

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

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# **Surfactant-Chelating Agent Interactions**

## **Impact on Bulk and Surface Properties**

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Gothenburg, Sweden, 2024

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Licentiatuppsatser vid Institutionen för kemi och kemiteknik

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Nr 2024:19

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Printed by Chalmers Reproservice

Gothenburg, Sweden, December 2024

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## **Abstract:**

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The influence of chelating agents on the self-assembly process in surfactant solutions remains largely unexplored and merits further study. Traditionally, chelating agents are seen as salting-out ions that promote surfactant separation. However, the opposite effect has been observed with iminodipropionate-based surfactants, where aminopolycarboxylate chelating agents increase the solubility of nonionic ethoxylated surfactants in mixed micellar systems. In this work, specific interactions between chelating agents and surfactants are hypothesized to influence both the self-assembly process and the macroscopic properties of surfactant formulations.

To investigate these interactions and their relationship to the chemical structures of the surfactant and chelating agent, NMR spectroscopy was employed, focusing on  $^{13}\text{C}$  chemical shift and line shape analysis. Moreover, the impact of these interactions on the formulation properties was assessed by measuring cloud point, viscosity, surface tension, and contact angle on hydrophobic surfaces.

The study reveals that interactions between the head group of amphoteric surfactants and chelating agents lead to the formation of oligomeric surfactant analogues with larger hydrophilic moieties, resulting in smaller, more spherical micelles. The strength and likelihood of these interactions depend on several factors, including the presence of oppositely charged moieties, neighboring groups near the interacting atoms, and the volume-to-length ratio of the surfactant. The interaction offers possibilities for tuning the aggregation behavior of systems containing surfactants and chelating agents, and consequently, the macroscopic properties of the formulation.

**Keywords:** Amphoteric surfactants, Chelating agents, NMR spectroscopy



## List of publications

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### Paper I

**The role of chelating agent in the self-assembly of amphoteric surfactants**

Josmary Velásquez, Lars Evenäs, Romain Bordes.

*Journal of Colloid and Interface Science*, 2024, vol. 676, p. 1079-1087.

### Paper II

**Amphoteric Surfactant-Chelating Agents Interactions: Impact on Bulk and Surface Properties**

Josmary Velásquez, Sarah Lundgren, Lars Evenäs, Romain Bordes.

*Manuscript*

## **My contributions to the Publications**

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### **Paper I**

Main author. Conducted all experimental work, data interpretation, visualization, and was responsible for writing and editing.

### **Paper II**

Main author. Conducted all experimental work except for surface tension and contact angle measurements in binary systems. Responsible for data interpretation, visualization, writing, and editing.

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# 1

## Introduction

Cleaning is the process of removing unwanted substances—such as dirt, infectious agents, and other impurities—from a surface. It is conducted in various contexts and employs numerous methods. Detergency refers to the process by which formulations of surface-active agents, commonly called detergents, are used to lift and displace unwanted deposits. In a typical cleaning process, there are multiple components: the object to be cleaned (substrate), the soil or unwanted deposit to be removed, the cleaning solution applied to the substrate, and often a mechanical or thermal action. Each of these components can vary in terms of properties, composition, and method of application.

The detergency process is inherently complex, due to the diverse and intricate nature of both soils and surfaces involved. Soils can be categorized into three types: organic, inorganic, a combination thereof. Organic soils, including food residues (such as fats, proteins, and carbohydrates), living organisms (like mold and bacteria), and petroleum-based substances (such as motor oil), are traditionally removed using alkaline cleaners or solvents. In contrast, inorganic soils—such as rust, mineral deposits, and scale—often require acidic or specialized cleaners to remove them effectively. The most challenging soils are of combined nature, which contain both organic and inorganic elements.

In addition to soil complexity, surface characteristics—such as roughness, porosity, and texture—affect the cleaning process, thereby influencing the adhesion between the soil and surface. The strength of this adhesion depends on factors like wettability and molecular

interactions, making it particularly challenging to remove soils when they share similar polarity with the surface.

Surfactants are central to detergent formulations, with their amphiphilic nature (possessing both hydrophilic and hydrophobic moieties) allowing them to migrate to interfaces and to decrease surface free energy, facilitating soil removal. The role of surfactants in influencing surface free energy and their relation to cleaning processes are presented in the section “Physicochemical Principles of Detergency.”

To achieve effective cleaning, formulations typically combine multiple ingredients beyond surfactants, including solubilizers and chelating agents. Solubilizers serve as coupling agents, integrating surfactants, solvents, and inorganic salts into a homogeneous solution. Chelating agents bind to divalent ions, enhancing the cleaning action of detergents.

The functions required of other essential ingredients in cleaning formulations are continuously evolving, shaped not only by technical needs but also by the practices and preferences of detergent producers and the regions in which they are used. One key aspect of this field is the availability of multiple, nearly equivalent technical solutions to achieve the desired outcomes. In this context, the result—achieving the necessary function—takes precedence, while the choice of ingredients is just one part of the process<sup>1-3</sup>. Often, different products or systems can be proposed to meet the same specifications with similar efficacy. For instance, hydrotropes and secondary surfactants can both be used to improve solubility, and similarly, chelating agents and some polymers can both be applied to control water hardness and prevent redeposition. The focus of this work will be on hydrotropes, secondary surfactants, and strong chelating agents, which play critical roles in cleaning formulations. Each of these components will be discussed in separate sections.

A common challenge in surfactant formulations involves the salting-out effect caused by chelating agents<sup>4,5</sup>, which leads to micellar growth and precipitation due to their strong hydration and water-structuring properties. A significant amount of information exists on interactions between traditional chelating agents, such as EDTA, and surfactants. However, molecular-level investigations into systems containing readily biodegradable chelating agents, such as MGDA and GLDA, remain unexplored. To address this gap, this work investigates how amine-based surfactants interact with chelating agents, the properties of

these interactions and the effects they have on bulk and surface properties of surfactant-based formulations.

The techniques used to evaluate these interactions and their effects on the surface and macroscopic properties of formulations are discussed in the experimental methods. To study the molecular interactions between amphoteric surfactants and chelating agents, a series of experiments by NMR spectroscopy were conducted, including analyses of chemical shift variations, line shape, and self-diffusion. To assess the effects of amphoteric surfactant-chelating agent interactions on the macroscopic properties, properties such as surface tension, contact angle, cloud point, and viscosity were evaluated.

## 1.1. Purpose and Objectives

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This study explores the interactions between surfactants and aminopolycarboxylic chelating agents, a relatively underexplored area despite their widespread industrial use. By gaining a deeper understanding of these systems, it is possible to design formulations that capitalize on these interactions to reduce salting-out effects, enhance the solubility of complex surfactant mixtures, and control surface properties. Ultimately, the goal is to provide insights that will guide the development of more efficient and sustainable cleaning formulations for various industrial applications.

The objectives of this work were divided into three main areas: (i) developing an experimental framework to identify the presence of interactions between surfactants and chelating agents, (ii) evaluating the structure-property relationships that drive these interactions, and (iii) assessing the effects of these interactions on the macroscopic properties of surfactant systems.

- (i) In Paper I, a detailed description of the NMR methods used to identify interactions between surfactants and chelating agents is provided, particularly focusing on the variation of chemical shifts with surfactant concentration. Paper II further expands on this framework by incorporating line shape analysis of  $^{13}\text{C}$  NMR signals, enhancing the methodology.
- (ii) The structure-property relationships driving the interactions between surfactants and chelating agents were primarily explored in Paper II. By analyzing a series of amine-based surfactants in combination with polycarboxylic acid-type chelating

agents, the study highlighted how various factors, such as branching, the nature of the surfactant head group, and the volume-to-length ratio of the surfactant, influenced the strength and characteristics of these interactions. This analysis provided key insights into how structural features of both components affect the overall system behavior.

- (iii) The effects of surfactant-chelating agent interactions on macroscopic properties, including cloud point, viscosity, surface tension, and contact angle, were evaluated in both Paper I and Paper II. These studies assessed how the molecular interactions influenced the overall behavior of the surfactant systems at the macroscopic level.



## Physicochemical Principles of Detergency

Effective detergency relies on multiple processes occurring simultaneously and synergistically. First, the cleaning solution must wet both the substrate and the soil, altering the interfacial properties at phase boundaries within the system. Simultaneously, simple solvation or liquid mediated removal of the dirt may occur. In many cases, mechanical agitation, such as rubbing or shaking, provides shearing action that helps separate the soil from the substrate and promotes mass transfer within the system. Once the soil detaches, it must be suspended, solubilized, or emulsified by the cleaning solution. Finally, the contaminated solution is removed (*e.g.*, by rinsing or wiping) to prevent redeposition on the surface.

Surfactants and chelating agents are crucial in detergent formulations. Simple cleaning products, like window cleaners, may rely solely on these two ingredients. However, more sophisticated formulations often contain a range of additives that improve cleaning performance and deliver specific benefits. Enzymes, for instance, are added to facilitate the hydrolysis of specific soils, bleaching agents to remove colored stains, and optical brighteners to enhance whitening. Polymers help prevent soil redeposition and inhibit crystal growth. Perfumes, dyes, and foam control agents adjust the sensory and functional properties of the product, while solubilizers help to integrate the different ingredients into a homogeneous solution. All ingredients are contributing to the overall efficacy of the detergent solution.

This study focuses on understanding the physicochemical behavior and molecular interactions in simple cleaning formulations, such as the one described in the preceding paragraph. The following sections will describe the key ingredients in cleaning products and explore their mechanisms of action, starting with surfactants and correlating their physicochemical properties to each stage of the cleaning process.

## **2.1. Surfactants**

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A typical detergent formulation relies heavily on surfactants—amphiphilic molecules that contain both hydrophilic (water-attracting) and hydrophobic (water-repelling) moieties. This dual affinity drives surfactants to migrate to interfaces, such as water-air or water-oil boundaries, resulting in a change in surface free energy. In this context, the terms "hydrophilic" and "hydrophobic" are often referred to as "lipophobic" (fat-repelling) and "lipophilic" (fat-loving), respectively.

Surfactants consist of an alkyl chain, typically with 8–22 carbon atoms, and a functional head group that interacts with water. Based on the head group, surfactants are classified as ionic or nonionic. Ionic surfactants dissociate into ions in water and are further divided into anionic, cationic, zwitterionic and amphoteric. Anionic surfactants have a negatively charged head group, while it is positively charged for cationic surfactants. Zwitterionic surfactants bear both positive and negative charges on the head group, whereas amphoteric surfactants change their ionization state with the pH of the solution. Nonionic surfactants, in contrast, have no ionic charge and therefore do not ionize in water. In detergent formulations, anionic and nonionic surfactants have historically been the most widely used, with nonionic surfactants valued for their superior ability to emulsify oils and remove organic soils.

### **2.1.1 Surfactant Solubility and Phase Separation**

The solubility of surfactants in different solvents is governed by several interrelated parameters. One of the primary factors is the structure of the surfactant, particularly the balance between its hydrophilic and lipophilic moieties. Surfactants with larger hydrophobic chains and smaller or less polar hydrophilic groups tend to have reduced water solubility but are more soluble in non-polar solvents. This structural balance directly

influences the behavior of the surfactant in different solvent environments, determining whether it predominantly dissolves in water or oil.

Temperature is another critical factor that affects surfactant solubility, and two concepts are widely used to describe this dependence: the Krafft temperature and the cloud point. The Krafft temperature, typically relevant to ionic surfactants, refers to the temperature below which surfactant molecules, when in a solution above the CMC, form insoluble hydrated solids with crystalline features. Above this temperature, the molecules form micelles.

While the solubility of many ionic surfactants increases with rising temperature, nonionic surfactants containing polyoxyethylene chains behave differently, showing decreased solubility as temperature increases. This is described by the cloud point, the temperature above which the surfactant solutions (typically at 1wt%) separate into a surfactant-rich phase and a dilute aqueous phase, initially visible as cloudiness. The onset of turbidity is influenced by factors like polyoxyethylene chain length and, to a lesser extent, the hydrophobic chain length, as well as surfactant concentration and cosolutes. There are two widely accepted models to explain this behavior<sup>6</sup>.

The first model attributes solubility to hydrogen bonds between water molecules and ether oxygen in the ethylene oxide chain. As temperature increases, these bonds weaken, leading to dehydration of the polyoxyethylene chains and decreased solubility.

The second model emphasizes the conformational flexibility of polyoxyethylene chains, which can adopt various structural forms with different energies and polarities. At lower temperatures, a low-energy, highly polar conformation dominates, reinforcing interactions with water. With increasing temperature, higher-energy, less polar conformations become more prevalent, reducing hydration and polarity. This shift favors stronger surfactant-surfactant interactions, closer head group packing, and an increased tendency for phase separation.

The Krafft point concept is generally not relevant for cleaning applications because the presence of impurities or additives in cleaning formulations lowers the Krafft point, much like solutes depress the freezing point of a solvent. In practice, this means the Krafft point for cleaning products is always below standard operating temperatures, making it less of a concern. In contrast, the cloud point is of critical importance. It affects both product shelf

stability and cleaning efficiency. Cleaning formulations are typically designed so that the cloud point is above room temperature, ensuring that the formulation remains stable and well-dispersed during storage. At the same time, the cloud point should be just above the optimal cleaning temperature, as numerous studies indicate that detergency is most effective near, but below, this threshold<sup>7,8</sup>. This balance maximizes both product stability and cleaning performance, making the cloud point a key consideration in detergent formulation.

### 2.1.2 Adsorption and Surface Activity

The amphiphilic nature of surfactants drives them to adsorb at interfaces, such as air/water or oil/water. When surfactant molecules migrate to these interfaces, they arrange themselves in a specific orientation: their hydrophilic heads face the aqueous phase, while their hydrophobic tails avoid contact with water. This process is driven by a reduction in free energy, as the removal of the hydrophobic segments from the water prevents the cavity formation needed to accommodate the hydrophobe in solution<sup>6,8,9</sup>. A phenomenon known as hydrophobic effect.

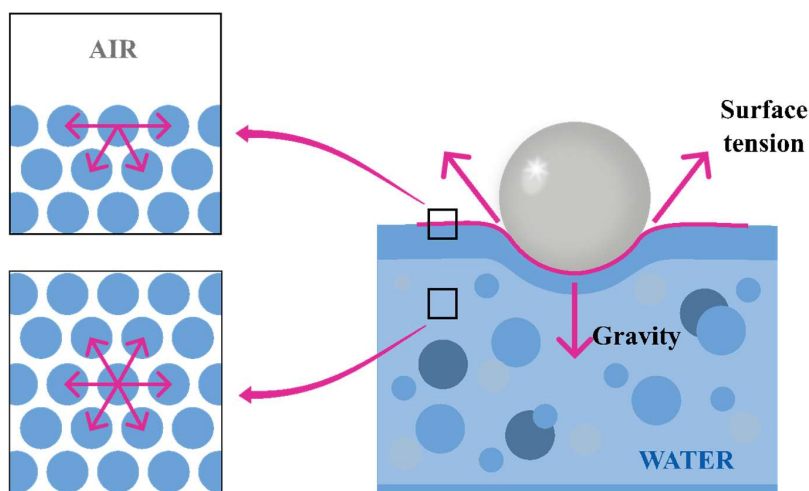


Figure 1. Illustration of surface tension at the liquid-air interface, highlighting the imbalance of cohesive forces experienced by molecules at the surface compared to those in the bulk. This results in higher energy for surface molecules.

At air-water or oil-water interfaces, the orientation of surfactants is relatively straightforward: the hydrophilic head group faces the water, while the lipophilic tail extends



into the second phase. However, the adsorption of surfactants at surfaces other than air, such as solid or oil/water interfaces, is more complex, as the process is influenced not only by the hydrophobic effect but also by the energy gained when interactions between the surface and surrounding water are replaced with interactions between the surface and surfactant molecules. As a result, the nature of the solid surface, in combination with the type of surfactant, determines both how the surfactant molecules adsorb and the morphology of the adsorbed layer.

One of the key effects of surfactant adsorption is the reduction of interfacial tension. Interfacial tension refers to the cohesive forces at the boundary between a liquid and another phase, such as air (denoted surface tension) or oil. Molecules at the surface of the liquid experience fewer cohesive forces than those in the bulk, due to the lack of neighboring molecules on one side; this imbalance in interaction results in a greater tendency for the molecules at the surface to interact with their neighboring molecules (Figure 1). In a solid, the excess energy is referred to as surface free energy.

When surfactants are introduced to water, they align at the interface, where interactions between the surfactant head groups and water molecules, along with van der Waals forces between the hydrophobic tails and the second phase (lipophilic, such as solid or oil), or between the tails themselves (if the second phase is air), balance the forces at the interface. These increased interactions at the interfacial region result in a decrease in the interfacial tension.

### **2.1.3 Wetting**

Wetting refers to the ability of a liquid to spread over a surface, displacing a second fluid, such as air. The extent to which a liquid spreads, known as wettability, depends on the properties of both the liquid and the surface. Wettability is governed by two types of forces: adhesive forces between the liquid molecules and the surface, promoting wetting, and cohesive forces within the liquid, which encourage the liquid to bead up. The balance between these forces determines whether the liquid wets the surface or forms a droplet.

To quantify wettability, the contact angle ( $\theta$ ) formed between the liquid and solid surface can be measured (Figure 2). According to Young's equation, this contact angle is related to the surface free energies between the solid, liquid, and the surrounding fluid (often air).

A smaller contact angle indicates better wetting, with angle less than  $90^\circ$  suggesting favorable wetting, meaning that the liquid spreads more across the surface. Conversely, a contact angle greater than  $90^\circ$  implies poor wetting, where the liquid tends to minimize its contact with the surface, forming a more spherical droplet.

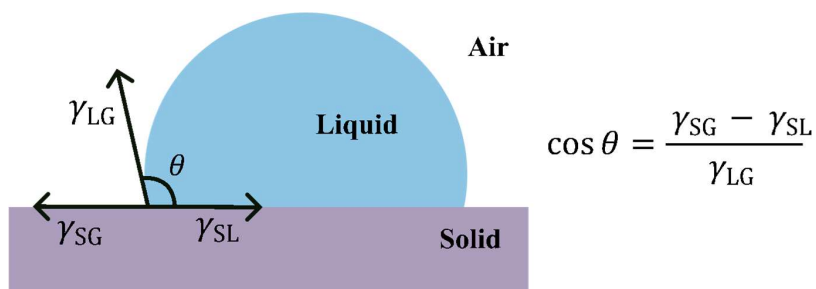


Figure 2: Contact angle measurement illustrating the variables in the Young's equation. The contact angle ( $\theta$ ) is shown at the interface where a liquid droplet meets a solid surface, with forces represented as surface tensions at the liquid-solid ( $\gamma_{SL}$ ), liquid-vapor ( $\gamma_{SG}$ ), and solid-vapor ( $\gamma_{LG}$ ) interfaces. The Young equation relates these forces to determine the equilibrium contact angle.

By lowering the interfacial tension at the interfaces between pairs of components - such as the detergent solution and the soil or the detergent solution and the solid surface - the adhesive forces binding the soil to the surface are diminished, facilitating its removal.

#### 2.1.4 Micellization

When a surfactant is added to water, it is initially present as single entities, or unimers, dissolved in the solution. As introduced earlier, the hydrophobic portion of each unimer disrupts the water structure, raising the free energy of the system. To counteract this, unimers migrate to interfaces, accommodating their lipophilic chains by orienting them away from the water. Another way to reduce free energy is through self-association, where unimers form micelles, incorporating the hydrophobic groups inward while the hydrophilic heads face the solvent. However, adsorption and micellization involve trade-offs, such as restricted molecular freedom and, for ionic surfactants, electrostatic repulsion within the micelle, which counteract this tendency. Ultimately, the occurrence and concentration above which micellization appears, reflect the balance between forces that promote and resist self-association.

Micellization can be demonstrated by measuring various physicochemical properties of the solution as the surfactant concentration increases. At the point of micelle formation, nearly all measurable physical properties of solutions undergo a sharp change (Figure 3), particularly those associated with the size or number of entities in solution, such as conductivity, light scattering, or osmotic pressure. This behavior is unique to systems undergoing self-association, other solutes show gradual changes in the properties as the concentration increases. This specific concentration above which self-association takes place is known as the critical micelle concentration (CMC), often determined by evaluating changes in surface tension.

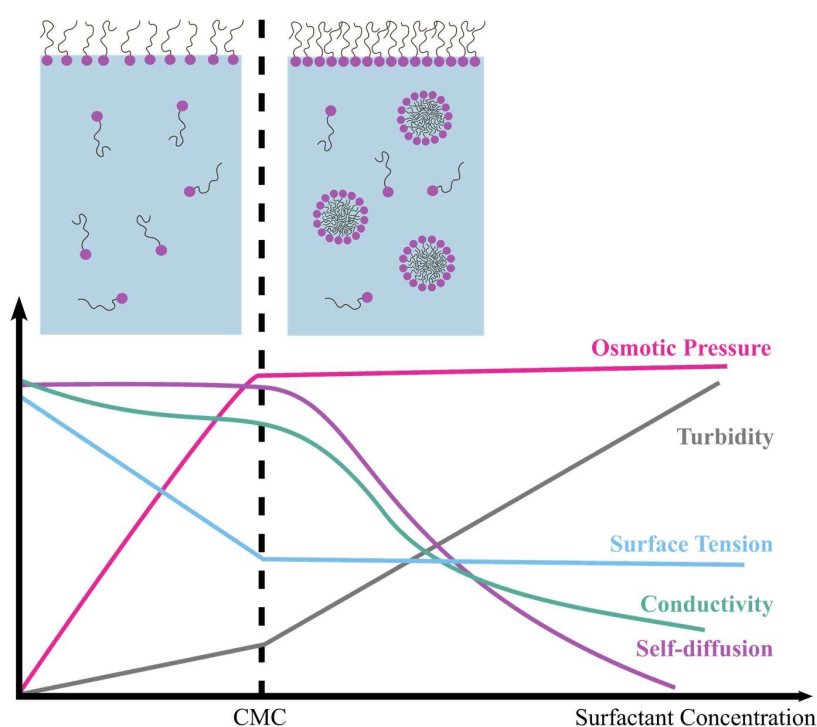
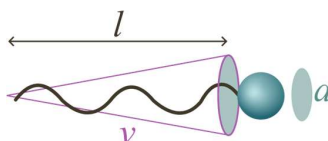


Figure 3: Plot illustrating changes in physicochemical properties—such as viscosity, surface tension, and turbidity—as surfactant concentration increases. The accompanying sketches depict the micellization process: at low concentrations, surfactant molecules are dissolved as individual units, while at higher concentrations, beyond the CMC, they aggregate into micelles.

While spherical micelles are the most commonly observed structures, surfactant molecules can self-assemble into a variety of geometries, including rod-like micelles, vesicles, and others. The shape of these aggregates is largely determined by the molecular structure of

the surfactant, and this relationship can be described using the Critical Packing Parameter (CPP). The CPP is calculated as

$$\text{CPP} = \frac{v}{a \cdot l}$$


The diagram illustrates a surfactant molecule. A double-headed arrow above the molecule is labeled 'l', representing the length of the hydrophobic tail. A purple shaded area at the end of the tail is labeled 'v', representing the volume of the tail. To the right of the tail is a blue sphere representing the hydrophilic headgroup, with a green shaded area next to it labeled 'a', representing the surface area of the headgroup at the aggregate surface.

where  $v$  is the volume of the surfactant tail,  $l$  the length of the surfactant tail, and  $a$  the surface area of the hydrophilic headgroup at the aggregate surface. It is well established that a CPP value of  $1/3$  corresponds to spherical micelles,  $1/2$  to cylindrical micelles,  $1$  to lamellar micelles, and values greater than  $1$  to reverse micelles. This parameter links molecular shape to aggregate geometry, influencing bulk properties such as the viscoelasticity of the solution<sup>10</sup> and solubilization capacity<sup>11</sup>.

Above CMC, micelles and unimers coexist in a dynamic equilibrium, where surfactant molecules continuously associate and dissociate from micelles. In this manner, micelles act as a reservoir of surfactant molecules, ready to migrate to new surfaces as they appear, such as when a surfactant solution spreads over a solid substrate.

### 2.1.5 Micellar Solubilization

When a third component, such as a hydrocarbon, is added to an aqueous surfactant solution, its behavior depends on the presence and type of micelles. Below the CMC, the solubility of the additive is similar to its solubility in water. Above the CMC, however, the solubility of the hydrophobic compound often increases significantly. For non-polar compounds like oils, micelles swell by incorporating some of the oil, allowing solubilization to occur within the lipophilic core of the micelle.

An important variable in the solubilization of oily matter in micellar systems is therefore the concentration of surfactant. Soil removal only becomes significant above the CMC<sup>12,13</sup>, and reaches its maximum at concentrations several times the CMC. At high surfactant concentrations (10-100 times the CMC), a substantial amount of oily matter can be solubilized, whereas at lower surfactant concentrations, only minor quantities of oil are solubilized. In the latter case, the remaining oil must be suspended in the solution in the form of a dispersion, e.g. as an emulsion, a topic that will be discussed later. Therefore, it

is essential that surfactant concentrations in cleaning formulations exceeds the CMC by several orders of magnitude to guarantee that micelles are present in sufficient quantities.

Solubilization in micellar systems is influenced not only by the nature of the additive but also by several formulation parameters, such as temperature, electrolyte concentration, and surfactant type. For instance, nonionic ethoxylated surfactants exhibit greater affinity for oil as temperature increases, leading to the formation of oil-in-water emulsions at lower temperatures and water-in-oil emulsions at higher temperatures. The temperature at which this inversion occurs is known as the Phase Inversion Temperature (PIT). At the PIT, the oil-water interfacial tension reaches a minimum, leading to maximum solubilization of non-polar materials. For both polyoxyethylene nonionic surfactants and polyoxyethylene nonionic - anionic mixtures the optimal oily soil detergency has been correlated with the PIT<sup>14,15</sup>. There is also a notable correlation between the PIT in emulsions and the cloud point in solutions of nonionic ethoxylated surfactants, which also extends to cleaning performance<sup>16-18</sup>.

### **2.1.6 Dispersions**

A dispersion refers to a system where small particles, droplets, or bubbles of one substance are distributed throughout another substance, the continuous phase, typically through mechanical energy input such as stirring or agitation. In cleaning processes, the main types of dispersions are emulsions, suspensions, and foams.

#### **Emulsions:**

An emulsion involves two immiscible liquids, oil and water, where one liquid is dispersed as tiny droplets within the other. The main difference between micellar solubilization and emulsions is that micellar solubilization is thermodynamically stable, while emulsions can only be kinetically stable; it implies that an energy input is required. Without stabilization, the liquids in an emulsion would quickly separate, *i.e.* they will form 2 macroscopic phases. To create a stable emulsion, an emulsifying agent, typically a surfactant, is used. Surfactants reduce the interfacial tension between the two liquids, allowing the droplets to form. Additionally, surfactants form an interfacial film around the droplets that prevents them from coalescing immediately. The stability of an emulsion depends on the strength of

this film and the reduction of interfacial energy, which can be enhanced by adding fine particles or creating steric and electrostatic barriers to prevent droplets from coalescing.

### **Suspensions:**

A suspension is a dispersion where non-soluble solid particles are distributed in a liquid phase. The stability of the suspension is a concern, as particles tend to settle or agglomerate without proper stabilization. To prevent this, electrostatic barriers are formed by adsorbing similarly charged ions or surfactants onto the particle surfaces, creating repulsion between particles. Additionally, steric barriers created by bulky molecules, such as non-ionic surfactants with long hydrophilic head groups, can prevent particles from clumping together by forming a physical shield around them.

### **Foams:**

Foams are dispersions of gas in a liquid or solid; the focus of this work is on liquid foams. These are systems in which gas bubbles are trapped within a thin liquid film. Like emulsions and suspensions, foams are inherently unstable.

Emulsions, suspensions, and foams, serve as medium to carry away dirt that has been removed from surfaces during cleaning. Foams, in particular, besides being a carrier also enhance the sensory properties of cleaning formulations, making them more appealing to users. In household applications foaming is associated by consumers with the quality of the cleaner and provides visual clues on the performance of cleaning products. In industrial and institutional (I&I) settings, foaming can bring benefits such as low-water cleaning and improved adhesion to vertical surfaces. However, many I&I cleaning processes require low-foaming formulations, especially when mechanical energy is involved, to prevent issues like pressure build-up or difficulties in rinsing large amounts of foam, which can flood industrial areas.

## **2.1.7 Soil Removal Mechanisms**

Cleaning and detergency are highly complex processes, largely due to the vast variety of soils, substrates, and ingredients in cleaning formulations. The following discussion focuses on the action of surfactants on soil removal process.

In general, cleaning takes place in two equally important steps: removing soil from the substrate and suspending the soil in solution to prevent redeposition. Soils that surfactants can remove are typically attached to the substrate either through physical adsorption (via van der Waals forces or dipole interactions) or by electrostatic forces. These soils are often further classified into particulate soil and oily soil.

Surfactants are effective in removing both types of soils, though the mechanisms involved are different.

Particulate soils tend to detach spontaneously when both the particle and the surface have similar net charges, which is often the case because both soils and surfaces typically carry a negative charge. If the two surfaces have opposite charges, removal is facilitated by actively inducing similar charges on both the soil and substrate surfaces. This creates a diffuse layer of counterions near the soil and substrate, which promotes an osmotic flow of water into the area, easing the desorption of solid particles. (Figure 4)

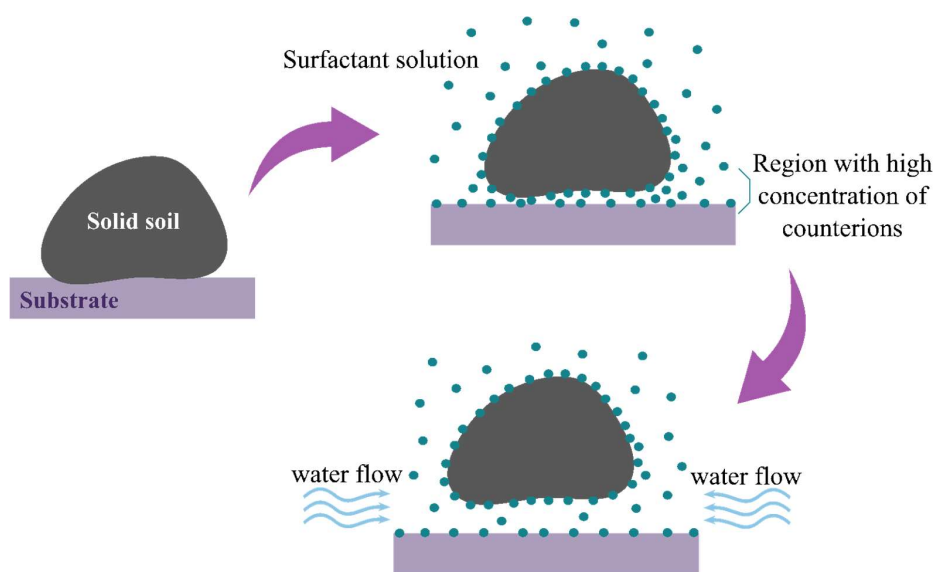


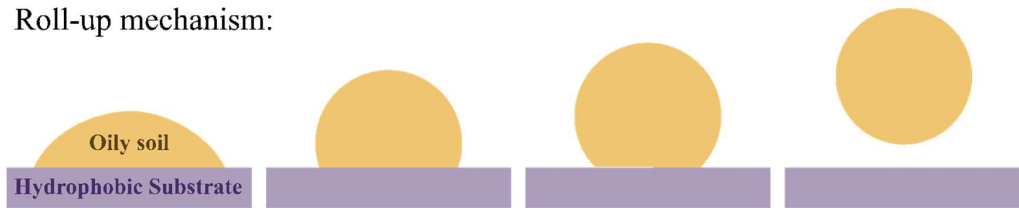
Figure 4. Mechanism of particulate soil detachment from surfaces. When both the particle and substrate have negative net charges, or like charges are induced, a diffuse layer of counterions forms, creating an osmotic flow of water into the interface. This flow facilitates the desorption of particulate soil from the surface.

A simple and effective way to induce charge formation on both soil and surface is to raise the pH of the surrounding solution. Increasing the pH can deprotonate neutral functional groups, such as carboxylic or phenolic groups, at the surfaces resulting in negative charges

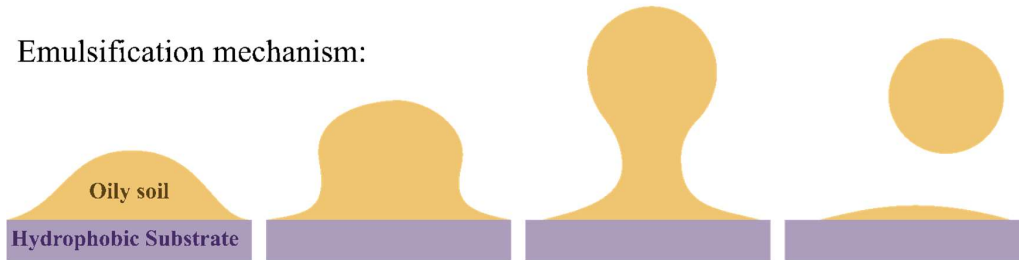
on both the soil and substrate; conversely acidification may protonate amines. This of course is highly dependent on the chemistry of the soil and the substrate.

Liquid soils are usually removed by the roll-back or roll-up mechanism, (Figure 5) which can also apply to solid soils that can be liquefied through thermal action or by the use of additives. In this mechanism, the contact angle of the liquid soil with the surface increases as surfactant from the cleaning solution enters the crevices between the soil and the substrate and adsorbs at both surfaces. The resulting osmotic flow may also promote the detachment of the soil, similar to the process with particulate soils described above.

Roll-up mechanism:



Emulsification mechanism:



Solubilization mechanism:



Figure 5. Mechanism of liquid soil removal from surfaces. In the roll-back or roll-up process, surfactants from the cleaning solution penetrate the crevices between the soil and substrate, increasing the contact angle of the liquid soil with the surface and creating an osmotic flow that aids in detachment. For hydrophobic substrates, however, soil removal relies on lowering the oil-water interfacial tension, allowing the surfactant to either solubilize or disperse the soil through micellar solubilization or emulsification.

For hydrophobic substrates, oily soil may wet the surface, rendering the roll-up mechanism less relevant. In that case, removal relies on reducing the interfacial tension between the oil



and the surrounding water. The surfactant primarily acts on the oil-water interface, while its adsorption at the substrate-water interface plays a less important role in soil removal.

When a sufficiently low interfacial tension is achieved by the surfactant, soil removal can occur via two distinct mechanisms, which may operate independently or in parallel: micellar solubilization and emulsification (Figure 5). In both cases, the oily soil is either solubilized or dispersed in the washing liquid.

Surfactants with appropriate structure adsorb at the liquid/soil and at the solid/soil interfaces, reducing the interfacial tensions in both cases. Lower interfacial tensions reduce the energy required to detach the soil from the surface, emulsify it with mechanical action or solubilize it within micelles.

It has recently been suggested that foams also aid in cleaning both oily and fine particulate soils through three key mechanisms: imbibition, wiping, and drainage<sup>19</sup>. Imbibition occurs when oil is drawn into the foam due to capillary forces. Wiping involves the movement of the contact line between oil, foam, and the surface, and is driven by the decay dynamics of the foam. Drainage occurs when the cleaning solution flows through the foam, utilizing capillary forces to pull fine particles into the liquid film of the foam.

In all the mechanisms mentioned above, equilibrium surface tension and surfactant adsorption values are not always reached, especially in high-speed or non-mechanical cleaning processes. In such cases, dynamic surface tension and adsorption processes become critical. Surfactants with higher diffusivity typically demonstrate superior soil removal performance under these conditions, as they are more effective at rapidly migrating to interfaces and reducing interfacial tension<sup>20</sup>.

## **2.2. Solubilizers**

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One challenge in formulating cleaning products is that the most effective surfactants for oil removal are often highly hydrophobic, and therefore require solubilizers to achieve a stable formulation, *i.e.* a one phase detergent systems where the active ingredients are in solution. The most common options used in industry for this purpose are hydrotropes and hydrophilic surfactants, referred to as secondary surfactants.

### 2.2.1 Hydrotropes

Hydrotropy, first defined in the early 20th century by Neuberg<sup>21</sup>, refers to the notable increase in the water solubility of hydrophobic compounds when specific water-soluble organic compounds, known as hydrotropes, are introduced. Hydrotropes possess both hydrophilic and hydrophobic regions. Structurally, hydrotropes are diverse, comprising both ionic and nonionic species. Their hydrophobic part can range from short alkyl chains to aromatic rings. While hydrotropes share some similarities with surfactants, such as their amphiphilic nature, they differ in their limited ability to self-assemble and their minimal effect on reducing surface tension. This distinction arises because their hydrophobic portions are typically too small to induce micelle formation.

In industry, hydrotropes are valued for their versatility. They have been used in a range of areas, including cosmetics, pharmaceuticals, and processes such as separation, solubilization, and extraction. They are also common additives in detergents, surfactants, and polymer formulations. Despite their long history and widespread use, the precise mechanisms by which hydrotropes enhance solubility remain a topic of debate. Several explanations have been proposed<sup>22</sup>:

1. Complex formation between hydrotrope molecules and solutes.
2. Solvent structure modification; this hypothesis suggests that hydrotropes alter the local structure of water, acting as structure breaker.
3. Self-association, the most widely supported hypothesis; it supports that hydrotropes self-associate with the substance to solubilize above a critical aggregation concentration, forming aggregates that behave similarly to micelles.

In surfactant solutions, hydrotropes play an additional crucial role by preventing the formation of crystalline phases within the surfactant solution itself, that can otherwise restrict the solubilization capacity of the solution. The mechanism by which hydrotropes function in these systems involves the creation of mixed micelles composed of both hydrotrope and surfactant molecules<sup>23-25</sup>. Due to the relatively large hydrophilic heads and small hydrophobic groups of hydrotropes, they typically form spheroidal rather than lamellar or liquid crystalline structures. This shift in aggregate geometry alters the natural association patterns found in pure surfactant solutions. By inhibiting the formation of

crystalline phases, hydrotropes enhance the solubility of surfactants in water and boost the solubilization capacity of the micellar solution<sup>8</sup>. Hydrotropic action, therefore, occurs at concentrations where hydrotropes begin to self-associate and form these mixed structures with surfactants<sup>26</sup>.

Unlike the well-established behavior of classical surfactants, hydrotropes continue to generate controversy in scientific literature<sup>22,27–30</sup>.

### **2.2.2 Secondary Surfactants**

Often secondary surfactants are added to improve solubility of highly hydrophobic surfactants in water. In such cases, one refers to mixed surfactant systems. In these systems, there is a cooperative self-association driven by the hydrophobic effect. Ideally, the formation of randomly mixed surfactant aggregates is favored because the hydrophobic effect is not specific to the nature of the polar group. When mixtures include different surfactant types, electrostatic interactions between head groups can promote association at lower concentration. As a result, these systems may exhibit synergistic behavior, leading to substantially lower CMC and lower interfacial tension than would be expected from the properties of the pure surfactants alone<sup>31–33</sup>.

The synergism arises primarily from non-ideal mixing effects in the aggregates. Due to these effects, the tendency to form aggregates in surfactant mixtures can differ markedly from that in pure surfactant solutions. A consequence of non-ideal mixing is that the composition at the interface or in the micelle can differ significantly from that of the unimers in solution. This distinction is important because surfactant adsorption depends on the unimer composition, while oil solubilization relies on the micellar composition. Typically, the most surface-active components tend to populate interfaces and micelles more than the more water-soluble components.

Secondary surfactants are often chosen as solubilizers over cheaper hydrotropes due to their multifunctional benefits in cleaning formulations. Unlike hydrotropes, secondary surfactants actively migrate to surfaces, aiding in cleaning. They offer high solubilization for hydrophobic surfactants at lower concentrations and contribute to foam and viscosity control. Additionally, they provide stability in alkaline and electrolyte-rich environments

and support formulation stability by solubilizing components such as solvents, perfumes, and dyes.

### **2.3. Chelating Agents**

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Chelating agents are molecules that attach to metal ions through two or more donor atoms, forming ring structures, a process known as chelation. These agents play a critical role in cleaning formulations by addressing a major challenge: water hardness.

In hard water, the presence of metal ions like calcium, magnesium, and iron can bind to surfactants, rendering them less effective or even causing them to precipitate out of solution. This in turn can reduce or fully deplete a detergent of its cleaning capability. Chelating agents prevent this by binding to the metal ions, keeping them soluble and preventing them from interfering with surfactant function.

Beyond their role as water softeners, chelating agents play a critical role in cleaning. Their ability to bind and sequester metal ions directly contributes to the removal of challenging soils. For example, in the removal of limescale, primarily composed of calcium and magnesium carbonates, chelating agents solubilize these metal ions, allowing the scale to be lifted from surfaces without the need for harsh acidic cleaning agents.

In addition to removing scale, chelating agents are effective in breaking down soils stabilized by metal ions, such as dairy residues that contain calcium. By binding to the metal ions within the soil matrix, the chelating agent weakens the attachment of the soil to surfaces. Chelating agents are also highly effective at treating metal oxide-based stains, such as rust.

Furthermore, most chelating agents provide a beneficial buffering effect, helping to maintain an alkaline pH. As discussed earlier, an alkaline pH deprotonates acidic soils and creates like charges on both the soil and the substrate. This leads to the formation of a diffuse layer of counterions between them, which promotes an osmotic flow of water into the area, lifting the soil.

Chelating agents can generally be classified as (i) hard chelating agents which would be those of the aminopolycarboxylic types, citric acid and sodium gluconate and (ii) soft ones which would be mostly of polymeric nature such as sodium polyacrylate. The former binds

strongly to metal ions with one chelating agent binding to one cation, the latter binds more loosely and the stoichiometry (ratio) of binding is variable. The focus in this research thesis is on hard chelating agents.

Aminopolycarboxylates are prominent metal chelators, with nitrilotriacetic acid (NTA) being the first commercially produced in 1936, followed by ethylenediaminetetraacetic acid (EDTA) in 1939. These chelating agents gained widespread use after 1967, when tripolyphosphates were banned in several countries. However, concerns over their ecological impact, toxicity, and poor biodegradability led to the search for more environmentally friendly alternatives. In the 1990s, methylglycinediacetic acid (MGDA) and tetrasodium glutamate diacetate (GLDA) emerged as popular replacements in several applications.

A common issue in formulations containing nonionic and/or ionic surfactants is the salting-out effect caused by chelating agents, which leads to micellar growth and precipitation. This effect is attributed to the strong hydration and water-structuring properties of the chelating agents. Beyond the salting-out effect, the detailed interactions between chelating agents and surfactants have been minimally explored. To the best of our knowledge, the existing literature can be divided into two main areas: studies on traditional chelating agents, such as EDTA, and research focused on practical applications, which often lack a comprehensive investigation into the chemical mechanisms driving these processes.

For example, Zhao *et al.*<sup>34</sup> studied the impact of EDTA on gemini cationic surfactants and found that the interaction led to the formation of oligomeric surfactant analogues, which self-assemble at lower concentrations than the CMC of the pure surfactant. This self-assembly is attributed to electrostatic binding between the carboxylate groups of EDTA and the ammonium group of the surfactant. Similarly, Soontravanich *et al.*<sup>35</sup> observed a synergistic effect on soap scum solubility at high pH when using a mixture of amine oxide-based surfactants and EDTA. The solubility was found to be significantly higher compared to chelate-free systems, likely due to the formation of mixed micelles between stearate anions and the surfactant, promoted by EDTA and chelated Ca<sup>2+</sup> ions.

Yunusov *et al.*<sup>5</sup> used molecular simulations to investigate surfactant-EDTA systems and found that EDTA disrupts hydrogen bonding between water molecules and between water and surfactants, suggesting its role as a salting-out agent. This disruption reduces surfactant

hydration and increases monolayer packing due to electrostatic repulsion. Additionally, their results showed that EDTA accumulates at the interface, thickening the interfacial layer, a trend also observed in systems containing both surfactant and chelating agent.

Studies on the interactions between amino acids and surfactants offer valuable insights into the effects of chelating agents on surfactant self-assembly. Yan *et al.*<sup>36</sup> found that, similar to the EDTA-surfactant system, the CMC of cationic surfactants decreases in the presence of amino acids, but also the aggregation number decreases, suggesting that these small molecules promote micelle formation. Chauhan and Sharma<sup>37</sup> proposed that amino acids could influence the hydration shell around the alkyl chain of the surfactant by interacting with its head group. Likewise, Kandpal *et al.*<sup>38</sup> observed that in systems with anionic surfactants and glycine, this interaction occurs at low surfactant concentrations, reaching a saturation point. Additional surfactant causes a regular micellization process in the presence of additives. Such interactions are well-documented, with most studies highlighting the key factors as the coexistence of a surfactant with an ammonium-based head group and an amino acid in aqueous solution<sup>39-41</sup>.

Most of the literature on GLDA and MGDA tends to emphasize on practical applications, such as enhanced oil recovery in oil fields<sup>42,43</sup> and cloud point extraction in water treatment<sup>44</sup>. These studies typically focus on performance metrics like recovery rates and surface tension variations under different experimental conditions, leaving a noticeable lack of molecular-level investigations into these systems. To address this gap, this work explores the interactions between amine-based surfactants and chelating agents, hypothesizing that these interactions can help prevent salting-out effects and even promote the solubilization of hydrophobic nonionic surfactants. This ability to solubilize hydrophobic surfactants is especially relevant in highly concentrated systems, such as those used in various industrial applications like cleaning, agriculture and oil field processes.



## Experimental Techniques

### 3.1. NMR to Explore Molecular Interactions in Surfactant Systems

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Nuclear Magnetic Resonance (NMR) spectroscopy operates on the principle that certain atomic nuclei, when placed in a strong magnetic field, will respond to electromagnetic perturbations by emitting signals. These signals are highly characteristic of the nucleus and depend on factors such as the strength of the magnetic field, the chemical environment, and the specific magnetic properties of the isotope being studied. Nuclei such as hydrogen ( $^1\text{H}$ ) and carbon-13 ( $^{13}\text{C}$ ), possess an odd atomic mass number, which gives them a magnetic moment and angular momentum, making them detectable by NMR.

In a typical NMR experiment, the nuclei are first aligned in a constant magnetic field ( $B_0$ ). A radiofrequency (RF) pulse is then applied to disturb this alignment, causing the nuclei to oscillate at a frequency known as the Larmor frequency, which is intrinsic to each type of nucleus in the applied field. This frequency, recorded as the chemical shift, varies according to the chemical environment of each nucleus, allowing NMR to differentiate between distinct molecular environments.

The unique strength of NMR spectroscopy lies in its ability to provide detailed insights into molecular structure and dynamics by detecting subtle interactions between nuclear spins and their surrounding environments. More importantly, NMR can independently observe each component in a complex mixture, allowing for an in-depth study of how individual surfactant molecules and other formulation ingredients behave and interact within the

mixture. Rather than focusing on the technical aspects of each NMR method, this section highlights the types of insights that NMR studies can offer for surfactant systems, specifically those methods that were employed in this research.

### 3.1.1 Chemical Shift Variations

Chemical shifts in NMR spectroscopy reveal valuable information about the electronic environment surrounding a nucleus, and by extension, the molecular environment of surfactants as they interact and aggregate. When surfactants begin to form micelles, changes in their chemical environment leads to observable changes of their NMR spectra<sup>45</sup>. This transformation—from individual molecules dissolved in solution to aggregated within micelles—can be tracked by monitoring these chemical shift changes.

Below the critical micelle concentration (CMC), the surfactant molecules primarily exist as isolated units, or unimers, within an aqueous environment, generating characteristic chemical shifts typical of this state. As the concentration reaches the CMC, the hydrophobic tail regions of the surfactants start to aggregate, moving into the micellar core, which is an aliphatic environment. This shift in environment leads to a distinct change in the observed chemical shift<sup>46</sup>,  $\delta_{\text{obs}}$ , which reflects a population average between micellized ( $\delta_{\text{mic}}$ ) and unimeric ( $\delta_{\text{uni}}$ ) states:

$$\delta_{\text{obs}} = \delta_{\text{uni}} \left( \frac{C_{\text{uni}}}{C_{\text{T}}} \right) + \delta_{\text{mic}} \left( \frac{C_{\text{mic}}}{C_{\text{T}}} \right) \quad (1)$$

Here,  $C_{\text{uni}}$  and  $C_{\text{mic}}$  are the free surfactant concentration and the concentration of surfactant in the micelles, respectively; and  $C_{\text{T}} = C_{\text{uni}} + C_{\text{mic}}$  is the total surfactant concentration. By plotting chemical shift variations as a function of surfactant concentration, the CMC can be determined, and, under favorable conditions, the aggregation number can be estimated<sup>47,48</sup>.

Similarly, dynamic molecular equilibria, such as binding interactions between two different molecules, alter the chemical environment of the atoms involved in the interaction. The fast exchange kinetics between bound and unbound states, relative to the time scale of NMR detection, leads to the observation of a population-weighted averaged chemical shift. In formulations where surfactants interact with secondary ingredients, the observed chemical



shift reflects contributions from surfactants in multiple states: as unimers, as part of micelles, and as surfactants interacting with secondary ingredients either in unimeric form or within micellar structures.

### 3.1.2 Analysis of Spectral Line Shape

Chemical exchange, a dynamic process where molecules transition between different states, such as free and bound forms, not only generates chemical shift variations in NMR spectra, but also influences the shapes of the NMR signals themselves. In a two-state system, where a molecule M binds to a ligand L to form a complex ML, the exchange rate  $k_{\text{ex}}$  is given by:

$$k_{\text{ex}} = k_{\text{on}}[\text{L}] + k_{\text{off}} \quad (2)$$

The appearance of an NMR signal depends on the relationship between the exchange rate  $k_{\text{ex}}$  and the frequency difference  $\Delta\omega$  between the free and bound states<sup>49,50</sup>. In the fast exchange regime ( $k_{\text{ex}} \gg \Delta\omega$ ), a single resonance appears at a chemical shift that represents a population-weighted average of the two states. In contrast, in the slow exchange regime ( $k_{\text{ex}} \ll \Delta\omega$ ), two distinct signals appear, representing the chemical shifts of the free and bound states, each weighted by their respective populations. When the exchange rate is intermediate ( $k_{\text{ex}} \approx \Delta\omega$ ), extensive line broadening occurs, reflecting the fluctuations between states at the time scale of the frequency difference.

This sensitivity to exchange kinetics, along with factors such as state population and chemical shift differences, makes line shape analysis a powerful tool for characterizing molecular equilibria and binding interactions. By examining changes in line shapes under various conditions, the strength and dynamics of interactions between surfactant molecules, or between surfactants and other components in a mixture, can be effectively assessed.

### 3.1.3 Diffusion NMR

Diffusion NMR, also known as Diffusion Ordered Spectroscopy (DOSY), NMR diffusometry or pulsed field gradient NMR, is a powerful technique used to measure self-diffusion coefficients of molecules in solution. This method combines RF pulses with

pulsed field gradients to analyze molecular movement, providing critical information about molecular size, shape, and interactions in complex chemical systems.

The fundamental pulse sequence in diffusion NMR is the pulsed field gradient spin-echo (PGSE) sequence. In this approach, magnetization is first excited by a 90-degree RF pulse, followed by a magnetic field gradient pulse that phase encodes the magnetization. It means that the spatial location of molecules is encoded before a delay, denoted diffusion time. After half of the diffusion time, a 180-degree RF pulse inverts the magnetization, and a second gradient pulse is applied to refocus the signal. Only spins belonging to molecules that have remained in the same location during the diffusion time will refocus completely, while those that have diffused reduce the intensity of the NMR signal. This attenuation of the signal is related to the self-diffusion coefficient, strength and duration of the gradient pulse, as well as the diffusion time.

In a diffusion NMR experiment, the gradient strength is incrementally increased, and signal intensity is measured at each step, with all other parameters kept constant. The results are analyzed by the signal integral intensity as a function of the so-called  $k$ -values, calculated using the equation:

$$\ln\left(\frac{S_{(2\tau)}}{S_{(0)}}\right) = -Dg^2G^2\delta^2(\Delta - \delta/3) \quad (3)$$

where  $g$  is the gyromagnetic ratio,  $G$  is the gradient strength,  $\delta$  is the duration of the gradient pulse, and  $\Delta$  is the time between the two gradients. For unrestricted diffusion and using a logarithmic y-axis, a linear trend is obtained, with the slope corresponding to  $-D$ , where  $D$  is the diffusion coefficient.

The self-diffusion coefficient provides insights into the molecular size and shape through the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\eta r} \quad (4)$$

where  $k$  is the Boltzmann constant,  $T$  is the temperature,  $\eta$  is the viscosity of the solvent, and  $r$  is the radius of the molecule. From the equation it is clear that larger molecules or

molecular assemblies have lower self-diffusion coefficients than smaller ones, and a molecule has a higher diffusivity in a low-viscosity solvent than in a more viscous solvent.

Diffusion NMR has diverse applications, including tracking molecular interactions and exchange, calculating association constants, studying encapsulation and molecular cages, and analyzing ion pairing and organometallic systems. It also provides information on molecular size and shape for small molecules, complexes, dendrimers, and polymers, making it invaluable for characterizing multicomponent systems.

### 3.1.4 Advantages and Limitations of $^{13}\text{C}$ NMR in Surfactant Analysis

While  $^1\text{H}$  NMR is widely used to analyze surfactant systems<sup>51-55</sup>,  $^{13}\text{C}$  NMR provides additional, direct insights into the carbon backbone of surfactant molecules<sup>47,56,57</sup>. A key advantage of  $^{13}\text{C}$  NMR is its ability to generate distinct signals for each individual carbon in the molecule, regardless of whether the carbon is bonded to hydrogen atoms. This feature enables more precise structural analysis, particularly in complex molecules or when investigating nonuniform changes in microenvironments. For instance, in sodium octanoate solutions, all eight carbons exhibit well-separated signals that can be unambiguously assigned<sup>48,58</sup>. In contrast,  $^1\text{H}$  NMR only identifies signals for methyl and methylene groups, making it challenging to resolve other parts of the molecular structure and monitor varied chemical shifts along the lipophilic chain.

Additionally,  $^{13}\text{C}$  NMR offers a broader chemical shift range<sup>47,48</sup>, attributed to the increased shielding experienced by heavier atoms with more electrons. This wider range is advantageous for detecting structural changes, such as micellization, as demonstrated in studies using  $^{19}\text{F}$  NMR for fluorosurfactants<sup>59-61</sup>, where the range in chemical shift provides more details on the molecular reorganization.

However,  $^{13}\text{C}$  NMR has certain limitations.  $^{13}\text{C}$  has a much lower natural abundance which gives a much lower sensitivity compared to  $^1\text{H}$  NMR, requiring higher sample concentrations or extended acquisition times to achieve sufficient signal strength. This drawback can make  $^{13}\text{C}$  NMR less practical for rapid or low-concentration measurements.

Despite these limitations,  $^{13}\text{C}$  NMR remains a valuable tool for studying surfactant systems, offering complementary information that enhances our understanding of complex formulations, particularly when multiple surfactants or additives are involved.

## **3.2. Surfactant Formulations: Key Properties**

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Designing an effective test for evaluating the functional performance of a surfactant formulation is often challenging, as no single laboratory test can replicate the wide range of real-world conditions and applications<sup>2</sup>. While specific tests exist for properties such as detergency, wetting, lubrication, defoaming, and dispersion, they cannot individually address the diverse needs of end users. Therefore, it is more practical to begin with quick, simple, and cost-effective tests to screen potential surfactants or formulations before proceeding to more complex functional evaluations.

Basic tests measuring properties like viscosity, cloud point, surface tension, and contact angle on hydrophobic surfaces can be conducted efficiently and provide critical insights into the physicochemical behavior of a formulation. In the context of this research, these preliminary tests help identify and control variables, establishing a more consistent foundation for a detailed study of surfactant interactions and behaviors.

The concepts of surface tension, contact angle and cloud point have been introduced in previous sections and the experimental methods or equipment used for such measurements are included in the papers supporting this research work. The relationship between surfactant solutions, micelles, viscosity and cleaning applications is presented here.

### **3.2.1 Viscosity**

Viscosity describes the resistance to flow of a fluid and is influenced by the interactions among its molecules, essentially acting as a form of molecular friction. Just as friction between solid objects affects movement, viscosity dictates the energy required to make a fluid flow.

In surfactant solutions, micelle shape directly impacts viscosity<sup>62</sup>. At low concentrations above the critical micelle concentration (CMC), micelles initially form spherical shapes, the simplest and most common morphology. However, as surfactant concentration increases, micellar growth may take place, leading to changes in size, shape and aggregation number. For shorter-chain surfactants, such as C8 or C10, micelles remain small and spherical even at relatively high concentrations (up to 40 wt%), resulting in a gradual increase in viscosity<sup>6</sup>, consistent with expectations for spherical particle dispersions. In contrast, longer-chain surfactants (C14 and above) form elongated micelles, eventually

developing into rod-like or thread-like shapes at higher concentrations. These elongated structures have greater surface area, which increases the likelihood of micelle-micelle interactions, leading to higher viscosity. These shape transitions are influenced not only by surfactant concentration or type, but also by changes in the solution conditions, such as temperature, presence of electrolytes and other physicochemical parameters.

Managing viscosity is critical in cleaning formulations, for technical, safety, and marketing purposes. Technically, increased viscosity improves adhesion, promotes even coverage, and enhances rinse-off efficiency. A thicker product allows a uniform coverage of surfaces, enabling longer contact time with contaminants, which is especially useful for applications on vertical surfaces. Higher viscosity also promotes the stability of colloidal particles, helping to preserve active ingredients and extend shelf life. However, viscosity must remain low to allow an easy dispensing. For safety, a thicker consistency reduces the risk of spills or splashes, and consumers often associate thicker products with higher quality and effectiveness.



# 4

## Results and Discussion

### 4.1. Demonstrating Intermolecular Interactions in Surfactant-Chelating Agent Systems

NMR spectroscopy was employed to study molecular interactions between chelating agent and surfactant. Systems were prepared with fixed chelating agent concentration while varying surfactant concentration, and  $^{13}\text{C}$  NMR spectra were recorded for analysis.

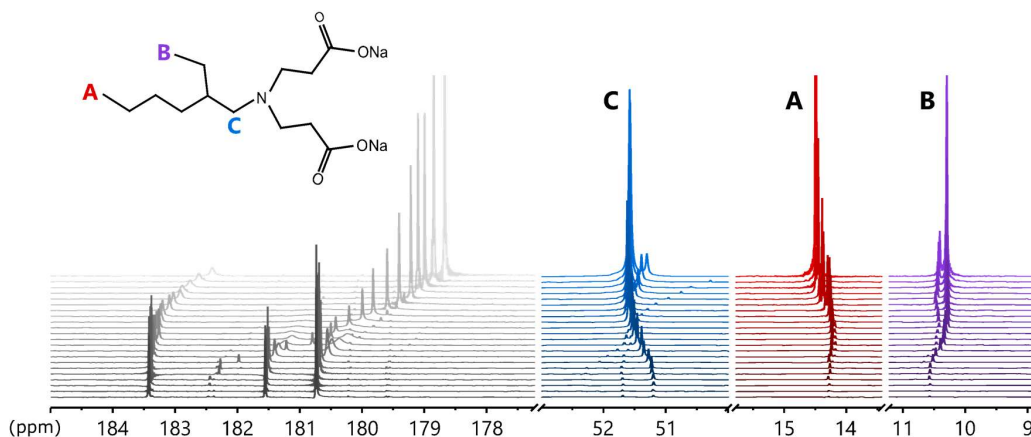


Figure 6. Evaluated regions of the  $^{13}\text{C}$  NMR spectra for the system containing 0.24 M GLDA at increasing amphoteric surfactants concentration. The surfactant signals discussed in the text are denoted by letters, as indicated on the molecular structure. The surfactant concentration increases progressively from bottom to top.

The presence or absence of intermolecular interactions was initially assessed by stacking the NMR spectra and visually inspecting changes in chemical shift or line broadening. A

typical example of the data is presented in Figure 6, which shows the stacked  $^{13}\text{C}$  NMR spectra of a system containing 2-ethylhexyliminodipropionate (BC8Amph) and GLDA as the concentration of surfactant increases.

Both chemical shift variations and line broadening were observed across the stacked spectra for both species, with more pronounced changes for the chelating agent. Since the concentration of GLDA remained constant, no intensity changes due to concentration variations were observed, eliminating the need for numerical evaluation of line width to distinguish between concentration effects and actual line broadening, thus facilitating visual inspection. Both chemical shift variations and line broadening observations suggest the presence of intermolecular interactions.

The next step in confirming intermolecular interactions in these systems was monitoring chemical shift changes as the surfactant concentration varies. This approach provides a more detailed description of the system and its interactions. Figure 7 presents the evolution of the chemical shift as a function of the reciprocal of surfactant concentration, in systems either without GLDA or at different constant GLDA concentrations. Here, the signals of carbon atoms along the lipophilic chain of the surfactant are tracked.

The system without GLDA (non-filled symbols) is discussed first. The chemical shift observed for the terminal carbon atoms in the surfactant molecule ( $C_A$  and  $C_B$  in Figure 7) varies with the reciprocal of surfactant concentration, following Eq. 1, which aligns with expected behavior for surfactant solutions<sup>46</sup>. At low concentrations, as the surfactant concentration increases ( $C_{\text{mic}} = 0$ ;  $C_T = C_{\text{uni}}$ ), the chemical shift remains constant, indicating the presence of surfactant molecules as unimers. At higher concentrations, however, the chemical shift moves downfield, suggesting that the environment around the methyl group changes due to micellization.

Figure 7 also shows the chemical shift of the methylene carbon atom  $C_C$  near the nitrogen atom, positioned close to the head group of the surfactant. This chemical shift exhibits minimal change as surfactant concentration increases, with only a slight decrease when forming micelles. This steady behavior suggests a microenvironment that remains constant after surfactant aggregation, as expected for carbon atoms at the micelle surface<sup>59</sup>.



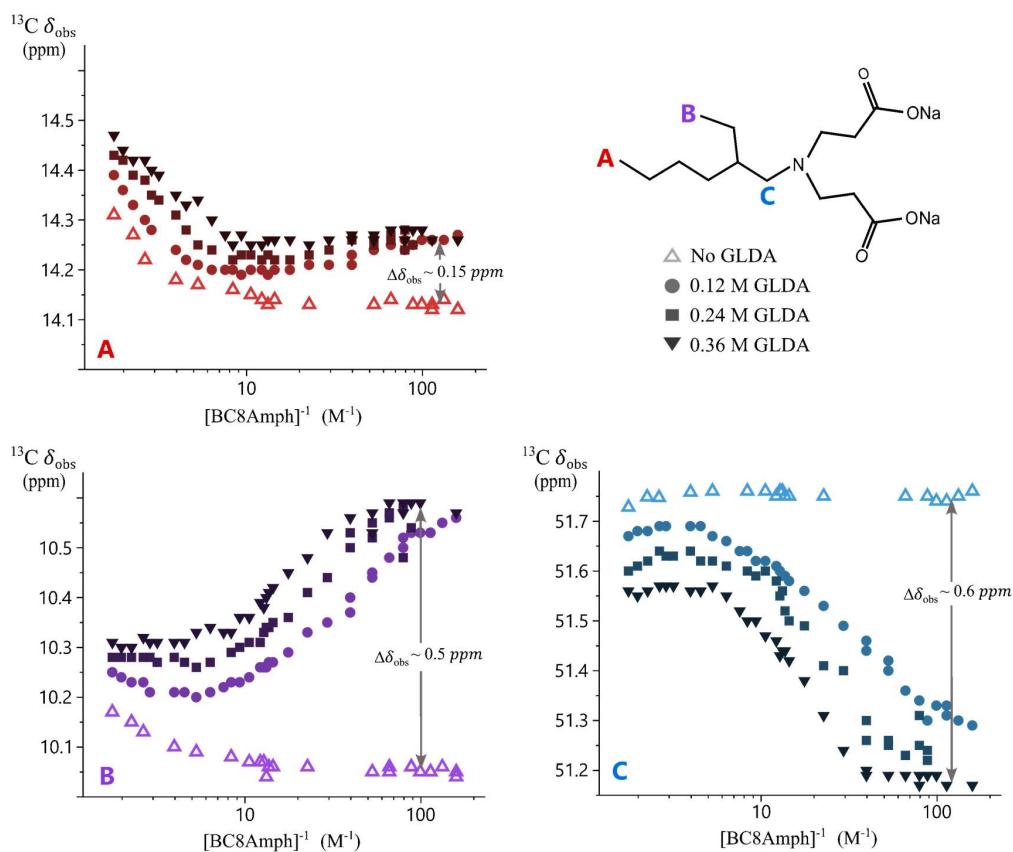


Figure 7. Observed chemical shift as a function of the reciprocal concentration of amphoteric surfactant (BC8Amph) in systems without additives and with different GLDA concentrations (0.12 M, 0.24 M, and 0.36 M). GLDA concentration increases with darker shading. Each plot represents a distinct signal for carbon atoms in the lipophilic chain, color-coded as indicated in the molecule. The x-axis is in terms of reciprocal surfactant concentration, so surfactant concentration increases from right to left along the axis.

In contrast, the variation in chemical shift at increased GLDA concentration (filled symbols in Figure 7) displays a distinct pattern. The presence of a salting-in or salting-out additive would typically change the chemical shift to a new value and move the inflection point to a higher or lower concentration, depending on whether micellization is promoted or hindered. However, the overall trend should remain. A change in the shape of the curve requires the introduction of an additional term in Eq. 1, which in these systems likely reflects an interaction between GLDA and either the amphoteric surfactant or the micelles. This altered curve shape thus clearly indicates that GLDA is interacting with the surfactant, rather than moving freely in the solution. Considering these interacting species, Eq. 1 can be revised as:

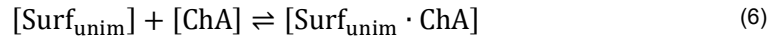
$$\delta_{\text{obs}} = \delta_{\text{uni}} \left( \frac{C_{\text{uni}}}{C_{\text{T}}} \right) + \delta_{\text{mic}} \left( \frac{C_{\text{mic}}}{C_{\text{T}}} \right) + \delta_{\text{uni+ChA}} \left( \frac{C_{\text{uni+ChA}}}{C_{\text{T}}} \right) + \delta_{\text{mic+ChA}} \left( \frac{C_{\text{mic+ChA}}}{C_{\text{T}}} \right) \quad (5)$$

where the two new terms, uni + ChA and mic + ChA, account for the surfactant interacting with the chelating agent (ChA) as a unimer or in the micelle, respectively.

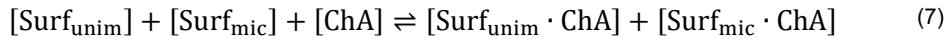
At low concentrations, Figure 7 shows that the chemical shift remains constant, and the degree of chemical shift change differs based on the carbon atom observed; atoms closer to the head group show a more significant shift than those further along the lipophilic chain. This difference suggests that GLDA is more concentrated around the head group of the surfactant, where the chemical shifts are more pronounced.

When the surfactant concentration increases, a new behavior can be observed. Here, the chemical shift patterns depend on the carbon atoms: the signals for the terminal methyl groups in the lipophilic chain shift upfield, with  $C_{\text{B}}$  - closer to the head group - displaying a steeper shift than  $C_{\text{A}}$ . In contrast, the signal for  $C_{\text{C}}$ , a methylene group close to the hydrophilic region, shifts downfield in the same range. In all the cases, the shifts are approaching that of a GLDA-free system. This shift pattern suggests that, at these concentrations, a growing portion of the added surfactant remains unbound to GLDA, therefore suggesting that the systems exist in a dynamic equilibrium, that could be described by:

below CMC:



above CMC:



where  $\text{Surf}_{\text{unim}} \cdot \text{ChA}$  and  $\text{Surf}_{\text{mic}} \cdot \text{ChA}$  refers to the complex formed between the chelating agent and the unimer, and a surfactant forming part of a micelle, respectively.

At even higher concentrations, a third distinct region is noted. The signal for C<sub>A</sub>, positioned at the far end of the chain, shows a downfield shift, while C<sub>B</sub> and C<sub>C</sub> shifts begin to level off.

For C<sub>A</sub>, the limited interaction with GLDA induces a minimal shift compared to the GLDA-free system, a behavior expected for a carbon atom that is distant from the head group where interactions predominantly occur. As such, the impact of GLDA-surfactant complexation on this carbon is negligible.

Conversely, C<sub>B</sub> and C<sub>C</sub> that are closer to the micelle surface, experience a more complex microenvironment. Here, their surroundings consist of the lipophilic core of the micelle, water molecules near the head group, and neighboring GLDA molecules. The resulting chemical shift thus reflects contributions from all these surrounding factors.

A similar analysis from the perspective of GLDA is included in Paper I, where it was also found that the most significant changes appeared in the low-field region of the <sup>13</sup>C NMR spectra, specifically in the signals from the carboxylic groups of both molecules. These findings provided a foundation for further analysis.

## **4.2. Understanding the Details of the Intermolecular Interactions**

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Building on prior knowledge, this study focuses on the low-field region of the <sup>13</sup>C NMR spectra, where signals from carboxylic groups exhibit the most significant variations. These changes provide important information on the interactions between amine-containing surfactants and polycarboxylic acid-type chelating agents. By tracking these regions, where the most pronounced shifts occur, the analysis captures critical insights into the molecular mechanisms governing these interactions. Abbreviations and chemical structures for the compounds studied are detailed in Figure 8.

To assess the necessity of the nitrogen atom for the interaction, two main criteria were evaluated. First, the direct effect the amine function on the differences in chemical shift and signal broadening for the carbonyl groups of NaCitrate compared to MGDA and GLDA in the presence of LC12Amph (Figure 9). The second criteria evaluated focused on the effect of the proximity to the nitrogen to the carbonyl group C4, comparing it to C5 and C6, in the GLDA molecule (Figure 9, middle spectra).

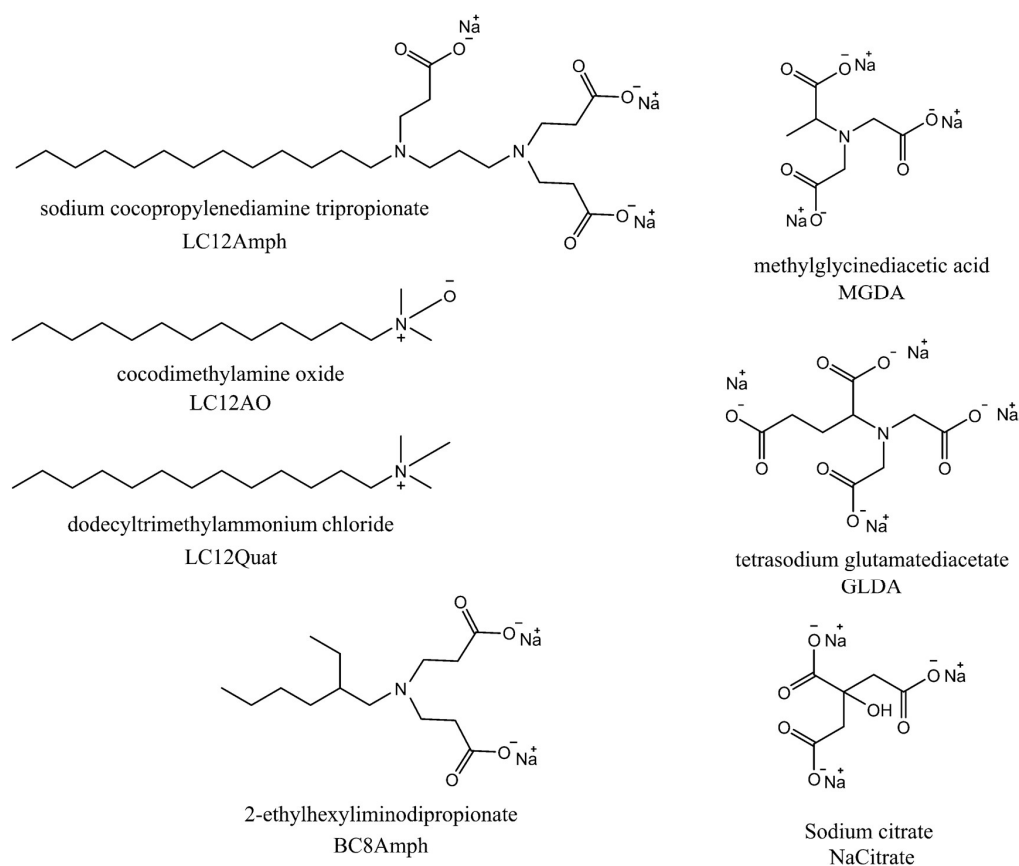


Figure 8. Chemical structures of the chelating agents and surfactants evaluated in this study. Surfactants include sodium cocopropylendiamine tripropionate (LC12Amph), cocodimethylamine oxide (LC12AO), dodecyltrimethylammonium chloride (LC12Quat), and 2-ethylhexyliminodipropionate (BC8Amph). Chelating agents include methylglycinediacetic acid (MGDA), tetrasodium glutamatediacetate (GLDA), and sodium citrate (NaCitrate). The abbreviated names used throughout the article are also indicated for clarity.

In both cases, a greater distance to the nitrogen atom or its absence minimized changes in chemical shift and signal broadening as surfactant concentration increased. Specifically, following the arrows in Figure 9, C4 exhibited small chemical shift variations compared to C5 and C6, while NaCitrate showed no changes in chemical shift or signal broadening. These observations highlight the critical role of the nitrogen atom in these interactions.

The following observations rely on the chemical similarity of the carbon atoms for the carbonyl groups, which, under similar interactions, would be expected to exhibit comparable chemical shifts variations. Therefore, differences in chemical shift variations among these atoms provide valuable insights into the interactions.

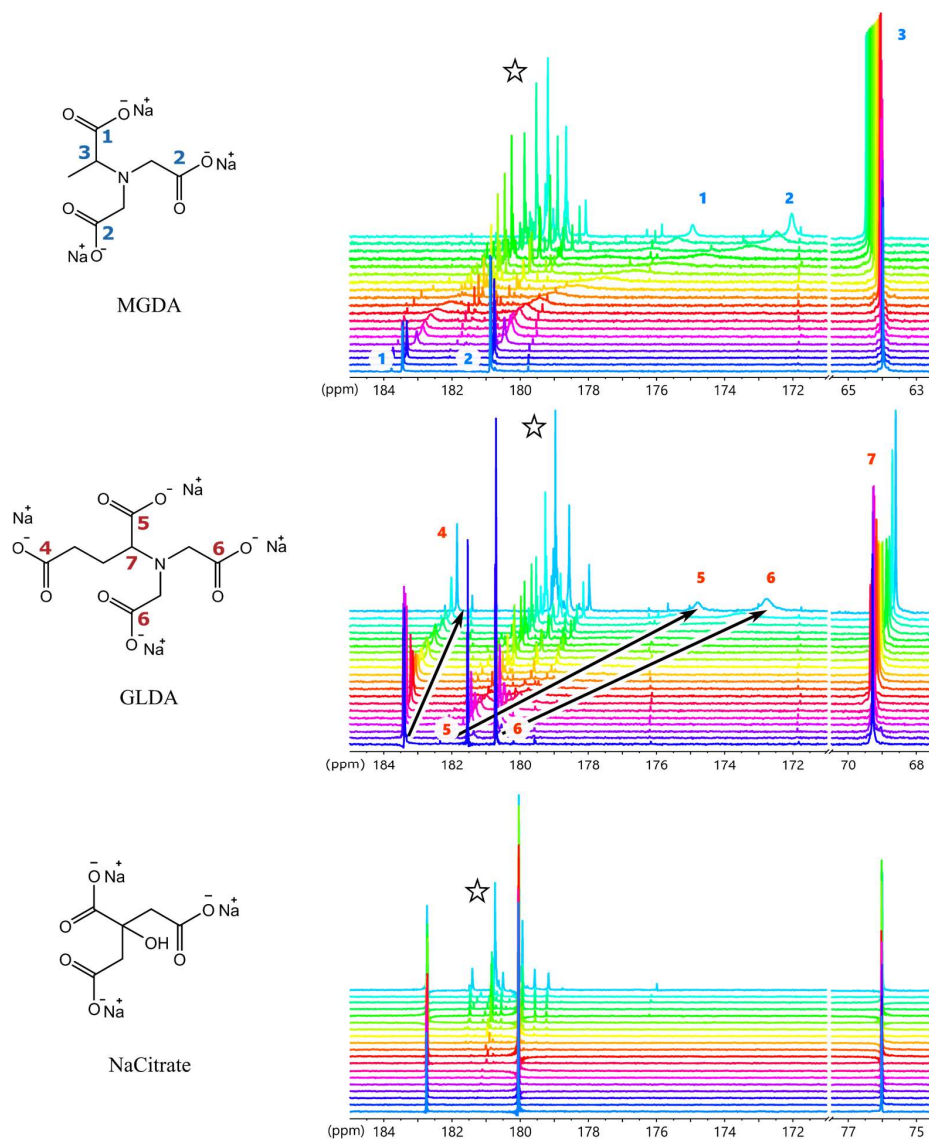


Figure 9. Region of the  $^{13}\text{C}$  NMR spectra analyzed for systems containing 0.24 M chelating agents with increasing concentrations of LC12Amph. The chelating agents, from top to bottom, are MGDA, GLDA, and NaCitrate. The signal of a methylene group (around 70 ppm) is used as a reference. Surfactant concentration increases from bottom to top. Surfactant signals are marked with a star, and chelating agent signals are labeled with numbers for consistency. The chemical shift changes for C4, C5, and C6 are highlighted with arrows.

For GLDA, comparable changes in the microenvironment of C5 and C6 would be anticipated, as interactions through C4 or C6 should similarly affect the chemical environment of C5; the same rationale applies to C6. This allows for the study of the effect

of steric hindrance by comparing chemical shift variations of C1 and C5, to C2 and C6 respectively, the latter pair having no neighboring groups.

To analyze the changes in the  $^{13}\text{C}$  NMR spectra, the chemical shift variation (top) and signal width at half-maximum intensity (bottom) as functions of the surfactant-to-chelating agent concentration ratio were evaluated. Results for systems containing LC12Amph with MGDA (left panel) and GLDA (right panel) are shown in Figure 10.

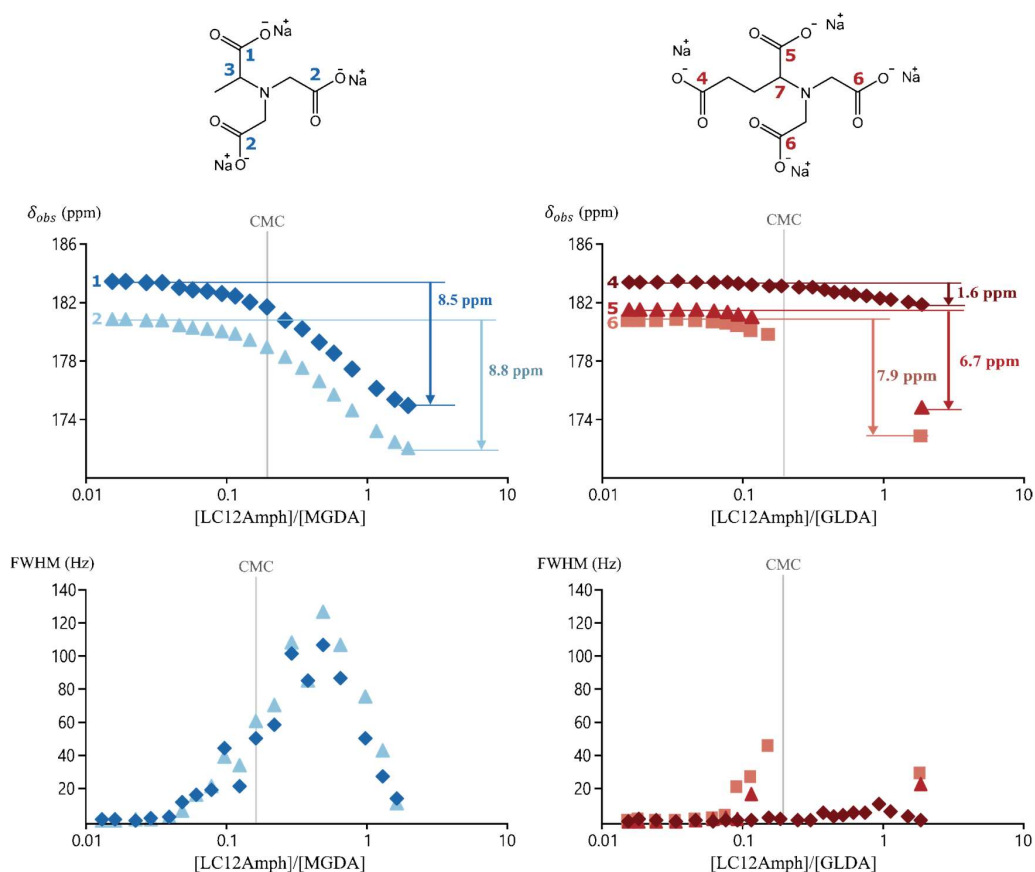


Figure 10. Chemical shift (top) and signal width at half-maximum intensity (bottom) as a function of the surfactant-to-chelating agent concentration ratio for systems containing LC12Amph with MGDA (left panel) and GLDA (right panel). The tracked signals correspond to carbons within the carboxylic groups of each chelating agent, with numbering provided in the accompanying chemical structures.

It is observed that the signal for C5 shows smaller chemical shift variations than that for C6, with a notable difference of approximately 1.2 ppm, accounting for around 20% of the total chemical shift change. A smaller difference was observed between C1 and C2 signals. This discrepancy can be attributed to the branching of the alpha carbons to both C1 and C5,

which likely induces steric hindrance, reducing the probability of interaction with the surfactant.

The nature of the branching also plays a role: C1 features a small methyl group in alpha position, while C5 contains a significantly larger propionic acid group. The propionic acid group exerts a more pronounced steric effect, leading to a greater reduction in chemical shift variation for C5 compared to C1. Additionally, the methyl group, in alpha position to C1, may increase the probability of interaction by enhancing the electronegativity of the neighboring carbonyl group, as it acts as an electron-donating group, reducing the difference in chemical shift variation between C1 and C2.

The study of changes in the width of the  $^{13}\text{C}$  signal, rather than its chemical shift, offers insight into the strength of the interaction instead of the degree of occupancy. This discussion focuses on the right side of Figure 10. Signal broadening in these systems reflects slower exchange rates, indicating longer residence times and stronger interactions.

For MGDA, signal broadening peaks with increasing surfactant concentration before sharpening, signifying initial strengthening of interactions followed by weakening due to micelle packing changes that favor surfactant-surfactant interactions. GLDA displays a non-monotonic broadening trend, with signals vanishing in the high-broadening region, suggesting stronger surfactant-chelating agent interactions and reduced molecular mobility compared to MGDA.

Comparisons between signals for the same chelating agent, such as C5 versus C6 and C1 versus C2, show similar broadening, indicating comparable interaction strengths for these carbons. This suggests that steric hindrance, while affecting the probability of interaction due to spatial accessibility, does not significantly influence interaction strength. In contrast, the minimal broadening of C4 across the concentration range points to weak interaction with LC12Amph.

The previous paragraphs revealed preliminary insights into how surfactant structure influences interaction strength. Building on this, the effect of the lipophilic chain of the surfactant was investigated. To this end, two surfactants (LC12Amph or BC8Amph) were selected and studied in the presence of MGDA. The plots of signal width as a function of the surfactant-to-chelating agent concentration ratio for these systems are compared in Figure 11.

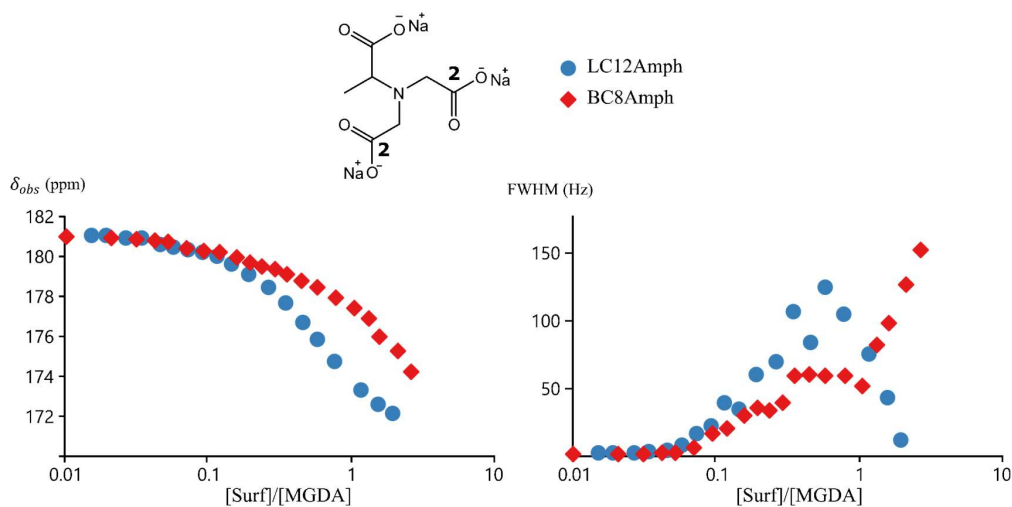


Figure 11. Chemical shift (left) and signal width at half-maximum intensity (right) as functions of the surfactant-to-chelating agent concentration ratio for MGDA with LC12Amph and BC8Amph. The tracked MGDA signal corresponds to a carboxylic carbon (C2), as highlighted in the accompanying chemical structure.

The main observation from the plot is the distinct trend for each amphoteric surfactant. For LC12Amph, signal broadening as a function of surfactant concentration reaches a maximum before sharpening. In contrast, BC8Amph shows a monotonic broadening under the same conditions. These differences arise primarily from variations in the length and shape of their lipophilic chains. LC12Amph, with its long, linear chain, displays strong self-association, resulting in better micellar packing and competitive head-to-head and head-to-chelating-agent interactions. Conversely, BC8Amph, more akin to a hydrotrope, has limited self-assembly capability. Its weaker head-to-head interactions and poor packing allow surfactant-chelating agent interactions to dominate, as the head groups remain distant within the aggregates.

To conclude this section, the effect of the nature of the head group of the surfactant on the interaction with the chelating agent was evaluated. For this purpose, LC12Amph, LC12AO, and LC12Quat were tested in systems containing MGDA. The resulting changes in chemical shift and signal broadening as functions of the surfactant-to-chelating agent concentration ratio are shown in Figure 12.

The comparison of amphoteric surfactants with amine oxide and quaternary ammonium-based surfactants reveals substantial differences in the chemical environment experienced



by the chelating agent as surfactant concentration increases. In systems with amphoteric surfactants, MGDA undergoes significant changes in its chemical environment, leading to pronounced chemical shift variations. By contrast, LC12AO and LC12Quat induce only minor shifts, noticeable only when the surfactant-to-chelating agent ratio exceeds one. These trends are consistent across all MGDA carbons, with carboxylic carbons (*e.g.*, C2) exhibiting larger variations compared to methylene carbons (*e.g.*, C3), as expected.

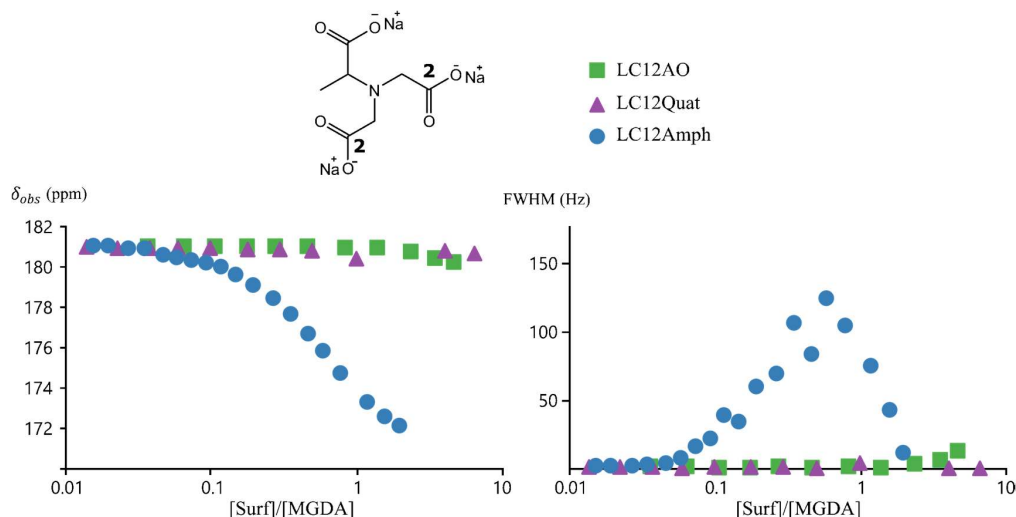


Figure 12. Chemical shift (left) and signal width at half-maximum intensity (right) as functions of the surfactant-to-chelating agent concentration ratio for MGDA with three different surfactants: LC12Amph, LC12Quat, and LC12AO. The tracked MGDA signal corresponds to a carbon within a carboxylic group (C2), highlighted in the accompanying chemical structure.

Signal width changes corroborate these observations: pronounced broadening occurs with the amphoteric surfactant, and no broadening with LC12AO or LC12Quat. These findings suggest that effective interactions require a surfactant with a head group featuring both positive and negative moieties. Additionally, the spatial separation between these moieties is crucial, as it must neither be too short (as in amine oxide) nor too long (as seen with the longest GLDA chain). Nevertheless, the head groups of LC12AO and LC12Amph differ not only in structure but also in electronic density, which may significantly influence surfactant-chelating agent interactions. The amine oxide group exhibits a harder, less delocalized electronic density, whereas the carboxylic group is characterized by a softer, more delocalized electronic density.

### 4.3. Effect of the Interactions on Bulk and Surface Properties

After establishing the interactions between surfactants and chelating agents on a molecular level, it is essential to explore how these interactions manifest in the bulk properties of formulations. Since the clouding temperature is a characteristic of polyoxyethylene-based surfactants, this study includes an ethoxylated decyl alcohol with four ethoxyl groups (C10E4), offering insights into the practical implications of surfactant-chelating agent interactions. The evolution of cloud point as a function of the concentration of MGDA is presented in Figure 13.

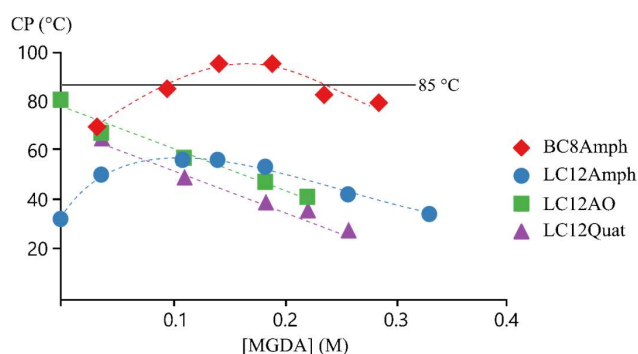


Figure 13. Evolution of the cloud point as a function of the concentration of MGDA, for formulations containing 6% C10E4 and one solubilizer: 6% BC8Amph, 6% LC12AO, 2% LC12Amph, or 1.3% LC12Quat. Data above 85 °C is indicative only, as measurements were capped at 80 °C. Dotted lines are included for visual guidance.

When non-interacting species are used to solubilize the nonionic surfactant, increasing the chelating agent concentration causes a salting-out effect, lowering the clouding temperature of the system. This behavior is observed in Figure 13 for systems with LC12Quat or LC12AO using MGDA, as well as in LC12Amph-NaCitrate (Figure 14) combinations. Similar trends are also reported for systems containing a water-soluble nonionic surfactant (decyl alcohol with eight ethoxylated groups) or sodium dodecyl sulfate as the solubilizer, combined with GLDA as the chelating agent (see Paper I).

When the nonionic surfactant is solubilized by an amphoteric surfactant, such as BC8Amph or LC12Amph (Figure 14), the cloud point increases with the chelating agent concentration until it reaches a maximum. This behavior can be explained using the CPP model. Specifically, the reduction in clouding temperature reflects a decrease in micellar size, likely due to an increase in the area occupied by the hydrophilic head group, caused by

complex formation between the chelating agent and the surfactant head group. This shift reduces the CPP, promoting the formation of smaller, more spherical micelles.

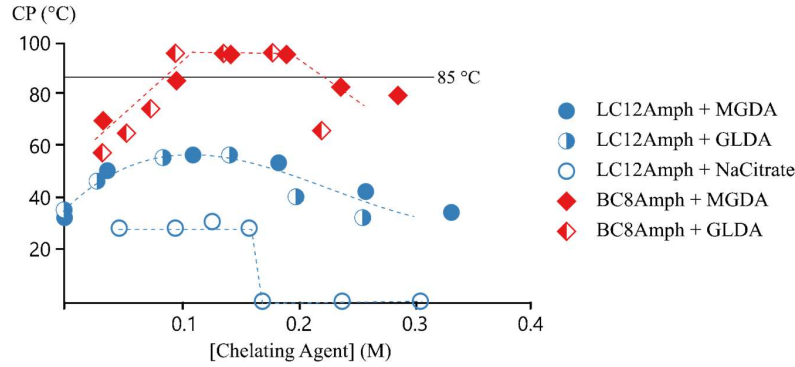


Figure 14. Evolution of the cloud point as a function of the concentration of chelating agent, for formulations containing 6% C10E4, one solubilizer: 6% BC8Amph or 2% LC12Amph and different chelating agents: MGDA, GLDA and NaCitrate. Data above 85 °C is indicative only, as measurements were capped at 80 °C. Dotted lines are included for visual guidance.

The CPP model takes into account variables such as the volume and length of the lipophilic chain, as well as the area of the polar region. The volume of the lipophilic chain ( $V$ ) and length ( $l$ ) can be calculated from the number of carbon atoms and methyl groups, using the formula

$$\frac{V}{l} = \frac{27(n_C + n_{Me})}{1.5 + 1.27n_C} \quad (8)$$

where  $n_C$  and  $n_{Me}$  represent the number of carbon atoms and methyl groups in the lipophilic chain, respectively.

The comparison of the volume-to-length ratios of the lipophilic chains for LC12Amph ( $21 \text{ \AA}^2$ ) and BC8Amph ( $23.2 \text{ \AA}^2$ ) reveals a clear correlation between these ratios and cloud point shifts. For BC8Amph, the cloud point change is more pronounced, with a 40 °C difference between low and high chelating agent concentrations. In comparison, LC12Amph shows a smaller shift of around 30 °C. This difference is attributed to the larger volume-to-length ratio of BC8Amph, which leads to a more significant change in CPP and consequently in micellar size and cloud point.

The viscosity of a solution is also influenced by the size of the aggregates. Since smaller aggregates result in lower viscosity, the behavior of viscosity in these systems mirrors that

of the cloud point. As the aggregate size decreases, the viscosity decreases accordingly. This trend is further discussed and compared in Paper I.

Since interactions in surfactant systems are being evaluated, it is equally important to understand their impact on the surface properties of formulations. This section concludes with an examination of surface tension and contact angle changes in binary systems of amphoteric surfactants with chelating agents and ternary systems incorporating nonionic surfactants.

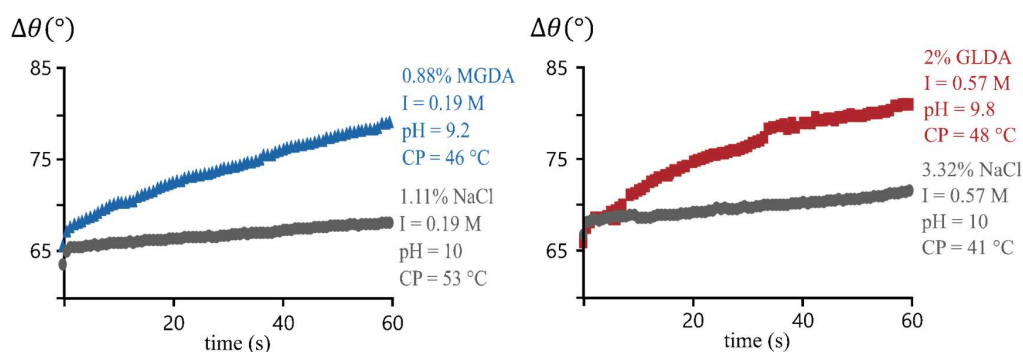


Figure 15. Changes in contact angle ( $\Delta\theta$ ) relative to water for ternary systems with LC12Amph and chelating agents: MGDA (left) and GLDA (right), compared to systems adjusted with NaCl and NaOH for equivalent ionic strength, pH, and cloud point.  $\Delta\theta$  values are calculated by subtracting the contact angle of water and that of the formulation, where a higher  $\Delta\theta$  indicates enhanced wetting of the soiled surface.

In binary systems, surface tension and contact angle remain largely unchanged, whether or not a chelating agent is present. This is consistent with the interaction occurring primarily in the bulk, where the hydrophilicity of the surfactant increases. According to the rule of mixtures for surfactants, the less hydrophilic surfactant dominates at the surface, reducing the likelihood of surfactant molecules interacting with chelating agents to migrate to the interface.

In contrast to the behavior in binary systems, ternary systems - selected for comparable cloud points, ionic strength, and pH levels and compared to systems adjusted with NaCl and NaOH to same conditions - exhibit notable differences in contact angle measurements on surfaces soiled with hydrophobic materials. Figure 15 presents the contact angle difference ( $\Delta\theta$ ), calculated by subtracting contact angle of water from the measurement of each formulation. A higher  $\Delta\theta$  indicates improved wetting.

For systems with LC12Amph and chelating agents, contact angle increases over time, showing greater changes compared to systems adjusted with NaCl and NaOH. This suggests that in ternary systems, interactions may promote the displacement of less hydrophilic surfactants to the surface or enable mixed surfactant systems at the interface to retain more water, improving soil wetting.



# 4

## Concluding Remarks and Future Work

The interactions between amphoteric surfactants and aminopolycarboxylic acid chelating agents were analyzed using NMR spectroscopy, focusing on  $^{13}\text{C}$  chemical shifts and line shape analysis. These interactions occur between the head group of the surfactant and the chelating agent species, in equilibrium with non-interacting species. When the interaction takes place, they form oligomeric surfactants with larger hydrophilic moieties, which increase solubility and enhance the capacity to solubilize non-water-soluble nonionic surfactants. In contrast, non-interacting species behave as typical chelating agents, causing a salting-out effect in solution.

Due to the molecular interaction and the resulting increase area per molecule of the hydrophilic head group, the critical packing parameter of the micelles decreases, resulting in smaller, more spherical micelles. In systems containing nonionic surfactants that are insoluble in water, this reduction in micelle size corresponds to a decrease in viscosity and an increase in cloud point, which facilitates the solubilization of larger amounts of nonionic surfactant.

Several important factors influencing the interaction between chelating agents and amphoteric surfactants were identified. The presence of oppositely charged moieties in both the surfactants and chelating agents is crucial for promoting a strong interaction. The positioning of these moieties also plays a significant role; the optimal distance of one or two methylene groups between positive and negative charges boosts the strength and likelihood of the interaction. Electron-donating groups and steric effects further modulate the interaction, either promoting or hindering the formation of these complexes.

Binary systems, *i.e.* surfactant and chelating agent, had only minor effects on surface tension and contact angle compared to surfactant solutions without chelating agents. However, the introduction of a nonionic surfactant in ternary systems magnified the interfacial effects, resulting in improved wetting behavior on hydrophobic surfaces. These findings suggest that the presence of a nonionic surfactant in systems containing amphoteric surfactants and chelating agents can enhance interfacial effects, making the system more effective for applications where surface wetting and stabilization are important.

These findings emphasize that by manipulating the interactions between surfactants and chelating agents, it is possible to avoid salting-out effects and enhance the solubility of complex surfactant mixtures. This approach can improve the performance of surfactant-based systems in practical applications, providing valuable insights for formulating and optimizing such systems.



## Acknowledgments

The Swedish Foundation for Strategic Research and Nouryon Surface Chemistry AB are gratefully acknowledged for their financial support.

This work would not have been possible without the contributions of many talented individuals:

- My academic supervisors, **Romain Bordes** and **Lars Evenäs**: It has been a real pleasure to have your guidance, challenges, and support. I hope you are enjoying the journey as much as I am... because I plan to stick around for some time!
- My industrial supervisors, **Sorel Muresan** and **Ulf Schröder**, and my examiner, **Martin Andersson**: Thank you for your interest in my work and for your valuable input.
- **Emelie Nero**, **Frida Jacobsson**, and **Sarah Lundgren**: Thank you for assisting in generating key data included in this work.
- **Louis Schwarzmayer**: Thank you for the engaging discussions and your readiness to help.

A heartfelt thanks to everyone at **Nouryon's Innovation Center in Stenungsund** and at the **Applied Chemistry Division at Chalmers** for making these spaces feel like home. Special thanks to those who check in on me and my work out of sheer care: **Steffen Brulls**, **Björn Englund**, **Sarah Lundgren**, **Smaragda-Maria Argyri**, **Frida Bilén**, and **Kinga Grenda**.

Thanks to **my friends** and **family**, your unwavering support means the world to me.

Finally, to **my beautiful daughter, Salomé Lobo Velásquez**. You are my greatest source of energy and inspiration. Your independence and willingness to help—both with small and not-so-small tasks—have been invaluable during demanding times. I don't think there are many kids like you, I consider myself the luckiest mom on earth!

Gracias... Totales!!!

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