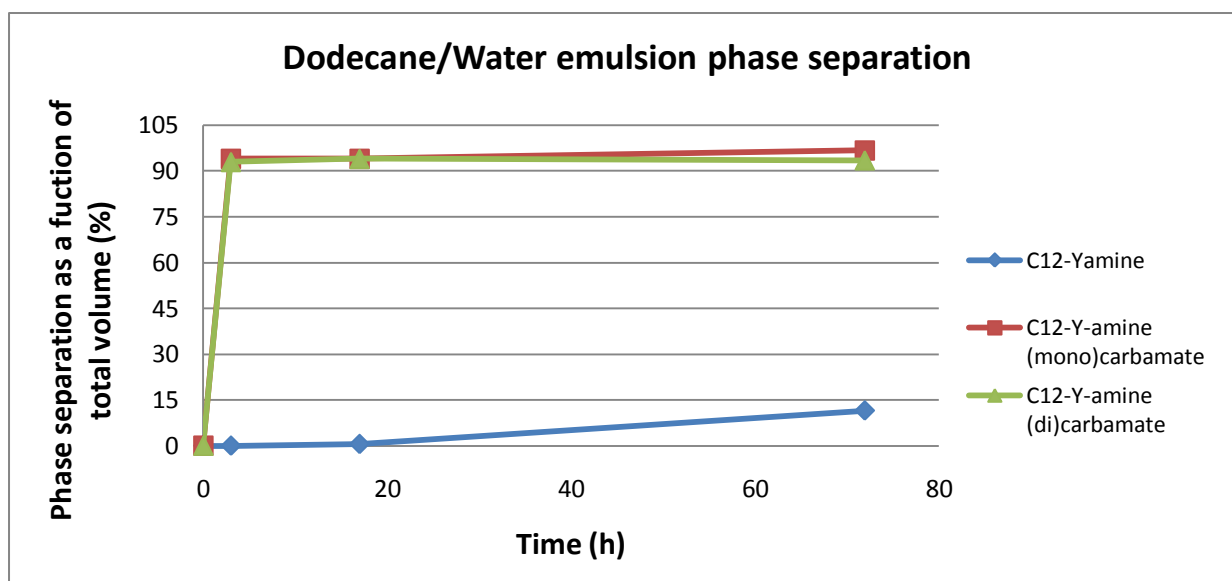


Diagram 3a Formation of Dodecane/Water emulsion separation.

Phase separations of xylene/water emulsions are shown in the diagram 3b. As indicated in the graph, C12-Y-amine creating emulsion with xylene and water was more stable than its carbamate forms. While the first phase separation in C12-Y-amine emulsion system could be observed at 144h, in C12-Y-amine (mono)carbamate emulsion system it was seen after 1,5h and in C12-Y-amine (di)carbamate emulsion system it was observed after 17h. Although in (mono)carbamate emulsion system, phase separation was observed earlier comparing to (di)carbamate emulsion system, (di)carbamate emulsion system completely lost its emulsion characteristic properties after 96h, which is much shorter duration as compared to the time (after 144h) of the highest phase separation of (mono)carbamate emulsion system. According to the diagram 3b, C12-Y-amine can be considered as the best emulsifier with respect to its carbamate forms.

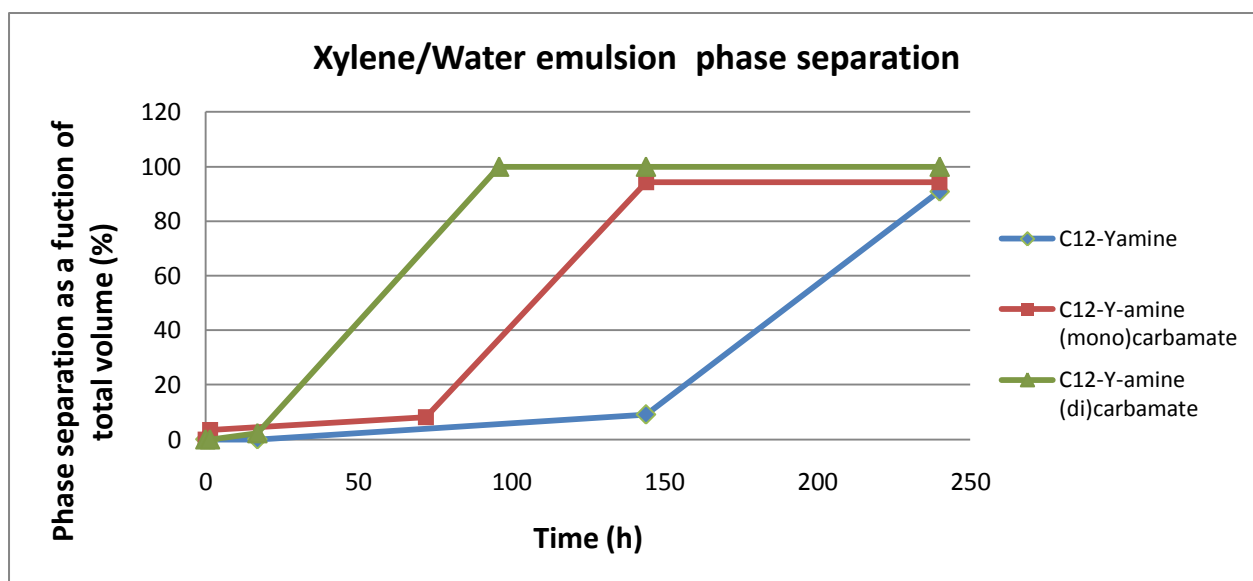


Diagram 3b Formation of Xylene/Water emulsion separation.

4.5 CMC

Du Noüy ring method was performed on KSV Tensiometer Sigma 70 at room temperature for measuring the surface tension and determining the CMC values of aqueous solution of C12-Y-amine and its two different carbamate forms. CMC determined results for C12-Y-amine and its carbamate forms are shown in the diagram 4.

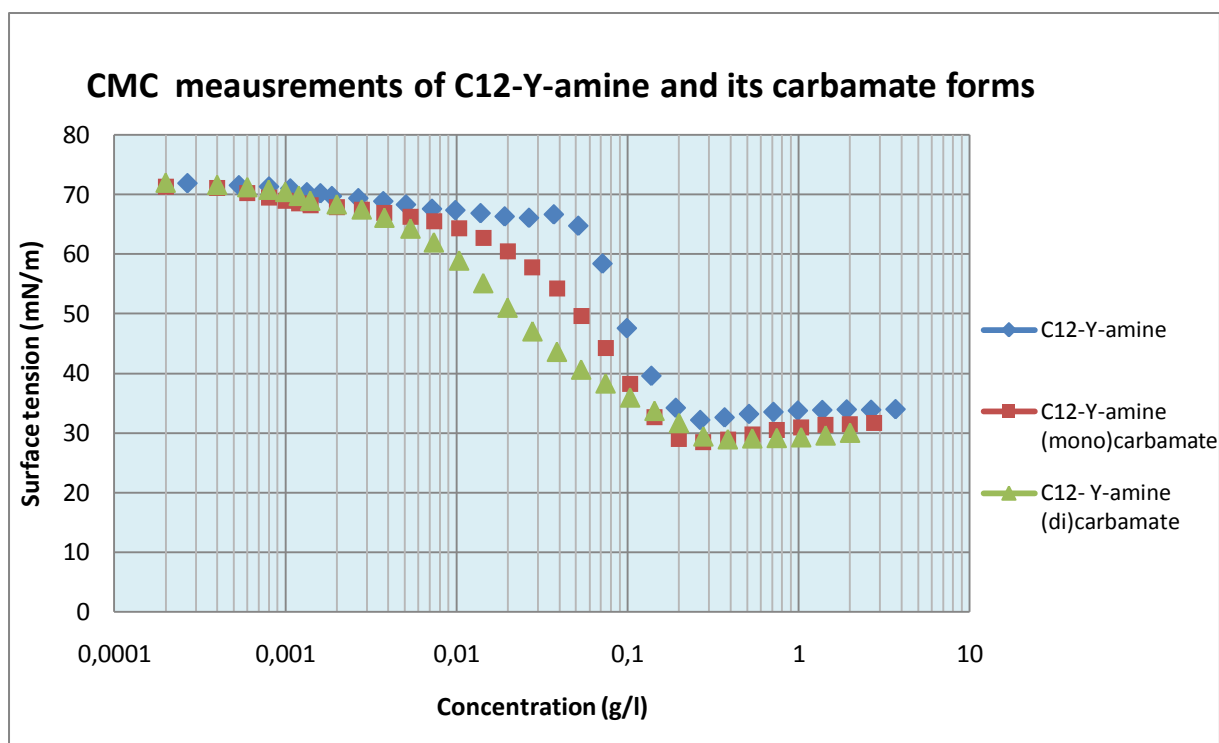


Diagram 4 CMC results of C12-Y-amine and its corresponding carbamate forms.

As indicated in the diagram 4, critical micelle concentration increased in the order of from low to high as; C12-Y-amine, C12-Y-amine (mono)carbamate, C12-Y-amine (di)carbamate. The approximate CMC values were measured at 0,50 mmol/l for the C12-Y-amine, at 0,58 mmol/l for the C12-Y-amine (mono)carbamate and at 0,73 mmol/l for the C12-Y-amine (di)carbamate respectively. Comparing the CMC results of C12-Y-amine before and after CO₂ exposure forms, amine form and its corresponding forms had similar CMC values to each other but slightly lower CMC value was determined for C12-Y-amine. This might be caused by the head groups of the carbamate forms. They have anionic charge groups and their head groups gain polarity and thus surface activity.

4.6 Toxicity Test with Microtox

For C12-Y-amine and its carbamate forms toxicity tests were performed with Microtox. EC₅₀ was calculated at two different time intervals (5 and 15 min). The results are shown in Table 3.

Table 3 Microtox toxicity test of C12-Y-amine and its carbamate forms

	EC₅₀ after 5 min	EC₅₀ after 15 min
<i>C12-Y-amine</i>	4.8 ppm	3.9 ppm
<i>C12-Y-amine (mono)carbamate</i>	15.6 ppm	12.4 ppm
<i>C12-Y-amine (di)carbamate</i>	35.7 ppm	24.0 ppm

The toxicity test indicates that C12-Y-amine can be considered toxic to the marine organism but its carbamate forms can be considered environmentally safe molecules. This can be the results of polar head groups because alkyl chains in both amine and its carbamate forms are the same but carbamate forms have charged head groups comparing to the original form.

According to Microtox test results C12-Y-amine (di)carbamate could be accepted as the most environmentally substance and C12-Y-amine (mono)carbamate might be considered to be intermediate environmentally safe substance but C12-Y-amine can be known toxic chemicals.

4.7 Algae Toxicity Test

The NOEC (No Observed Effect Concentration) and LOEC (Lowest Observed Effect Concentration) estimations were determined for C12-Y-amine, C12-Y-amine (mono)carbamate and C12-Y-amine (di)carbamate. The values of ErC₁₀ and ErC₅₀ could be considered as estimations only with the reason of the test concentrations that are spaced widely. (See Table 4)

Table 4 Algae toxicity test of C12-Y-amine and its carbamate forms

	NOEC	LOEC	ErC₁₀	ErC₅₀
<i>C12-Y-amine</i>	0.01 ppm	0.1 ppm	0.0181 ppm	0.0552 ppm
<i>C12-Y-amine (mono)carbamate</i>	< 0.01 ppm	0.01 ppm	0.00361 ppm	0.069 ppm
<i>C12-Y-amine (di)carbamate</i>	0.1 ppm	1 ppm	0.26 ppm	0.9 ppm

Since the characteristic of test chemicals is poorly soluble, it was observed that excessive variation occurred between replicates in the C12-amine (mono)carbamate. The results are sufficient to determine the toxicity estimation, that was between C12-Y-amine and C12-Y-amine (mono)carbamate, which was surprisingly similar, yet precise distinction between two chemicals was impossible through a screening study. Also according to aquatic toxicity results, C12-Y-amine and its corresponding carbamate forms indicated toxicity to algae and further testing needs to be done.

4.8 Reverse Reactions

4.8.1 Synthesis of C12-Y-amine from C12-Y-amine (mono)carbamate

The C12-Y-amine (mono)carbamate was successfully switched back to C12-Y-amine form with N₂ gas exposure and applied heating at 95°C for 4h (Figure17).

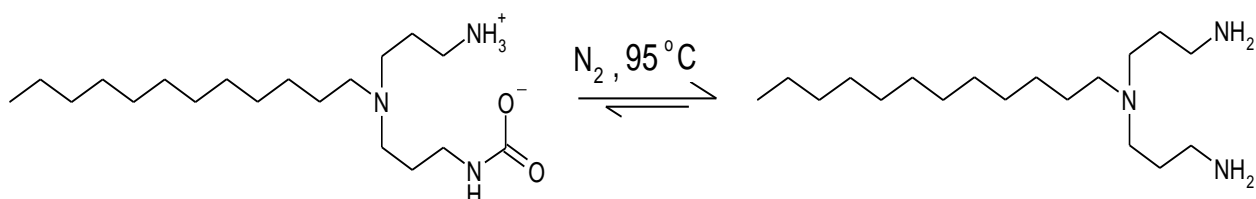


Figure 17 Reversed reaction of (mono)carbamate

The conversion of C12-Y-amine (mono)carbamate back to C12-Y-amine was proven by ^1H NMR (Figure 18). After N_2 gas treatment and heating applied, the signal of the methylene group at 3.0-3.1ppm was reduced as the original amine form was switched back by carbamate salt after 4h.

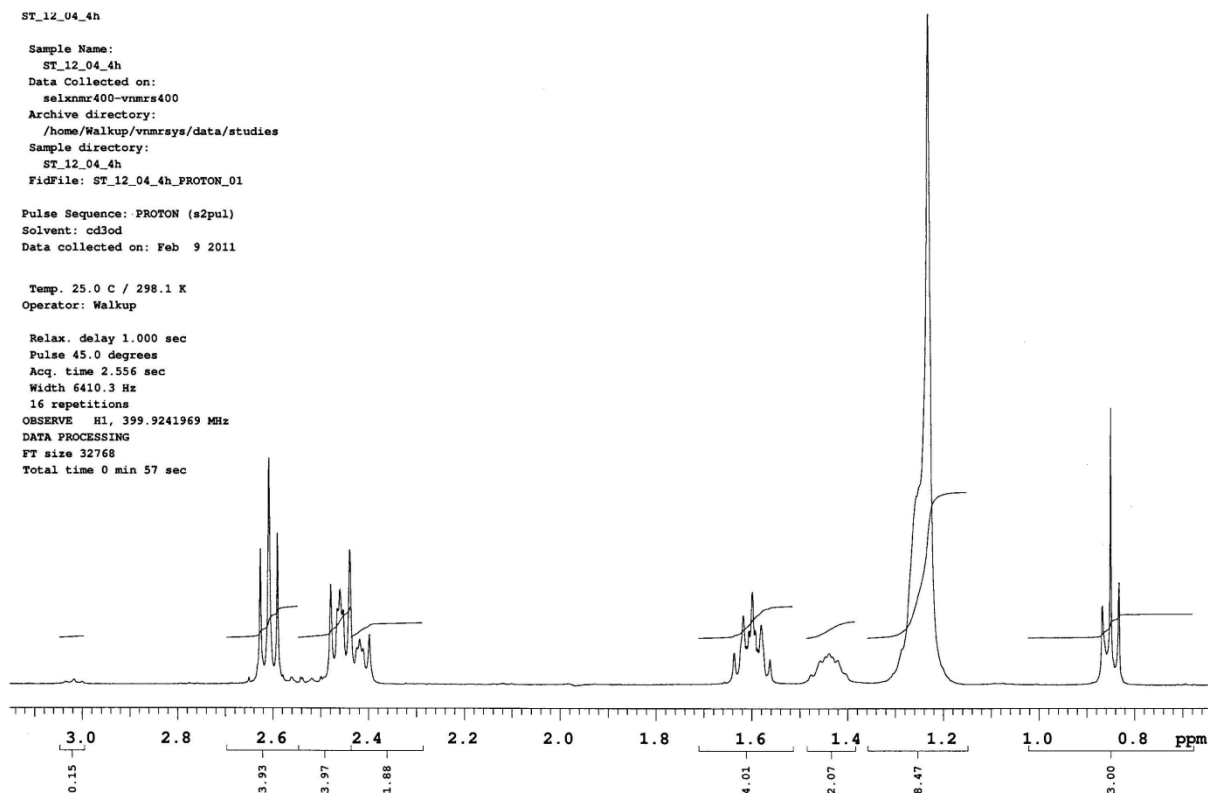


Figure 18 ^1H NMR spectrum of reversed (mono)carbamate upon heating at 95°C and expose N_2 gas (CD_3OD)

4.8.2 Synthesis of C12-Y-amine from C12-Y-amine (di)carbamate

The reversing of C12-Y-amine (di)carbamate to its original amine form was performed with N_2 gas exposure and heating applied at 95°C for 6h. (Figure 19)

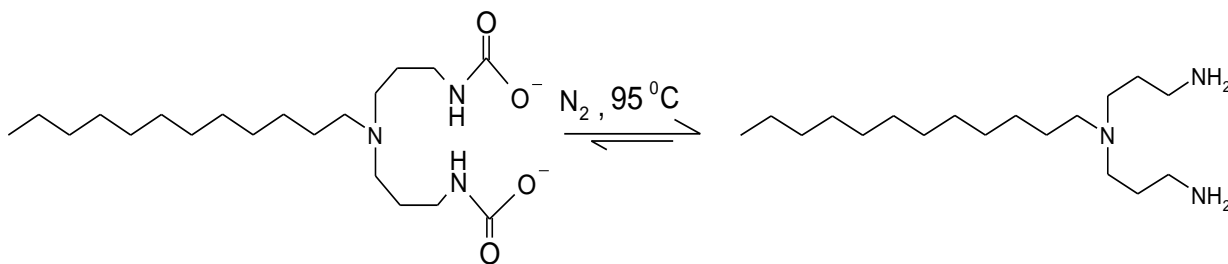


Figure 19 Reversed reaction of (di)carbamate

The conversion of C12-Y-amine (di)carbamate to its original amine form (C12-Y-amine) was identified by NMR spectrometer. The ^1H NMR spectrum of reversed C12-Y-amine (di)carbamate showed similar to C12-Y-amine (mono)carbamate ^1H NMR spectrum. After N_2 gas exposure and heat application, the methylene group signals at 3.0-3.1ppm was decreased as the original amine form was switched back by (di)carbamate salt after 6h (Figure 20).

The differences between (mono)carbamate and (di)carbamate reversibility to form its original amine form is that (di)carbamate reversing reaction needed more energy to switch it back to C12-Y-amine. This can be explained as (di)carbamate form has more carbamate group than (mono)carbamate form and the reversal of (di)carbamate required more energy.

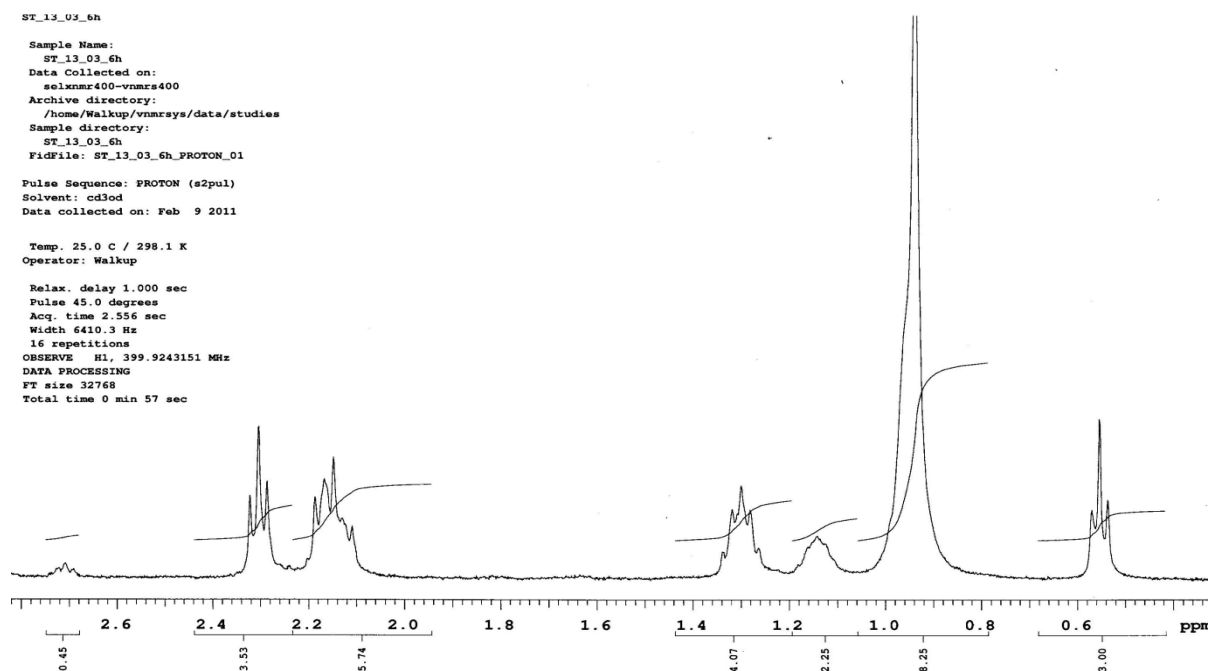


Figure 20 ^1H NMR spectrum of reversed (di)carbamate upon heating at 95°C and expose N_2 gas (CD_3OD)

5 Conclusion

N, N-di(propylamino) dodecylamine (C12-Y-amine) was purified via vacuum distillation and its corresponding two carbamate forms were synthesized to examine the ability as a switchable surfactant.

N, N-di(propylamino) dodecylamine (C12-Y-amine) easily reacted with CO₂ to produce its corresponding carbamate forms. An optimal formation of (mono)carbamate forms was a consequence of reaction temperature at 50°C, a high CO₂ flow with stirring and an optimal formation of (di)carbamate forms was a result of reaction temperature at 50°C, a high CO₂ flow accompanying with adding NaOH, and stirring.

Reversibility of the surfactant from its corresponding carbamate forms to the original amine form was accomplished with a high N₂ gas flow and stirring at 95°C. The reversibility concept is favourable environmentally and economically due to the possibility of recovering and reusing the compounds in different beneficial applications.

Although the surfactant molecule was reversibly changed to another form by activation of triggers, there was no indication of significant changes in the surface activities. According to CMC measurements, carbamate forms have slightly lower surface activity when compared to original amine forms. It was considered that charged groups in the carbamate forms gain polarity and thus surface activity.

Microtox test indicated that C12-Y-amine is toxic but its corresponding carbamate forms are environmentally friendly. On the other hand, algae toxicity test estimations indicated higher toxicity for C12-Y-amine and its (mono)carbamate but lower for its (di)carbamate form.

Emulsion studies were performed for both amine form and its corresponding carbamate forms. Emulsions consisting of C12-Y-amine had long term stability whereas its corresponding carbamate forms had very short term stability.

All in all, the C12-Y-amine is a switchable surfactant meaning that it switches from amine to its corresponding carbamate forms by heating in CO₂ atmosphere and it switches back to the amine form by N₂ exposure and heating.

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