Self-assembly Behavior in Systems Containing Surfactants and Chelating Agents

Understanding the Influence of Surfactant Head Groups and Chelating Agents on Cleaning Solution Properties

Master's thesis in Materials chemistry

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Abstract

Cleaning products play a crucial role in effectively maintaining a healthy and hygienic living environment. In all cleaning formulations ingredients like chelating agents and surfactants are essential for the products' performance. This study investigates the self-assembly of surfactants in the presence of chelating agents and their influence on the physicochemical properties and cleaning efficiency of cleaning formulations. The formulations consist of a nonionic surfactant, a chelating agent and a secondary surfactant. Three amine-based secondary surfactants were evaluated, including an amphoteric surfactant, an amine oxide, and a quaternary ammonium compound (quat). The chelating agents evaluated were L-glutamic acid N,N-diacetic acid tetrasodium salt (GLDA), methylglycine N,N-diacetic acid trisodium salt (MGDA), ammonium citrate and citric acid.

The study focuses on how these components affect clouding temperature, viscosity, foaming, wettability, and surface tension. Results show that clouding temperature, viscosity, and foaming are notably impacted by the choice of secondary surfactant and chelating agent, whereas surface tension remains unchanged. Amphoteric surfactants, in particular, reduce the salting-out effect of chelating agents like MGDA and GLDA, likely due to the similarity between their molecular structures. This interaction is hypothesized to lower the critical packing parameter (CPP), leading to smaller, more spherical micelles that increase solubility, raise clouding temperature, decrease viscosity, and improve foaming. These changes could enable higher concentrations of active ingredients, resulting in more concentrated, energy-efficient products with reduced packaging needs.

Cleaning performance tests on model soils revealed that formulations combining amphoteric or amine oxide surfactants with GLDA or MGDA were most effective across various surfaces and soil types, especially at higher concentrations of chelating agents. These findings suggest that combining amphoteric surfactants with GLDA or MGDA could lead to the development of more concentrated, sustainable cleaning products.

Keywords: Surfactants, Chelating agents, Surface cleaning, MGDA, GLDA, Citric acid, Ammonium citrate, Quat, Amine oxide, Amphoteric.

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Frida Jacobsson and Emelie Nero, Gothenburg, June 2024

List of Abbreviations and Acronyms

Below is the list of abbreviations and acronyms that have been used throughout this thesis listed in alphabetical order:

CMC	Critical micelle concentration
CP	Cloud point
CPP	Critical packing parameter
GLDA	L-glutamic acid N,N-diacetic acid tetrasodium salt
MGDA	Methylglycine N,N-diacetic acid trisodium salt
Quat	Dodecyltrimethylammonium chloride

Nomenclature

Below is the nomenclature of indices and parameters that have been used throughout this thesis.

Indices

S	Solid
L	Liquid
G	Gas

Parameters

γ_{SG}	Surface tension of the solid
γ_{SL}	Interfacial tension between liquid and a surface
γ_{LG}	Surface tension of the liquid
θ	Contact angle between a liquid drop and a surface
S	Spreading coefficient

Contents

1

Introduction

1.1 Background

Cleaning products play a crucial role in effectively maintaining a healthy and hygienic, as well as aesthetic living environment. These products range from household degreasers to the toughest industrial and institutional cleaning solutions. In all cleaning formulations ingredients like surfactants and chelating agents are essential for the products' performance [1].

A company that specializes in this field is Nouryon, a global specialty chemicals leader. This project will be carried out in collaboration with Nouryon Surface Chemistry in Stenungsund and the Division for Applied Chemistry at Chalmers University of Technology. The main goal for Nouryon, within the cleaning market, is to discover sustainable, natural and cost-effective products and formulations. Nouryon is a distributer of surfactant cleaning solutions to custumers who dilute and modify these solutions in various ways to produce different cleaning products. One of Nouryon's biggest challenges is to increase the concentration of the active ingredients in their products. More concentrated products uses less energy when manufactured and transported and also requires less resources for packaging [2]. This decreases the cost of the products and reduces their environmental impact.

In order to achieve efficient cleaning, the surfactants are very hydrophobic and therefore present a poor solubility in water. To solubilize these hydrophobic surfactants more hydrophilic surfactants are added as solubilizers, which in this project will be referred to as secondary surfactants. When these two surfactants are mixed, the combination will promote the formation of micelles and improve the solubilizing capability [3]. Unfortunately, for these hydrophobic surfactants to be soluble in water, in combination with the secondary surfactants, the amount of water must be sufficiently high [2]. This prevents formulations of highly concentrated solutions. If the surfactant solutions could be more concentrated, more cleaning products could be made from the same amount of solutions produced making it more cost-effective and sustainable.

In 2021, a patent was filed by Nouryon claiming the discovery of a cleaning formulation containing a chelating agent and an amphoteric surfactant that worked better at dissolving the hydrophobic nonionic surfactant in water than just the amphoteric surfactant alone. This allowed to reduce the water content in the solution making it possible for more concentrated liquid cleaning formulations.

Chelating agents are chemicals that control the reactivity of metal ions [4]. In hard water, calcium and magnesium ions leaves residues on surfaces and enhance the bonding of dirt. The chelating agents "catch" these ions, improving the cleaning power of the product. However, introducing chelating agents to surfactant systems usually promotes salting out of the surfactants dissolved in the water [5]. This means that with increasing concentration of chelating agent the solubility of the surfactant decreases. When chelating agents were introduced to systems containing both nonionic surfactants and amphoteric surfactants this was not the case. This deviant behaviour is not well understood and neither is how it affects the cleaning abilities of these systems. Therefore different surfactant-chelating agent systems will be studied to evaluate the behaviour and properties of those systems to determine what sets them apart and if other deviations are found.

1.2 Aim

This work aims to evaluate how the properties of systems containing nonionic surfactants, chelating agents and amine-based secondary surfactants are influenced by the nature of the secondary surfactants' head group and the type of chelating agent. The effect of the different components have on the systems' cleaning abilities will also be evaluated.

1.3 Research questions

The following questions are at the centre of this study: How does the nature of the secondary surfactants' head group and the type of chelating agent influence the physicochemical properties of the formulated systems? What is the impact of varying the type of chelating agent and secondary surfactant on the cleaning performance of the systems? What underlying mechanisms can explain the observed variations in the properties and performance of the formulated systems, particularly regarding the influence of the secondary surfactants' head group and the type of chelating agent?

2

Theory

2.1 Cleaning

Cleaning is a broad concept. A general definition can be that it is the process of removing undesired elements like dirt, pathogens, and various contaminants from either an object or its surroundings. Depending on the type of cleaning, different processes are used. In this report the focus is on cleaning of hard surfaces using a cleaning agent in combination with water. These cleaning agents are usually referred to as detergents.

Dirt adheres to surfaces by different forces, for example van der Waals forces and electrostatic interactions [6]. To remove the soil, interactions between the components in the cleaning agent with the soil and the surface are required. Some soils are water-soluble and some are water-insoluble, making the use of the right detergent, to achieve the wanted effect, crucial. The fact that there are near endless combinations of different soils and surfaces is why the research and development of new and improved detergents is still very relevant and why there are a lot of patented cleaning processes. Modern detergents are typically customized to suit the requirements of each particular application.

To effectively clean a surface, the water, along with the detergent, must sufficiently wet the surface. This requires the washing water to spread evenly across the dirty surface. In other words, it must have a low contact angle, which is achieved by low surface tension. Contact angle and wetting will be described more thoroughly in sections 2.5.1 and 2.5.3 respectively. After the water has wet the surface the detergent can interact with the soil and start the process of removing it. When the soil is removed from the surface and dispersed in the water it must be prevented from readsorbing onto the surface. The soil removal process is explained further in section 2.6.

2.1.1 Cleaning formulation components

The definition of a detergent is "a surfactant (or a mixture containing one or more surfactants) having cleaning properties in dilute solutions" [7]. In household settings, the term "detergent" is typically used when talking about laundry or dishwashing detergent. Such products consist of blends of different compounds, where not all of them are considered to be surface active. In this report, these cleaning mixtures will be referred to as cleaning formulations. Cleaning formulations can consist of surfactants, polymers, chelating agents, solubilizers, biocides etc [1]. For the cleaning formulations formulated in this project, a nonionic surfactant, a solubilizer (secondary surfactant) and a chelating agent were mixed together with water. The nonionic surfactants' main role is to remove the soil from the surface, the solubilizer is used to dissolve the nonionic surfactant in the water, i.e raise the cloud temperature, and the chelating agent is used to decrease the effects that hard water has on the surfactants.

2.2 Surfactants

The active ingredient in a cleaning formulation, the surfactant, is a molecule that is amphiphilic. It has a hydrophilic head group and a hydrophobic alkyl chain, often referred to as the tail. The surfactant, or surface active agent, has an affinity for interfaces. At an interface, surfactants reduce the interfacial tension [6]. Not all surfactants migrate to the interface, there are also surfactants in the bulk, dissolved as unimers, or in micelles.

The polar group of a surfactant can be charged or non-charged, dividing surfactants into different classes: nonionic and ionic. Ionic surfactants can either be positively charged or negatively charged, or both, which divides them into the categories: cationic, anionic and zwitterionic [8].

2.2.1 Nonionic surfactants

Nonionic surfactants are commonly used in detergency, both household and industrial, and has an important role as an emulsifier. The polar group of a nonionic surfactant is usually a polyoxyethylene consisting of 5-10 ethylene oxide units. It can also be a polyhydroxyl group. Since nonionic surfactants are neutral, they are normally compatible with all other types of surfactants. Ethyleneoxide based surfactants are stable to pH, electrolytes and hard water. Their physicochemical properties are, however, dependent on temperature. Increased temperature reduces the hydrogen bonding between the polar groups and the water molecules , resulting in a higher hydrophobicity of the surfactants at elevated temperatures, often referred to as cloud point [9]. Foaming is more active below the cloud point [10], and above the cloud point the surfactant act as a defoamer [11]. A disadvantage with nonionic surfactants is that they can be harmful to skin, since they can be oxidized in air [8].

2.2.2 Ionic surfactants

In an aqueous solution, the head group of an ionic surfactant dissociates into ions [12]. Anionic surfactants become anions, cationic surfactants become cations and zwitterionic surfactants dissociate into both anions and cations [8]. This happens by the dissociation of their counterions, which still are in close contact to the surfactant. Anionic and cationic surfactants are normally incompatible and would precipitate upon mixing [13]. Zwitterionic surfactants are however commonly suitable in mixtures with other classes of surfactants [14]. Ionic surfactants are partly used to increase the cloud point, or solubility, of a nonionic surfactant [15].

2.2.2.1 Anionic surfactants

Anionic surfactants holds the majority of the surfactant market, and it is estimated to be around 70%. Its success comes from low manufacturing costs and ease of production [8]. Detergency, both industrial and household, and pesticides are the main applications of anionic surfactants [16]. Anionic surfactants are used as wetting, spreading, emulsifying, foaming and dispersing agents [17]. The success of anionic surfactants in detergency is because of their ability to bind to and remove positively charged particles as clay. They also generate more foam than other classes of surfactants [15].

Common polar groups for anionic surfactants are sulfonate, sulfate, carboxylate and phosphate, which are combined with counterions as sodium, potassium, ammonium, magnesium, calcium and protonated alkyl amines. The choice of counterion can increase the solubility of the surfactant in oil or water, or both depending on their intended application [8].

2.2.2.2 Cationic surfactants

Cationic surfactants are most frequently used in fabric softeners, personal care (e.g. conditioners), antistatic agents, corrosion inhibitors, particle dispersants and emulsifiers [18]. Their field of application comes from their positive charge, which enables adsorption to most surfaces, which are normally negatively charged [8]. Cationic surfactants contain nitrogen-based functional groups as amine or quaternary ammonium, referred to as quats, where the central nitrogen atom is bonded to four alkyl or aryl groups [8]. Commonly halides as chloride and bromide act as counterions in quats [19].

Quats are stable in regard to pH. They have disadvantages in personal care products since they can cause skin irritation and allergies. Another disadvantage of quats is their harmfulness to the environment since they are commonly toxic to aquatic life and show low degradability [13] [19].

2.2.2.3 Zwitterionic surfactants

The interest in zwitterionic surfactants and their unique properties has significantly increased in the recent years. They have outstanding interfacial activity, low CMC [20], and low eye and skin irritation which creates possible applications in personal care [8]. The downside with zwitterionic surfactants is the increased manufacturing cost and therefore they only hold about 5% of the market. This also contributes to limited research within the field [20]. A zwitterionic surfactant which behavior is depending of the pH and which can dissociate into both anions and cations is called amphoteric [8].

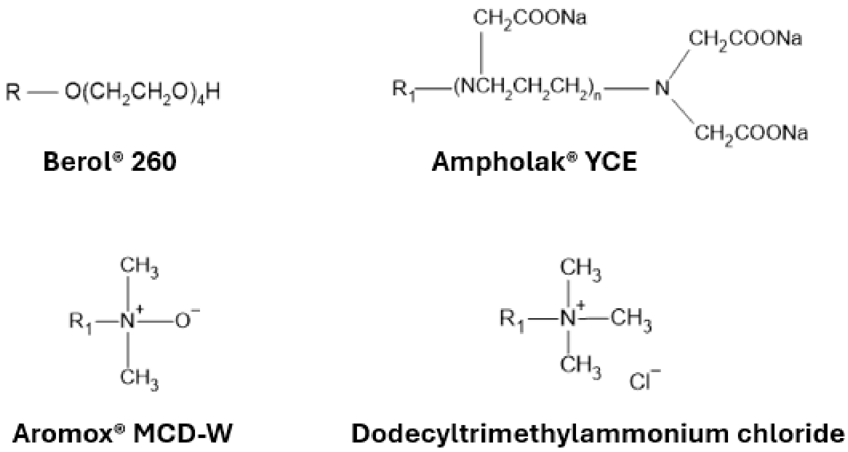
Groups that contain a positive charge are quaternary ammoniums, imidazoliums, pyridiniums and phosohoniums, which are combined with anionic carrying groups as carboxylates, sulfonates or sulfate groups in the polar head group. The positive and negative charge in the head group is separated by a small segment such as methylene. Zwitterionic surfactants have larger head groups than regular ionic surfactants, which result in bigger micelles and lower CMC [20].

pH influences a system containing amphoteric surfactants. At low pH, they are positively charged and at high pH they are negatively charged [21]. At the isoelectric point, the amphoteric surfactant does not carry a charge and it resembles a nonionic surfactant in terms of physicochemical properties [22]. Foaming, wetting and detergency are properties known to be affected by the pH dependence of amphoteric surfactants [8].

One type of zwitterionic surfactant is amine oxides. At high pH they are neutral and at low pH they behave as cationic surfactants [23]. This phenomenon is useful in making pH-responsive systems. Anionic surfactants can also influence the amine oxides to become cationic surfactants. Some authors refer to amine oxides as nonionic or cationic surfactants [8]. Applications of amine oxide surfactants are in detergency, cosmetics and drug delivery as they have good skin compatibility and great dispersing and foam boasting ability [8],[24]. Straight-chain dimethyl amine oxides form spherical micelles at least up until the alkyl chain of the surfactant is 12 C long, and from at least 18 C they form rod-like micelles [23].

2.2.3 Surfactants in this project

The surfactants used in this project are presented in Figure 2.1. The same nonionic surfactant is used in all formulations and is called Berol® 260. It is a $C_9 - C_{11}$ alcohol ethoxylate with four ethoxylate units. The secondary surfactants investigated are an amine oxide-based surfactant, an amphoteric surfactant and a cationic surfactant. They are used to solubilize the nonionic surfactant Berol® 260. The amine oxide based surfactant is called Aromox® MCD-W, with the chemical name: cocodimethyl amine oxide. The second surfactant is Ampholak® YCE which is an amine-based amphoteric surfactant of propionate type. Its chemical name is sodium cocopropylenediamine propionates. The last surfactant is a quat, a cationic surfactant, with the chemical name dodecyltrimethylammonium chloride. All three secondary surfactants have the same length of the lipophilic chain represented by R_1 in Figure 2.1. It is 12 carbons long.



Berol® 260

Ampholak® YCE

Aromox® MCD-W

Dodecyltrimethylammonium chloride

Figure 2.1: Molecular structure of the surfactants: Berol® 260, Ampholak® YCE, Aromox® MCD-W and dodecyltrimethylammonium chloride.

In Table 2.1 the physicochemical properties: pH, viscosity, density, cloud point and surface tension of the surfactants are presented.

Table 2.1: Physicochemical properties of Berol® 260, Aromox® MCD-W, Ampholak® YCE and dodecyltrimethylammonium chloride.

Surfactant	**pH**	**Viscosity** $[mPa]$	**Density** $[kg/m^3]$	**Cloud point** $[°C]$	**Surface tension** $[mN/m]$
Berol® 260	7-9.5^a	50^a	960^a	55-59^a	27^a
Aromox® MCD-W	7-8^b	50^b	960^b	-	30^b
Ampholak® YCE	6-7^c	$\leq$ 150^c	1047^c	-	39^c
Quat	4-7.5^d	-	930^d	-	33^e

[a] Data adopted from *Nouryon Product data sheet Berol 260* [25].
[b] Data adopted from *Nouryon Product data sheet Aromox MCD-W* [26].
[c] Data adopted from *Nouryon Product data sheet Ampholak YCE* [27].
[d] Data adopted from *Chemical book: dodecyltrimethylammonium choloride* [28].
[e] Data adopted from *Parchem Product specification dodecyltrimethylammonium chloride* [29].

2.3 Interface adsorption and micellization

Interfacial tension is referred to as the amount of energy required to create a unit area of interface between two immiscible phases. It can also be described as a result of an imbalance in forces, which is described in Figure 2.2 c). In the bulk of a liquid, a molecule experiences the same molecule and therefore the same force in all directions, resulting in a net zero force. At an interface, a molecule experiences a net force inwards the bulk since it lacks bulk molecules in the opposite direction, causing the interface to contract. Reduction in interfacial tension is favoured by a close-packed interface and the maximum reduction in interfacial tension is reached when micelles, large aggregates of surfactants, start to form in the bulk [8].

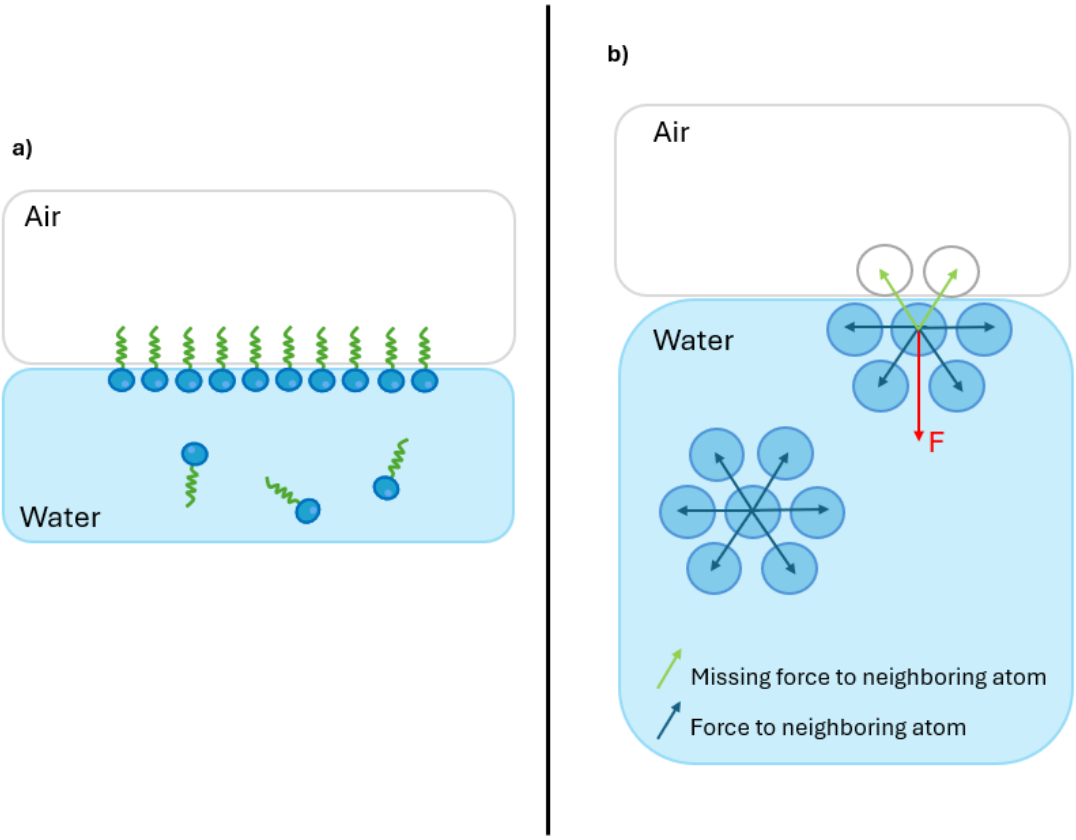


Figure 2.2: (a) a monolayer of surfactants between the air-water interface and (b) the origin of surface tension caused by an imbalance in forces of a molecule located at an interface.

The interfaces between air-water, oil-water and solid-water attract surfactants, where they form a monolayer, see Figure 2.2 a). The surfactant locates itself with its hydrophilic part in the polar phase and its hydrophobic part in the non-polar phase. The driving force of surfactants migrating to an interface is to minimize the interaction with water and is called the hydrophobic effect. Electrostatic interactions also influence surfactant adsorption at interfaces for ionic surfactants. In an aqueous medium, a surfactant binds with its counterion, known as counterion binding. This interaction fixes the counterion's position, preventing it from moving freely within the medium. The counterions are governed by a balance of energy and entropy, where energy attracts the counterions to a charged surface and entropy makes the counterions want to be spread out in a solution. The assembly of counterions close to a surface is called the double layer, which is governed by an electrostatic force and entropy. High counterion binding is achieved when the electrostatic force is bigger than the entropy, which happens when the surface charge increases [8].

2.3.1 Critical micelle concentration

At the critical micelle concentration the first micelle forms. No more surfactants migrate to the interface, and as a result, the surface tension has reached its minimum. CMC can be measured with different techniques since many properties have a characteristic change at CMC, e.g. surface tension or solubilization. CMC depends on e.g. the length of the alkyl chain, the type of polar group and the type of counterion. The dependence of the length of the alkyl chain is according to Traub's rule: adding one methylene group to the alkyl chain decreases the CMC with a factor of two or three for ionic respectively nonionic surfactants. Ionic surfactants have a much higher CMC than nonionics, and within the ionic group, anionic surfactants have marginally lower CMC. The counterion is also important for the CMC [8].

CMC also depends on physical properties. For ionic surfactants, CMC is independent of temperature, while for ethylene oxide nonionic surfactants the CMC decreases with increasing temperature. Addition of electrolytes is the most important property which influences the CMC for ionic surfactants. The effect is more predominant in long-chained surfactants [8].

The properties of a surfactant system are highly dependent on CMC, e.g. solubility, surface tension and turbidity as seen in Figure 2.3. It shows that solubilization requires a concentration much higher than CMC and how the surface tension decreases drastically until CMC is reached.

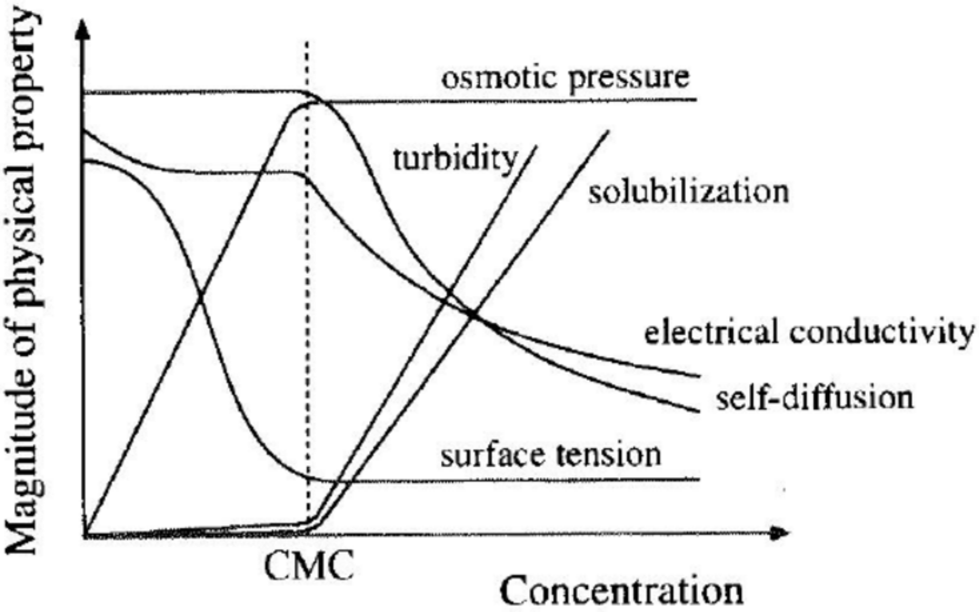


Figure 2.3: Physicochemical properties dependence on CMC [30].

2.3.2 Micelles

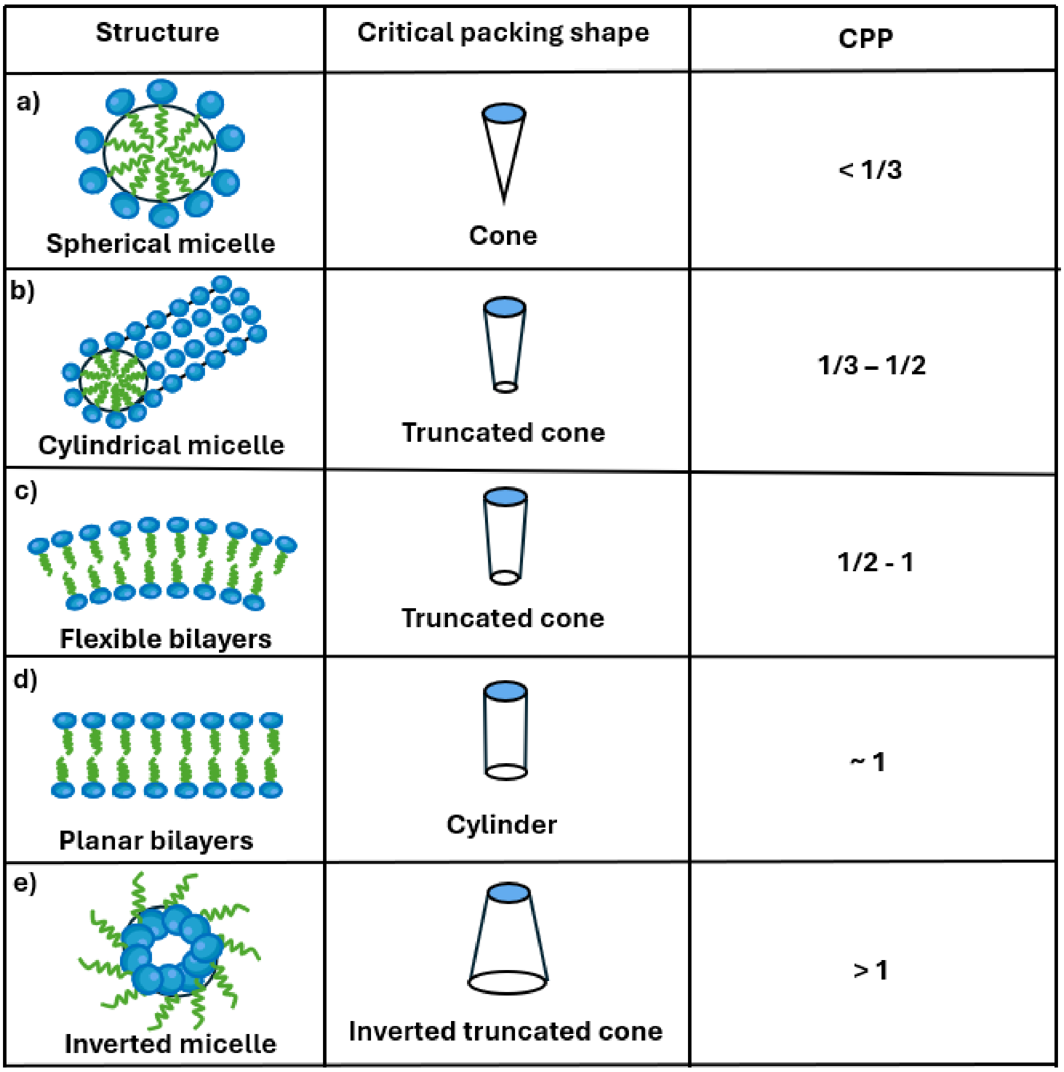
The driving force for micelle formation is hydrophobic interactions [8]. In an aqueous solution above the CMC, the hydrophilic heads face the water and the surfactants' tails face each other, where the alkyl chains are held together by Van der Waals forces [8][31]. The alkane interior has lower energy than an alkyl chain in water. Besides the attractive forces between alkyl chains causing micelles to form, there are also opposing forces from the polar group. They are comprised of charge-charge repulsion and hydration of the polar group. This creates an equilibrium preventing micelles from growing endlessly. The opposing forces of ionic surfactants are more predominant than for nonionic surfactants, partly because of their head-to-head repulsion, however, mostly because of their counterion binding [8]. Nonionic surfactants have therefore a much larger force for micelle formation. It is a difference of about 100 times [32]. The CMC for nonionic surfactants are therefore at significantly lower values than for ionic surfactants.

Micelles are typically spherical. The micelle has a radius typically between 1.5-3 nm, which is the size of an extended alkyl chain of a surfactant. The alkyl chains are, however, not extended in the micelle [8].

Micelles consist of a defined number of surfactants called the aggregation number. It is dependent on the type of surfactant, temperature and electrolyte addition, and is used to describe the size and shape of micelles [33].

Micellar growth for ionic surfactants is influenced by their structure, where longer alkyl chains promote growth. If the temperature of the system is increased, growth will decrease, however, increased surfactant concentration supports growth. The counterion also has a major influence, it can either prohibit or promote growth depending on which type it is. Addition of cosolutes to the system also has an effect, where salt, medium to long-chain alcohols and aromatics induce the growth, while alkanes and other non-polar solutes inhibit growth [8]. Nonionic micelles behave differently than ionics. A smaller polar group leads to increased growth of polyoxyethylene based micelles, where 4 to 6 oxyethylene units are most favorable. There is no or little growth with 8 or more oxyethylene units. Temperature influences nonionic surfactant-based micelles in contradiction to ionic ones; higher temperature induces growth. While higher surfactant concentration also promotes growth for nonionic surfactants [8].

Micelles are regularly described as spherical, however, they can also possess other structures such as cylinders, bilayers and vesicles. Factors influencing the structure are hydrophobic interactions, electrostatic repulsion, hydration or steric hindrance and packing considerations. Concentration of surfactant, temperature and addition of salt to the system can also influence the micelle structure [34]. Micelles and their structure can be studied with different techniques as NMR and light scattering techniques [31]. Presented in Figure 2.4 is (a) a spherical micelle, (b) a cylindrical micelle, (c) a flexible bilayer, vesicle (d) a planar bilayer and (e) a reversed micelle.



Structure	Critical packing shape	CPP
a) Spherical micelle	Cone	< 1/3
b) Cylindrical micelle	Truncated cone	1/3 – 1/2
c) Flexible bilayers	Truncated cone	1/2 - 1
d) Planar bilayers	Cylinder	~ 1
e) Inverted micelle	Inverted truncated cone	> 1

Figure 2.4: Different structures of micelles with their critical packing shape, where the blue circle represents the head and the cone represents the tail. The CPP of each structure is also noted.

2.3.3 Critical packing parameter

The geometry of micelles can be defined by the critical packing parameter, CPP, which is a dimensionless number. It describes the relationship between the area of the polar group, a, extended chain length, l, and volume, v, of the hydrophobic tail of the surfactant according to equation 2.1.

$$CPP = \frac{v}{a\, l_{\text{max}}} \tag{2.1}$$

The area of the head group is influenced by electrolyte addition for ionic surfactants and temperature for nonionic surfactants. Including salt in an ionic surfactant solution will increase the CPP and promote the formation of cylindrical micelles instead of spherical ones. This is due to closer packing of the surfactants in the micelles because the salt screens head-to-head repulsive forces [8].

If the critical packing parameter is below one third, the surfactants will form a spherical micelle. Typically nonionic surfactants with large head groups and ionic surfactants in absence of electrolytes form spherical micelles [8]. The CPP for other micelle structures is noted in Figure 2.1. If the CPP is increased a little then cylindrical micelles will form. Around one bilayers are formed, and above one reversed micelles are the dominant structure.

2.3.4 Mixed micelles

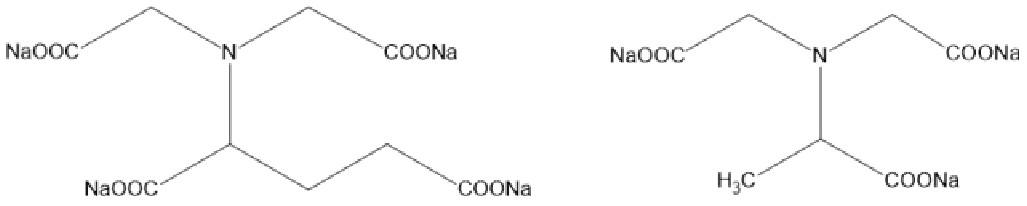
In most applications, there are not only one but several different types of surfactants in the system which can form mixed micelles [8]. These micelles show enhanced performance. They are used as solubilizers and suspension or dispersing agents [35]. Mixed micelles between nonionic and ionic surfactants are most commonly found on the market [8]. It owns its success to decreased electrostatic repulsion [35].

Mixed micelles have enhanced properties from their single surfactant micelles by e.g. reduced CMC, increased foaming and beneficial rheological properties [36]. The properties of a system containing mixed micelles will be influenced by the interaction of the two surfactants and their relative surface activity, described in CMC. For a mixed micelle, the CMC is influenced by both surfactants in the mixture [8]. The stability of a mixed micelle depends on the structure of the single surfactants in the mixture. Similar length of the alkyl chains favours stability of a nonionic-nonionic micelle. This phenomenon is also present in nonionic-ionic micelles, however, head group interactions are of greater importance to consider for those micelles [35].

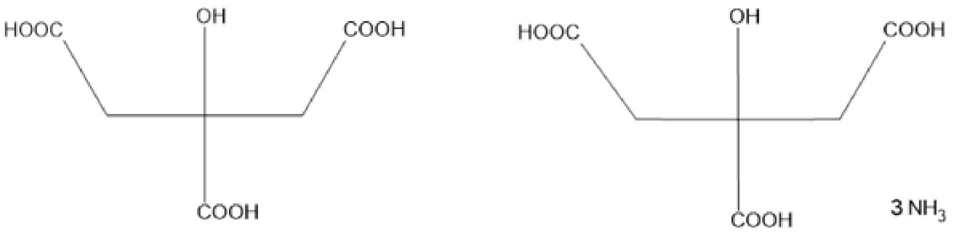
2.4 Chelating agents

Chelating agents are used in detergency to remove ions such as Ca^{2+}, Cu^{2+}, Fe^{3+} and Mg^{2+} from water, since they affect the surfactant solubility and thereby their cleaning ability. The ions will adhere to surfaces and leave residues, making the surface appear dirty even after cleaning. The residues contribute to adhesion of dirt and bacteria. The foaming ability can also be affected, where an increase in hard water leads to a decrease in foaming [37]. Chelating agents bind to metal ions and form ring complexes with them. A chelating agent has two or more functional groups which can donate an electron pair to the metal. Typical functional groups are NH_2 and acidic groups as $COOH$, SO_3H, OH and SH. These functional groups must be located within the molecule to allow ring formation with the metal. The chelate ring is usually five or six-membered, however, some four-membered rings exist [38]. Different chelating agents have an affinity for different metal ions.

The chelating agents investigated in this project are Methylglycine N,N-diacetic acid trisodium salt (MGDA), L-glutamic acid N,N-diacetic acid tetrasodium salt (GLDA), citric acid and ammonium citrate tribasic, which are presented in Figure 2.5. MGDA and GLDA contain a central nitrogen atom and all four chelating agents have at least three carboxylic acid groups, which can bind to metal ions. MGDA and GLDA have sodium counterions, while ammonium citrate has NH_4^+ and citric acid only H^+.



GLDA **MGDA**



Citric acid **Ammonium citrate tribasic**

Figure 2.5: Molecular structure of GLDA, MGDA, citric acid and ammonium citrate tribasic.

GLDA is an environmentally friendly chelating agent due to its biodegradability and biobased source. Up to 86% of the raw material used for GLDA is biobased and GLDA is degraded within 28 days to an extent over 60%. GLDA is produced by monosodium glutamate (MSG), which is naturally occurring in different foods as corn. GLDA is stable in regard to temperature and has high solubility across the entire pH-range [39]. MGDA is also a biodegradable surfactant, with a degradability over 68%. It has similar properties to GLDA, that it is stable in regard to temperature. MGDA has a higher chelating ability than citrates [39]. The solubility of MGDA and GLDA in water increases with increasing pH. The highest solubility is found when they are fully ionized, which happens at high pH. GLDA has higher solubility than MGDA in the whole pH-range.

Citric acid is an organic acid with many applications, e.g. the use as a chelating agent [40]. Also, salts of citric acid as ammonium citrate are good chelating agents [41].

2.5 Properties

Understanding certain properties of surfactants and detergents is crucial as they significantly impact performance in various ways. Below are these key properties, which provide insight into the cleaning process, described.

2.5.1 Cloud point

At a specific temperature, the solubility of a nonionic surfactant in water at 1 wt% sharply decreases, resulting in the solution becoming turbid. The temperature at which this happens is called the cloud point, CP, referring to the cloudy appearance [6]. This behaviour is reversible and the solution will become clear again upon cooling. The solubility of nonionic surfactants in water is due to the formation of hydrogen bonds between the hydroxyl (-OH) and ethoxy groups (-CH_2CH_2O-) of the head groups and the hydrogens in the water molecules [6]. When the temperature is increased the conformations of the ethoxy groups will change into conformations with higher statistical weight and less or no dipole moments. With no dipole moments the surfactants will no longer be polar and they will interact less favorably with water, causing the surfactants to become insoluble. This is the reason why the cloud point is not very influenced by the length of the alkyl chain but all the more influenced by the length of the polar head group, for example a polyoxyethylene chain. The cloud point is also highly dependent on the size of the micelles, larger micelles will give lower CP [8]. Above the cloud point there will be two phases, one water-rich phase and one surfactant-rich phase, and the nonionic detergent will therefore not be useful above the CP. In general, the nonionic surfactants are optimal for detergency when used just below their CP, but above their CMC [42].

The clouding of nonionic surfactants can be altered by the addition of cosolutes [8]. By addition of electrolytes the CP can be either increased or decreased depending on the type of salt. If the cloud point is increased by the addition of cosolutes it's referred to as salting in and if the cloud point is decreased it's salting out. The Hofmeister series ranks the order in which salts influence solubility [43]. Anions have a stronger effect than cations and some anions and cations are shown in the series below.

$$Citrate^{3-} > SO_4^- > CH_3COO^- > Cl^- > Br^- > I^- > SCN^-$$

$$Ni^{2+} > Ca^{2+} > Li^+ > Na^+ > K^+ > NH_4^+ > (CH_3)_4N^+$$

The ions to the left are more hydrated than the ones on the right and are classified as water structure makers. This means that they tend to bind more water than the surfactants, leading to stabilization of the surfactant structure which will cause salting out behaviour. Larger ions, like SCN^- or $(CH_3)_4N^+$, are considered less polar than smaller ions like Citrate^{3-} or Ni^{2+} and exhibit reduced affinity for water. They thus become concentrated near the oxyethylene groups, which will cause the surfactants' structure to unfold, leading to increased solubility and cloud point.

By introducing ionic surfactants the formation of mixed micelles occurs and this can increase the solubility and the cloud point as well. The mixed micelles will then carry a charge, making it significantly more challenging to achieve the formation of a concentrated surfactant phase due to the adverse electrostatic interactions resulting from the entropy of the counterion distribution [8]. Mixed micelles might also alter the CPP and therefore the size and shape of the micelles which will lead to a change in the cloud point.

2.5.2 Viscosity

Studying viscosity helps with formulating surfactant solutions with desired rheological properties, ensuring they meet specific application requirements. There are no ideal viscosity values for detergents, it all depends on what type of detergent that is produced and in which market and country it's being sold etc. [44]. A detergent should have a viscosity that will make the delivery of the cleaning agents efficient. An excessively high viscosity can impede the flow of the detergent, while a viscosity that's too low may compromise its stability or its ability to effectively remove dirt and stains.

For surfactant solutions, the viscosity is weakly dependent on the formation of spherical surfactant aggregates, micelles. If the surfactant self-assembly behaviour creates bigger cylindrical or thread-like micelles the viscosity will increase more intensely [8]. When the concentration of surfactants is increased the viscosity is also increased. For the spherical micelles at low concentration, the viscosity increase is only dependent on the micelle size but at higher concentrations it's also due to micelle-micelle interactions, causing the viscosity to drastically increase at elevated concentrations. For micelles that are not spherical, a small increase in the concentration will highly affect the viscosity whereas for spherical micelles the concentration has to be relatively high to cause significantly higher viscosity.

2.5.3 Wettability

Wetting is the ability of a liquid to spread on a surface and the degree to which it spreads is referred to as wettability [8]. The wettability is dependent on the nature of both the surface and the liquid drop. Wetting influences the spreading, penetration and adhesion of cleaning agents on surfaces. In Figure 2.6 an illustration of a liquid drop on a surface can be seen and how the spreading is affected by different forces.

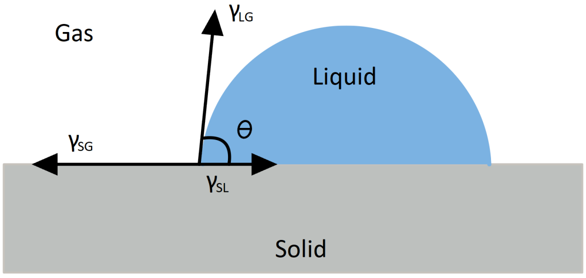


Figure 2.6: Illustration of the forces acting on the drop and the contact angle related to Young's equation.

θ is describing the contact angle between the drop and the surface. If considerable spreading occurs the contact angle will be low and the liquid-solid and the liquid-gas interfacial areas will increase. If the liquid is water this means the surface is hydrophilic. A rule of thumb is that when the contact angle for water is below 90° the surface is hydrophilic and when it's close to or above 90° the surface is hydrophobic. The γ_{SG} is the surface tension of the solid, measured in mN/m. It's usually referred to as the surface free energy, and this force strives to increase the spreading of the drop. Therefore spreading is excessive on solid materials with a high surface energy. The γ_{LG} describes the surface tension of the liquid and γ_{SL} is the interfacial tension between the liquid and the surface. From Figure 2.6 Young's equation can be derived

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos\theta \tag{2.2}$$

where the horizontal component of the surface tensions, $\gamma_{LG}\cos\theta$, and γ_{SL} work against spreading. Spreading occurs until equilibrium is reached and the resultant force is zero.

Quantifying the wettability of a solid surface can be difficult as it is not easy to assess the surface free energy and the interfacial tension. Materials with a high surface energy such as metals, glasses and ceramics usually promote total wetting, making the contact angle zero. However, on low-energy surfaces such as polymeric materials the wettability is difficult to quantify. A rule, however, is that for a liquid to spread on a surface the surface free energy must be higher than the surface tension of the liquid.

From equation 2.2 a spreading coefficient can be derived

$$S = \gamma_{SG} - \gamma_{SL} - \gamma_{LG} \tag{2.3}$$

indicating that spreading will always occur if $S>0$. This equation demonstrates that wetting can be promoted either by decreasing γ_{SL} and γ_{LG} or by increasing γ_{SG}. By adding a surfactant both the surface tension of the liquid and the interfacial tension will decrease, as described in section 2.2. It is also possible to promote wetting by modifying the surface into becoming more hydrophilic which will increase the value of γ_{SG} and decrease the value of γ_{SL}. If a surface is made dirty the wettability of the surface may change. The surface can become more hydrophobic due to oily soil with low polarity and there can also be less spreading due to a more uneven topography.

For a surfactant to be a good promoter of wetting, known as wetting agent, it should be able to move rapidly to the newly created surface and have a strong driving force for the liquid-solid interface as well as effectively reduce the surface tension. Another important condition is that there are a sufficient amount of free surfactants that are not in the form of micelles.

The viscosity of the surfactant solution can affect the wetting of the surface. If two solutions with the same surface tensions are compared, the one with higher viscosity will spread more slowly but will not necessarily have lower wettability. The initial contact angle will not be affected by the viscosity [45].

2.5.4 Foaming

The definition of a foam is a dispersion of a gas in a liquid or solid, however this work is limited to liquid foams. The appearance of foams is determined by their foam number, which is described by the ratio between gas and liquid. If the amount of gas is low, i.e a low foam number, the gas bubbles will be spherical and the liquid lamellae between the bubbles will be thick. In the opposite case, the liquid lamellae will be thin and planar. The region where three bubbles meet is called the Plateau border, see Figure 2.7 [8].

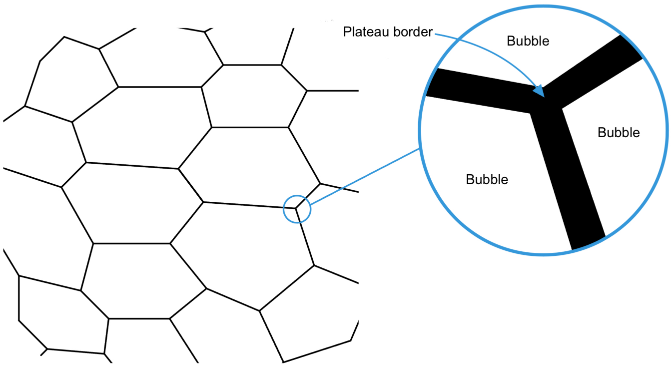


Figure 2.7: Foam with a high foam number and a zoom in on the plateau border where three bubbles meet.

To form a liquid foam the liquid must be a mixture as pure liquids can not foam. One of the components in the mixture must be surface active, for example a surfactant, to lower the surface tension in the liquid-gas interface. This enables the liquid to spread and form a stable film over the gas phase, called the foam film. The foam film promotes the formation of smaller, more numerous bubbles, resulting in a more stable foam structure [8]. To form a foam the foam film must also exhibit surface elasticity, meaning that if the foam film has been stretched there must be a force pulling it back to its original state, see Fig 2.8. The force is due to the change in the surface tension gradient which is trying to pull back the lamellae to reduce the created higher surface tension and return to equilibrium. For this to happen the transportation of the surfactant from the bulk to the stretched surface must be slower than the restoration of the lamellae. If that's not the case the surfactants will end up lowering the surface tension of the stretched region, removing the surface tension gradient, resulting in a permanent stretch and weakened lamellae.

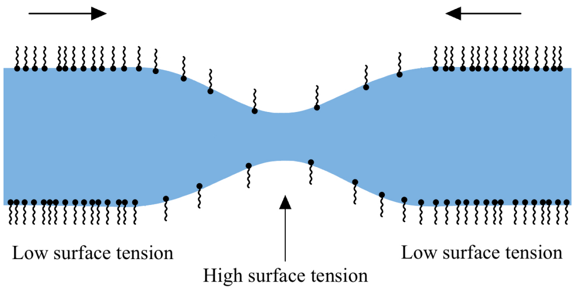


Figure 2.8: A stretched lamellae showing the uneven concentration of surfactants and how this influences the surface tension.

There are four different forces acting on foams, gravitational forces, pressure difference in Plateau borders and lamellas, pressure difference of the gas in bubbles of different sizes and repulsion between charges at the interfaces [8]. The gravitational force causes the liquid to drain between the bubbles, destroying the foam, and can be reduced by increased viscosity of the bulk liquid or by introducing solid particles or emulsion droplets. The gravitational force, as well as pressure differences between plateau border and lamellas and between bubbles of different sizes, are all destabilizing forces. If the surfactants coating the walls of the lamellae are carrying a charge the repulsion between these charges can help stabilize the foam [32]. When the foam is collapsing the lamellae will shrink and the head groups of the surfactants will come closer together and an electrostatic repulsion will arise preventing further shrinkage of the lamellae. In contrast to the other three forces this is a stabilizing force.

The critical packing parameter, CPP, is important to assess and a vital tool to understand when describing foaming and foam stability. When the CPP increases the surfactants pack closer together at the liquid-air interface resulting in higher cohesion. This increases both the elasticity and the viscosity of the liquid lamellae, giving it strength that results in high foamability and good foam stability [8]. Foamability does not continuously increase with CPP however, at a certain value it will start decreasing. This is because the foamability will decrease if the thin liquid film between the bubbles is broken. Breaking of the film is usually onset by the formation of a hole in it. The formation of holes correlates with the CPP, and a surfactant with a higher CPP exhibits a stronger tendency to create holes. The reason for this is that the energy required to form a hole in surfactant systems with a low CPP is much larger than for systems with a high CPP due to the high curvature of the hole created. Therefore highest foamability is obtained where these two phenomena balance each other.

At the air-water interface, the interaction between the water molecules and the surfactants is dependent on the surfactants' charge. Cationic surfactants, as quats, at the monolayer has been shown to attract the oxygen atom of water molecules, turning the hydrogen atoms towards the solution. For anionic surfactants such as SDS (sodium dodecyl sulphate), it has been shown to be the opposite behaviour, where they attract the hydrogens of the water molecules [46]. Between the hydrogen of the water molecules and certain headgroups as sulphates of anionic surfactants there will be formation of hydrogen bonds. This is not the case in cationic surfactants, since the hydrogens pointt towards the bulk, not exposed to create hydrogen bonds with the surfactant head group. The hydrogen bonds allow for a denser packed interface which leads to a higher foamability and greater foam stability [47].

Foaming is affected by temperature. At temperatures above the cloud point of the surfactant solution foaming will be low due to the phase separation. The surfactant-rich phase will act as an antifoam and reduce the foamability [48]. At temperatures slightly below the cloud point, the foam ability is the highest. This applies to nonionic surfactants as the polyoxyethylene chain will contract at higher temperatures, giving a higher CPP value [8]. As long as the new higher CPP value does not promote the formation of holes, this is the case. There isn't a class of surfactants that are better foamers, however, within a class of surfactants there is an optimal CPP that will give the optimal packing at the interface and the most stable foam [32].

2.6 Soil removal process

The mechanism of removing soil from a surface is different depending on the type of soil present and the type of detergent formulation. There are two types of soil, oily soil and particulate soil. Oily soil is in liquid form and usually refers to petroleum products such as engine oil and vegetable oil while the particulate soil refers to unwanted solid particles attached to the surface [8]. Particulate soil can be hydrophilic as well as hydrophobic. Both these soils adhere to the surface as a consequence of van der Waals forces and electrostatic interactions between the contaminants and the surface [49]. When the contaminants are removed from the surface it's also important that readsorption is prevented.

2.6.1 Electrostatic stabilization

If the surface and the particulate soil particles are both negatively charged the cleaning is relatively easy. This is because of electrostatic stabilization. When the soil particles and the surface have the same charge there will be an accumulation of oppositely charged counterions around the contact zone. This will lead to an osmotic flow of water into this zone that will cause the particle to desorb from the surface [8]. However, if the soil particles and the surface are not of the same charge, i.e. the particles have a positive or neutral charge, electrostatic stabilization is not possible unless the pH is raised. A raised pH will deprotonate neutral and positively charged functional groups and give them a negative charge or a neutral charge respectively. This will give both the surface and the soil a negative net charge which will make the removal of the soil particles easier. The same electrostatic stabilization mechanism can be applied when hydrophobic particles are attached to hydrophobic surfaces. This situation, however, requires the addition of surfactants. Anionic surfactants will create a negatively charged monolayer on the particles and the surface, which again will promote an osmotic flow of water, see Figure 2.9. The same process is possible for cationic surfactants, but then the possibility for readsorption is higher because the desorbed particles will be positively charged while the surface will most likely have a net negative charge. For nonionic surfactants, the osmotic flow will be due to the high concentration of polyoxyethylene chains in between the particles and the surface. This is more related to steric stabilization as opposed to electrostatic stabilization.

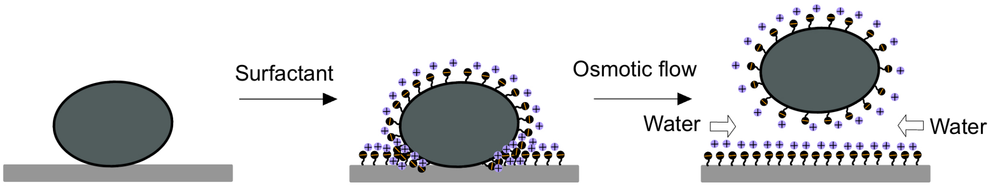


Figure 2.9: Hydrophobic particle attached to the hydrophobic surface is removed by the addition of anionic surfactants. Due to the high concentration of counterions, an osmotic flow of water will cause the particles to detach.

2.6.2 Roll-up mechanism

The so called roll-up mechanism is applied to oily soils but has a similar principle as described above. When the oil is attached to a moderately hydrophilic surface, causing the contact angle to be around or above 90°, a surfactant solution is needed to remove the oil [8]. The surfactants will enter the area between the oil and the surface and attach to both surfaces leading to an osmotic flow that will detach the soil, see Figure 2.10. This does not work if the surface is completely covered in oil as the surfactants won't be able to reach the surface and detach the soil.

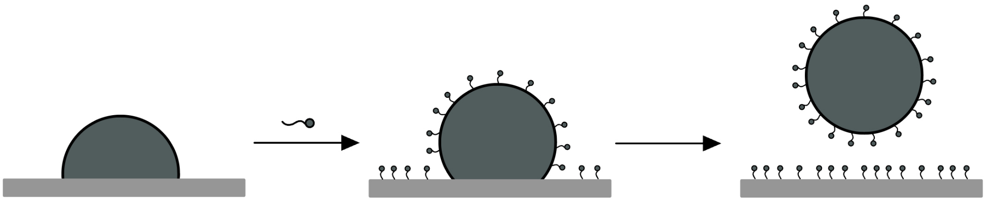


Figure 2.10: The roll-up mechanism for oily soil attached to moderately hydrophilic surface.

2.6.3 Emulsification

Both emulsification and solubilization, see section 2.6.4, are mechanisms applied when the surface is hydrophobic and wetting by the oil occurs. The removal of the oil is then based on lowering the interfacial tension between the oil and the surrounding water as opposed to the oil and the surface. Emulsification takes place when the interfacial tension is so low that the oil is deformed, creating an elongated drop [8]. The elongated drop will eventually "neck" and a free oil drop is formed, see

Figure 2.11. The oil drop will be stabilized by a monolayer of surfactant, preventing it from readsorbing to the surface. For the emulsification mechanism to succeed some mechanical action is often required as well.

Figure 2.11: The emulsification mechanism.

2.6.4 Solubilization

The solubilization mechanism does not require mechanical action but is taking place spontaneously. A microemulsion is formed from the surface of the soil. For maximum efficiency the microemulsion should be bicontinuous. The surfactants interact with the soil-water interface, solubilizing the soil into a microemulsion generated around the surface of the soil [8]. This creates a new surface on the remaining soil and fresh contact is established with the detergent solution, making new microemulsions, see Figure 2.12. If the surfactant solution is above its CMC and the concentration of surfactants is in excess in comparison with the oily soil direct solubilization into micelles might occur. The occurrence and rate of this is enhanced when surfactant-rich phases are present in the cleaning solution [50]. These phases exist when the surfactants are above their cloud points. The phases rich in surfactants can either directly dissolve the oily soil or engage with it to create intermediary phases abundant in surfactants, such as microemulsions with a large oil content, as previously mentioned. Given suitable conditions, these intermediary phases can then be emulsified into the washing solution. The effectiveness of solubilization can therefore be explained by the phase inversion temperature (PIT).

Figure 2.12: The solubilization mechanism. The soil is solubilized in a microemulsion.

The PIT is the temperature at which the oil-water interfacial tension is at a minimum for an oil-water-surfactant system. The cloud point, which is usually used to characterize surfactant systems, does not take the oil phase into account, which the PIT does. This is the reason why the PIT is the temperature of relevance for solubilization. To obtain the most effective solubilization the cleaning should be done at the phase inversion temperature [8]. When the oily soil molecules are larger than the tail of the surfactant, which is often the case, the PIT is larger than the cloud point. This means that the cleaning should take place at a temperature above the cloud point. For oil molecules smaller than the surfactant tail it's the opposite.

3

Methods

The methodology was divided into formulation preparation, determination of physicochemical properties related to detergency and examination of the cleaning ability.

3.1 Formulation preparation

The cleaning formulations prepared contained a nonionic surfactant, a secondary surfactant and a chelating agent in an aqueous solution. The nonionic surfactant was the same in all formulations. There were three different secondary surfactants and four different chelating agents tested in a matrix system, see Table 3.1.

Table 3.1: Components for the different cleaning systems evaluated.

Nonionic	Secondary surfactant	Chelating agent
Berol 260	Ampholak YCE	Ammonium citrate
Berol 260	Ampholak YCE	Citric acid
Berol 260	Ampholak YCE	GLDA
Berol 260	Ampholak YCE	MGDA
Berol 260	Aromox MCD-W	Ammonium citrate
Berol 260	Aromox MCD-W	Citric acid
Berol 260	Aromox MCD-W	GLDA
Berol 260	Aromox MCD-W	MGDA
Berol 260	Quat	Ammonium citrate
Berol 260	Quat	Citric acid
Berol 260	Quat	GLDA
Berol 260	Quat	MGDA

For every system, different concentrations in the range 0.5 - 9 wt% of the chelating agent were prepared. A formulation without the chelating agent present was also prepared for every system and used as a reference. The concentration of the nonionic surfactant was fixed at 6 wt%. For the secondary surfactant, the concentration varied in a range between 1.9-6 wt%. The concentration of the secondary surfactant was determined with regard to the clouding temperature of the system. The clouding temperature was aimed to be under 80°C for every concentration of chelating agent used in a certain system.

The chemicals used were Dodecyltrimethylammonium chloride (≥98%, Sigma-Aldrich), Ammonium citrate tribasic (≥97%, Sigma-Aldrich), Aromox® MCD-W (Nouryon), Ampholack® YCE (Nouryon), Berol® 260 (Nouryon), Citric acid, Methylglycine N,N-diacetic acid trisodium salt (Nouryon), L-glutamic acid N,N-diacetic acid trisodium salt (Nouryon), Perylene (≥99%, Sigma Aldrich), Rhodamine B (≈95%, Sigma Aldrich) and Sodium hydroxide.

3.2 Physicochemical properties

Different physicochemical properties were determined for the cleaning formulations to be able to compare them and see the differences and later be able to discuss their different cleaning abilities.

3.2.1 Clouding temperature

The clouding temperature of all the cleaning formulations was measured by filling a test tube to about a third with the formulation and placing a thermometer inside. The test tube was then heated by lowering it into a hot water bath at approximately 80°C. When the formulation in the test tube was visibly turbid it was taken out and cooled down slowly in room temperature while stirring with the thermometer. The temperature at which it was possible to clearly see through the formulation again was noted as the clouding temperature. The clouding temperature was determined to have a 2°C margin of error.

If the cleaning formulation didn't become turbid before reaching 80°C the clouding temperature was noted as "above 80 °C". This is because the heating water will start boiling and this will give unreliable results. It's also hard to measure a clouding temperature below room temperature as this would require cooling the sample instead of heating it. The clouding temperature of formulations that were turbid at room temperature were therefore noted as "below room temperature".

3.2.2 Viscosity

The viscosity of the formulations was measured by a Brookfield DV-I+ viscometer. A spindle is immersed in the liquid sample and driven through a calibrated spring. The resistance of the fluid against the spindle's movement is measured through spring deflection, which is assessed using a rotary transducer. The viscometer gives the results in units of centipoise [cP], which is equivalent to milliPascal-seconds [mP·s], and the measurement range depends on several factors: the spindle's rotational speed, its size and shape, the container it rotates within, and the calibrated spring's full scale torque. The torque appears in units of dyne-centimeters or Newton-meters but is expressed as a percentage.

The S18 spindle was used for the measurements and its corresponding container. The rotational speed was set to 100 rpm for all measurements except for some of the samples with amine oxide, where the speed was set to 60 rpm due to the higher viscosity. When the measurement was initiated the temperature was noted and then the viscosity and the torque were documented after three, five and ten minutes. The mean viscosity was then calculated.

3.2.3 Contact angle

The contact angle of the different formulations on different soiled surfaces was evaluated using an optical tensiometer from Attension. The sessile drop setting was used which measures the contact angle, as described in section 2.5.1, against time using a camera. The surfaces used were ceramic, glass and a metal with a vehicle finish that were soiled according to the method described in section 3.3.1. The surface was placed in the goniometer and the contact angle of three water droplets was measured before the contact angle of three droplets of each formulation was measured. The droplets were placed on the surface with the help of a syringe and a small needle. The mean value of the contact angle of the three different drops for each formulation was calculated to get as real a value as possible as the surfaces might not be totally uniformly soiled. The difference between the contact angle of the water drops and the drops of the cleaning formulations (°water - °cleaning formulation) was calculated to be able to compare contact angles between plates as two different plates are not identically soiled. A lot of plates were used to be able to fit measurements for all the formulations. The water almost always had a higher contact angle than the cleaning formulations so if the difference was high that meant the contact angle of the cleaning formulation was low.

For the metal plates the measurements were done at Nouryon. The same method was used but the dosage of the droplets onto the surface was automatic. This enabled the droplets to have the same volume. The dosage volume was set to a fixed volume of 4 μL.

3.2.4 Foaming

The cleaning formulations' ability to foam and their foam stability was evaluated by measuring the foam height using the Ross-Miles method. The Ross-Miles foam analyzer (RMFA) is an optical instrument consisting of a high cylindrical vessel, which can be heated, and a 200 ml Ross-Miles pipette. The method is a standard method, ASTM D1173-07, and is carried out at 50°C and with a 0.05% surfactant solution in demineralized water.

0.35 g of cleaning formulation was dissolved in 699.65 g of demineralized water in a 1 litre beaker that was covered with parafilm and put in a 55°C water bath until the solution reached a temperature of 50°C. 50 ml of the solution was measured in a measuring glass and poured into the cylindrical vessel which was heated to 50°C. The 200 ml Ross-Miles pipette was filled and the solution was poured on top of the 50 ml already in the cylindrical vessel creating a foam. The measurement was started at the same time and recorded the foam height for 400 s. If the foam had decomposed before the 400 s were out the recording was stopped early. This measurement was done twice for all the samples to get an average.

3.2.5 Surface tension

Surface tension of the samples was measured with a Sigma 70 force tensiometer and a so called Du Noüy ring. The Du Noüy ring is made of platinum and is connected to a hook that is connected to a very sensitive balance. The ring is lowered into a vessel with the current liquid. When the ring is then slowly lifted from the liquid the force required to raise the ring from the surface of the liquid is recorded. The surface tension is then calculated using the force required and the perimeter of the ring.

Surface tension was only measured on the cleaning formulations used for the cleaning tests. This was done to examine whether the surface tension of the solutions differed a lot from each other. Approximately 30 ml of the solution was poured into a vessel specifically suited for the force tensiometer. The container was placed in the machine and the measurement was initiated. The probe setting was the mini-ring which has a radius of 4.815 mm. The vessel used has a diameter of 46 mm and a maximum volume of 40 mL. The heavy phase was set to water but the density was manually changed for every sample to match the liquid being measured. Air was the setting for the light phase.

3.2.6 Other measurements

The pH was measured on all samples using a 744 Metrohm pH meter at room temperature. The density of the samples used for surface tension measurements was evaluated by adding 1 mL of solution to a 10 mL measuring glass and then weighing it. This gave an approximate value of the density in the unit of g/mL or g/cm^3.

3.3 Cleaning

The cleaning ability of the formulations was evaluated in a macroscopic and a microscopic way through a so called black box test and fluorescence microscopy respectively.

3.3.1 Black box

A black box test is a macroscopic non-mechanical cleaning test. The basic principle is that a surface is soiled and then the cleaning formulation is poured onto the surface to optically determine the cleaning ability.

The surfaces used were ceramic, glass and metal with a vehicle finish. The ceramic and glass plates were soiled with a kitchen soil, symbolizing household kitchen cleaning. For the metal plate a soil collected from an engine was used, symbolizing industrial and vehicle cleaning. The soil was evenly distributed on the surface using a paper tissue or a cloth. For the glass and the ceramic, the plates were dried at room temperature for one hour, while only half an hour for the metal plates. The soiling process, including amount of soil and distribution process, was aimed to be the same on every plate, however, since it depends on handicraft, only formulations on one plate should be compared and not between plates.

In the cleaning phase, the plate was put in a vertical position. Three diluted cleaning solutions with a volume of 10 ml and a concentration between 5-17 % were poured on the soiled surface at once, letting the excess formulation run off. After about 30 s the plate was rinsed with water. The cleaning ability was determined visually. If the formulation was able to wash of all the dirt it was considered to have a good cleaning ability, otherwise not.

The cleaning formulations for a plate were chosen so that either a secondary surfactant or a chelating agent were fixed and the other varied. For each plate the solutions chosen had the same clouding temperature, in an interval off ± 4°C, and the same pH. If the pH was too low for a formulation it was raised by addition of NaOH.

3.3.2 Fluorescence microscopy

Fluorescence microscopy was used to evaluate the microscopic cleaning ability. Both the soil and the cleaning formulation were labelled with a fluorescence marker of different wavelengths. The formulations' ability to clean were optically assessed by dropping two drops of them on a soiled surface and see the cleaning effect with the microscope. Pictures were also taken with the microscope before and after the cleaning formulation was added to the soiled surface.

The instrument used was Axio Imager.Z2m (Zeiss, Germany) with the following filters: transmitted brightfield, Rhodamine B (565 nm) and DAPI (465 nm). Glass with a soil that contained 20 wt% lambert soil, 30 wt% white spirit, 50 wt% corn oil and 0.1 wt% pyrene was used. After the plates were soiled they were left to dry for four days. The cleaning formulations were labelled with Rhodamine B.

4

Results and discussion

4.1 Physicochemical properties

4.1.1 Clouding temperature

The clouding temperature of the systems listed in Table 3.1 was determined, and the concentrations of secondary surfactants used are detailed in Table 4.1. The concentrations of the secondary surfactants are the ones that resulted in a clouding temperature between room temperature and 80°C. It is apparent from this table that amine oxide was required in a higher concentration to be able to solubilize the nonionic surfactant. However, when citric acid was used as the chelating agent the amount of secondary surfactant needed to solubilize the nonionic surfactant was reduced for all systems.

Table 4.1: Concentration of the secondary surfactant used in the cleaning formulations.

Concentration secondary surfactant	**Chelating agent**
1.5 wt% Amphoteric	Citric acid
1.9 wt% Amphoteric	MGDA
2 wt% Amphoteric	GLDA
2.6 wt% Amphoteric	Ammonium citrate
0.9 wt% Amine oxide	Citric acid
5 wt% Amine oxide	Ammonium citrate
6 wt% Amine oxide	MGDA
6 wt% Amine oxide	GLDA
0.7 wt% Quat	Citric acid
1.3 wt% Quat	MGDA
1.3 wt% Quat	Ammonium citrate
1.5 wt% Quat	GLDA

In Figure 4.1, it is clearly seen that citric acid has a behaviour significantly different compared to the other chelating agents. When citric acid is used the clouding temperature rises with increasing concentration, contrary to the typical salting out effect associated with chelating agents. Another thing that stands out is that for the formulations containing the amphoteric surfactant the clouding temperature shows a distinct increase until the concentration of GLDA and MGDA is approximately 4 wt%. When ammonium citrate is used the effect is not as clear, however, a small plateau can be seen before the clouding temperature decreases above 1 wt% of added chelating agent. The behaviour observed in the systems containing the amphoteric surfactant in combination with, particularly GLDA and MGDA, was anticipated based on previous research findings [2]. These findings suggest that this behaviour is caused by specific interactions between the amphoteric surfactants' head groups and the chelating agent, leading to decreased CPP. The theory behind the interactions is that the head group of the amphoteric surfactant is similar to the structure of the chelating agent and that they can interact because of molecular ressemblances. The lower CPP promotes the formation of smaller and more spherical micelles that are more easily dissolved, hence the higher clouding temperature. When the concentration of chelating agent gets too high the solubility will decrease because the amount of free chelating agent molecules will increase and the salting-out effect will dominate.

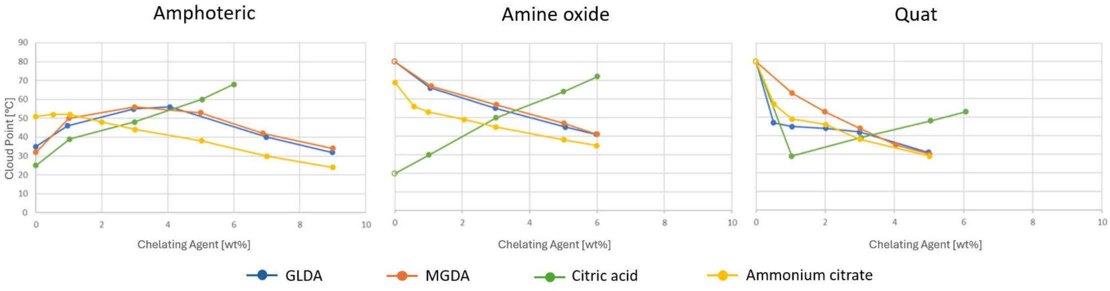


Figure 4.1: Clouding temperature of cleaning formulation systems containing an amphoteric, amine oxide or quat secondary surfactant against chelating agent concentration.

The clouding temperature behaviour seen for the amphoteric secondary surfactant was not observed when the amine oxide and the quat was used. This was an interesting result as all three secondary surfactants are amine-based and therefore the prediction was that they would behave similarly. However, aside from all secondary surfactants containing a nitrogen atom, the head groups are quite different, see Figure 2.1. The head group of the amphoteric surfactant is very similar to GLDA and MGDA, see Figure 2.5, as they all contain -N$(CH_2COONa)_2$. This is in line with the theory that the interactions are because of "like dissolves like". The ammonium citrate is not as similar to the amphoteric head group as GLDA and MGDA, it contains carboxylic groups but no nitrogen. This could be the reason why the effect of the ammonium citrate is not as prominent as it is for GLDA and MGDA. The head groups of the amine oxide and the quat are not at all similar to the chelating agents in the same way as the amphoteric. Therefore, they do not interact with each other in the same way and the chelating agents might be freely floating around in the solution. This would cause salting out as the anion of GLDA and MGDA is very similar to the anion of ammonium citrate, citrate^{3-}, which is a strong water structure maker, see the Hofmeister series in Section 2.5.1.

The anion of citric acid is also citrate^{3-} but is not salting out as the other chelating agents. This is highly counterintuitive considering the literature and the reason why this is happening is not clear. Some literature findings, [51][52], suggest that citric acid can act as a co-surfactant as well as a chelating agent. Miyazaki *et al.* found that citric acid, at low concentrations of 0.6 wt%, could inhibit the binding of calcium ions to the anionic surfactant surfactin [51]. They also discovered that citric acid acted as a cosurfactant as the interfacial tension was decreased to less than a tenth as compared to the interfacial tension between the pure surfactin solution and oil. To confirm citric acid as a cosurfactant in this study, surface tension measurements should be done on the formulations containing citric acid. The citric acid also lowers the pH, which was a potential reason for its behaviour. However, low pH as an explanation was ruled out as this hypothesis was tested by lowering the pH with HCl only, and this did not solubilize the nonionic surfactant. Since citric acid exhibited behaviour contrary to that of the other chelating agents, it was omitted from further analysis due to its unexpected performance.

4.1.2 Viscosity

The results from the viscosity measurements are presented in Figure 4.2, where it can clearly be seen that the formulations containing amine oxide have significantly higher viscosity. The reason for this is probably correlated to the higher concentration of amine oxide compared to the amphoteric and the quat, as presented in Table 4.1. At a higher concentration of surfactants there will be micellar growth causing more micelle-micelle interactions leading to increased viscosity.

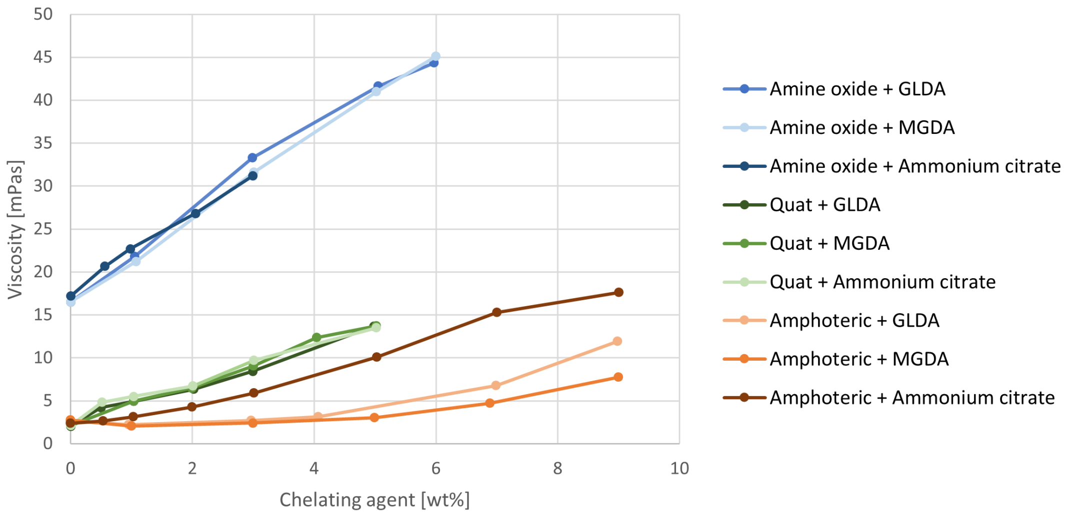


Figure 4.2: Viscosity behaviour in cleaning formulations containing 6 wt% nonionic, a secondary surfactant with concentration according to Table 3.1 and a chelating agent: Ammonium citrate, GLDA and MGDA respectively at 22°C.

From Figure 4.2 above it can be seen that the viscosity increases with increasing concentration of chelating agent. While the type of chelating agent does not seem to play a major role for the amine oxide and the quat this is not the case for the amphoteric. For the amphoteric, the viscosity is increased to a higher degree by ammonium citrate. Another interesting result is that GLDA and MGDA do not immediately increase the viscosity in combination with amphoteric surfactant. In Figure 4.3, the viscosity and clouding temperature for amphoteric secondary surfactant with chelating agent can be seen side by side. This shows how clouding temperature and viscosity have an intrinsic correlation in these cases.

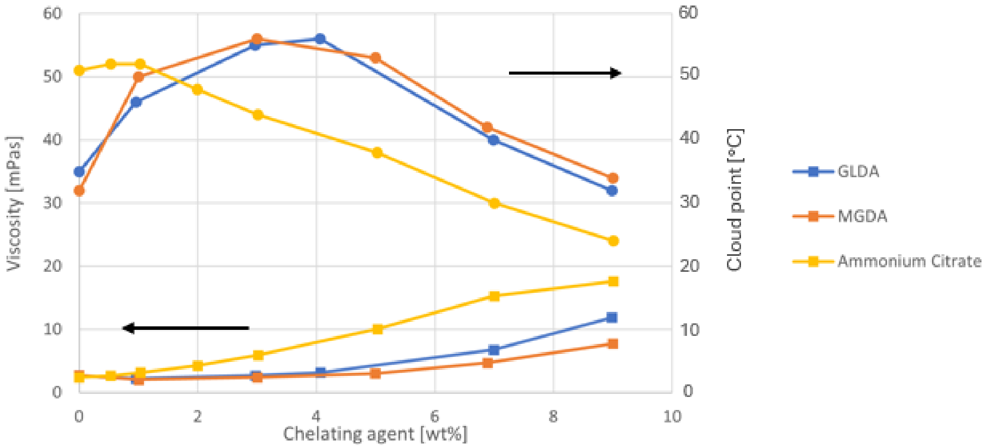


Figure 4.3: Viscosity and clouding temperature behaviour in cleaning formulations containing 6 wt% nonionic, an amphoteric secondary surfactant with conentration according to Table 3.1 and a chelating agent: Ammonium citrate, GLDA and MGDA respectivly at 22°C. The squares and the circles indicate the viscosity and clouding temperature measurements respectively.

It can be seen in the figure above that the viscosity starts to increase first around 5 wt% of added GLDA or MGDA. This is the same amount of chelating agent at which the clouding temperature starts to decrease. For the ammonium citrate the viscosity increases directly with the addition of chelating agent concentration. However, from 0 wt% chelating agent to 1 wt% the viscosity is pretty constant, which correlates to the clouding temperature being constant between these concentrations as well. Between 0 and 1 wt% of GLDA and MGDA the viscosity decreases slightly while the clouding temperature increases steeply. These findings support the hypothesis suggesting an interaction between GLDA and MGDA with the amphoteric surfactant, which encourages the formation of smaller, more spherical micelles. As stated before spherical micelles show lower viscosity than larger, elongated ones. Because there is probably no interaction between the chelating agents and the amine oxide and quat the steady increase in viscosity in Figure 4.2 for these formulations shows that the micelles are steadily growing when chelating agent concentration is increased.

In formulations where the chelating agent does not interact with the secondary surfactant, the viscosity remains unaffected by the type of chelating agent used. GLDA and MGDA, which are suspected to interact with the amphoteric surfactant, influence the viscosity similarly. However, after 4 wt% GLDA, the viscosity increases more steeply. GLDA is a slightly bigger molecule than MGDA and has four COO^- sites while MGDA has three, which is probably why GLDA is somewhat better at salting out.

4.1.3 Foaming

The foam height was tested for formulations without chelating agents, only containing 6 wt% nonionic surfactant and a secondary surfactant in the concentrations mentioned in Table 4.2. The table below shows the initial foam height.

Concentration secondary surfactant	Initial foam height [mm]
6 wt% Amine oxide	67
5 wt% Amine oxide	57
2.6 wt% Amphoteric	41
2 wt% Amphoteric	43
1.9 wt% Amphoteric	45
1.5 wt% Quat	31
1.3 wt% Quat	30

Table 4.2: Initial foam height for formulations only containing a nonionic surfactant and a secondary surfactant.

After 300 s the decrease in foam height for amine oxide was only about 10 mm, while for quat and amphoteric it was about 25 mm. The quat had therefore almost no foam after 300 s. Amine oxide had the highest foamability and stability, however, it could be expected since the formulation with a higher concentration of amine oxide also had higher foaming. When increasing the surfactant concentration more surfactants will be at the interface and therefore the foam is stabilized to a higher degree [53]. Previous studies have shown that the head group of the surfactant can influence the foamability and stability [54]. Petkova *et al.* reported that foamability and stability will only occur above a certain surfactant concentration which depends on the specific surfactant [55]. However, the scope of the project was to determine the influence of chelating agents on secondary surfactants, and therefore the effect of the secondary surfactant itself was not investigated further.

The foaming of the system when adding a chelating agent is more interesting and is presented in Figure 4.4. The figure shows the formulations listed in Table 4.3. There was a distinct decrease in foaming for the quat-containing formulations when chelating agents were added. The initial foam height decreased from 30 to 10 mm and the foam did not even last 50 s. The stability of the foam is dependent on electrostatic interactions, hydration and van der Waals forces [53]. The solutions used for the foaming test were highly diluted, meaning that properties as viscosity and pH are close to the ones of water. At neutral pH, the amine oxide and amphoteric will be neutral. The quat is cationic, which gives the interface a positive charge and an electrical double layer which helps stabilize the foam film. However, when salt is added, the initial foam height decreases because the bubbles rapidly coalesce. This happens due to the rupture of the thin aqueous films, which is caused by a reduction in the repulsion from the electrical double layer [53].

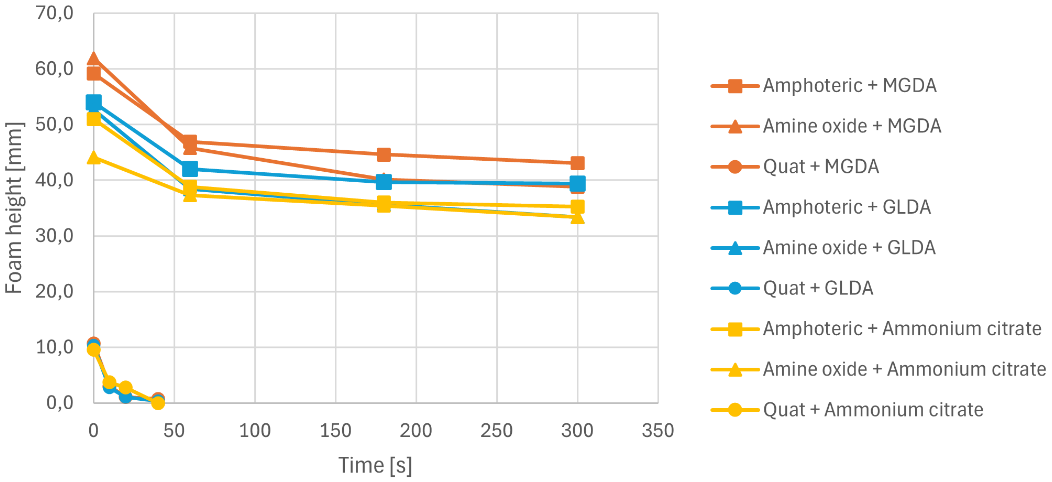


Figure 4.4: Foaming behaviour according to Ross-Miles test at 50°C for the formulations listed in Table 4.3.

In Figure 4.4 the foam height for respective chelating agent is similar for amine oxide and amphoteric. Compared with the initial foam height for the formulations without chelating agents presented in Table 4.2, the initial foam height decreased when adding chelating agents to amine oxide based formulations and it increased for the amphoteric containing formulations. The initial foam height is dependent on the diffusion of the surfactant to the interface, which is affected by addition of salt [53]. Therefore, addition of chelating agents to amine oxide-based formulations seems to increase the diffusion to the interface decreasing foam.

For the formulations containing the amphoteric secondary surfactant, there is an increase in the foamability and stability of the foam when adding a chelating agent. This effect is clearly shown in Figure C.1 and it is more predominant for MGDA and GLDA. For ammonium citrate the initial change in foamability is minimal, however, when increasing the concentration of chelating agent, the foamability increases. For the formulations containing amine oxide or quat the behaviour is opposite; adding a chelating agent decreases the foamability, shown in Figures C.2 and C.3. For ammonium citrate there is minimal change when adding a low-concentration chelating agent, however, increasing the concentration of the chelating agent decreases the foamability.

The foaming behaviour for the formulations containing the amphoteric secondary surfactant is believed to depend on the interaction between the secondary surfactant and the chelating agent. In Figure 4.5 the initial foam height and clouding temperature of the same system are presented as a function of chelating agent concentration. It is clear that the foam height increases when MGDA is added, represented by the point at 1 wt%. At the plateau in clouding temperature at 3 wt% and 5 wt% MGDA there is also a plateau in foam height. After the plateau the foam height increases to 7 wt% to decrease again to 9 wt% MGDA. This trend is also observed for GLDA. This behaviour indicates that the interaction between the amphoteric surfactant and MGDA/GLDA influences the foamability of the cleaning formulations. As previously stated, this interaction leads to a decrease in CPP, which is the reason why the foamability decreases or reaches a plateau.

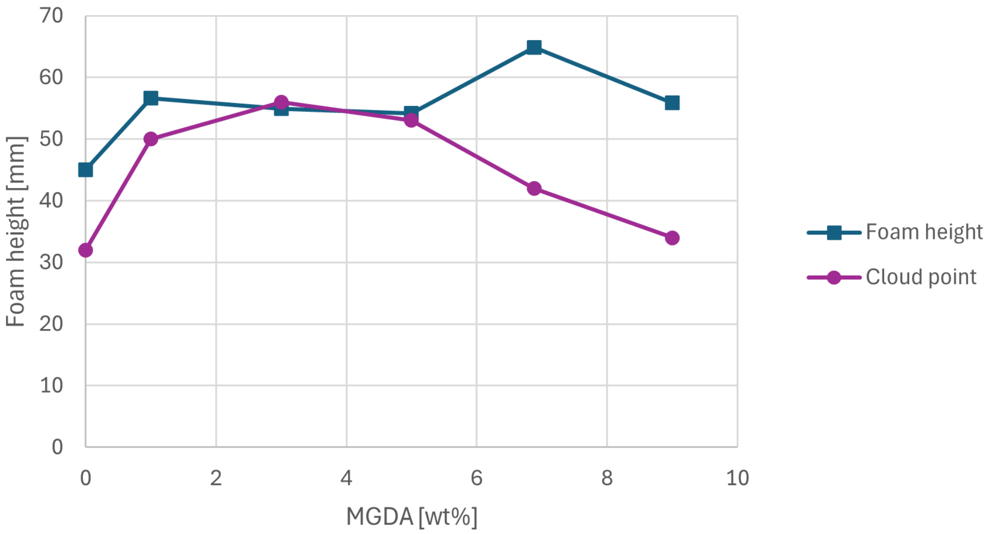


Figure 4.5: Foam height and clouding temperature as a function of MGDA concentration for a cleaning solution containing 6 wt% nonionic and 1.9 wt% amphoteric surfactant.

Figure 4.4 also describes the influence of the type of chelating agent on the foamability. MGDA yielded the highest foam height, while there was no remarkable difference between ammonium citrate and GLDA. For the formulations in Table 4.4 MGDA also had higher foam height than GLDA, which can be seen in Figure C.6. Ammonium citrate, however, had a different behaviour which can be explained by a greater variation in foaming dependent on which concentration of chelating agent used for ammonium citrate. MGDA seems to increase the foamability slightly for formulations with amine oxide or amphoteric secondary surfactants compared to GLDA. The reason for this could be that MGDA is a smaller molecule or because it has one less COO^- group than GLDA, which makes it less effective at salting out or interacting with other molecules.

4.1.4 Contact angle

The contact angle varies with secondary surfactant. When quat is used as the secondary surfactant the contact angle is lower than the rest, which can be seen in Figure 4.6. Figure 4.6 shows the delta angle, meaning the difference between the contact angle of water and the formulation of the same soiled surface. A high delta angle means a low actual contact angle. The behaviour of the quat is observed for all surfaces and all chelating agents. Figure 4.6 also shows that amine oxide gives the highest contact angle, which also can be seen for the other chelating agents.

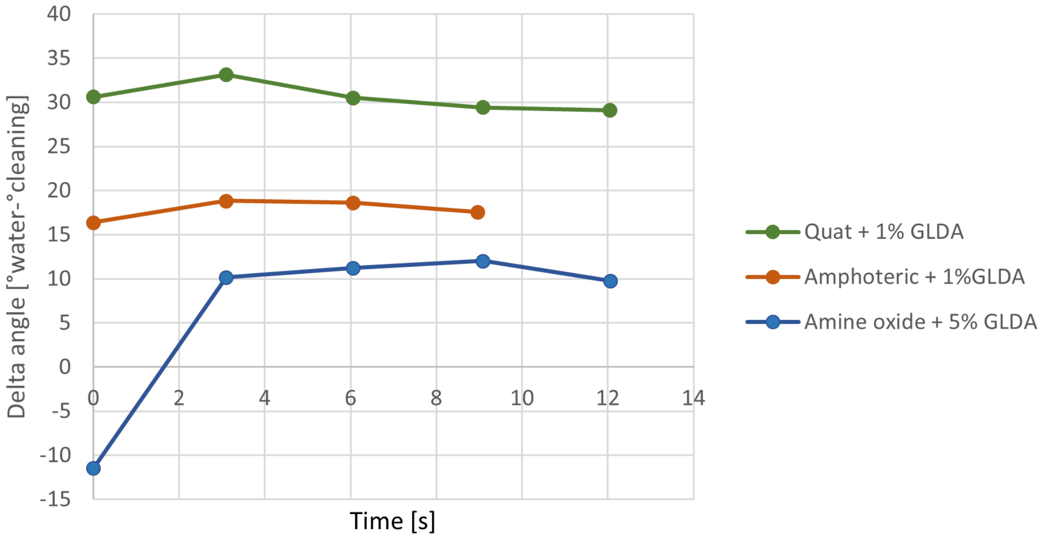


Figure 4.6: Difference in contact angle between water and the cleaning formulation on ceramic with kitchen soil. All formulations contained GLDA, where the secondary surfactant is varied.

Table 2.1 presents a difference in surface tension between the secondary surfactants, where amphoteric has the highest surface tension of 39 mN/m and amine oxide the lowest of 30 mN/m. The quat has a surface tension close to amine oxide of 33 mN/M. In Table 4.4 the surface tension for the cleaning formulations is presented, where amphoteric still has the highest surface tension above 27 mN/m. However, the formulation containing the quat has a lower surface tension than the one containing amine oxide. It is reasonable that quat has lower contact angle than amphoteric as seen in Figure 4.6 since it has lower surface tension, both when looking at the secondary surfactant alone and for the cleaning formulation. It is also clear here that it is the secondary surfactant which is the reason, since they have the same amount of chelating agent. The behaviour of the amine oxide is deviant, it has the highest contact angle while having low surface tension. One notable thing is that the amine oxide formulation contains a higher amount of salt in comparison with the quat and the amphoteric. Higher amount of salt increases the surface tension, however, this is not seen in Table 4.4. This suggests that the difference in contact angle is dependent on more than the surface tension. The soil could also influence the contact angle due to variations in the interaction between different surfactants and the soil.

Figure 4.7 shows an indication of dependence in the initial contact angle for amphoteric with GLDA on its interaction. The surface used was glass with kitchen soil. The concentrations of GLDA (1,3 and 4 wt%) which are on the plateau in clouding temperature gives a lower contact angle, while the concentrations after the plateau (7 and 9 wt%) gives a higher initial contact angle. This behaviour is also observed for ceramic with kitchen soil.

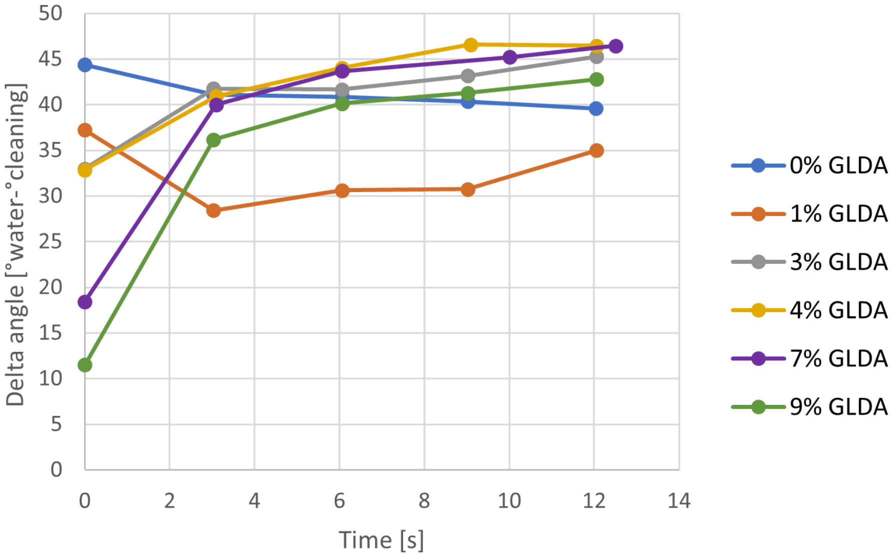


Figure 4.7: Difference in contact angle between water and the cleaning formulation on glass with kitchen soil, where the formulations contained 2 wt% amphoteric and varying concentration of GLDA.

For the contact angle measured on ceramic and metal, there is no effect in changing the concentration of chelating agent. This was observed clearly since there was very little difference between the contact angle from 2-12 s when the concentration of a chelating agent was changed. This trend was observed for all combinations of secondary surfactants and chelating agents. For ceramic and metal, the same plate was used for one system, meaning the contact angle measured for different concentrations of chelating agent within a system was measured on the same plate. This eliminates errors from the soil process. For glass there are bigger differences between the contact angle within a system, however, no clear trends are observed. The differences in contact angle are therefore believed to depend on soiling errors, since a new glass plate was used for every concentration of a chelating agent within a given system.

4.2 Cleaning

Cleaning tests were carried out on the formulations presented in Tables 4.3 and 4.4. In Table 4.3 the secondary surfactant was fixed and the chelating agent varied, meaning that the effect of the chelating agent could be studied. The clouding temperature and pH needed to be the same for the formulations that were being compared in the black box test and therefore the pH was adjusted for some formulations. In Table 4.4 the chelating agent concentration was fixed instead and the effect of the secondary surfactant could be studied. The viscosity, the foam height and the surface tension of these formulations are also presented in these tables. There were no significant differences in surface tension between the systems, indicating that the value is determined by the nonionic surfactant and that there is no direct influence of the secondary surfactants or the chelating agents used.

Table 4.3: Concentration and physicochemical properties of the cleaning systems with fixed secondary surfactant and varying chelating agent.

Cleaning system	[Surfactant]	Chelating agent	Clouding temperature [°C]	pH	Viscosity [mPas]	Foam height [mm]	Surface tension [mN/m]
Amphoteric	1.9 wt%	7 wt% MGDA	42	10.8	4.71	64.9	27.0
	2 wt%	7 wt% GLDA	40	10.6	6.76	51.4	27.0
	2.6 wt%	3 wt% Ammonium citrate	44	10.5	5.91	51.0	27.4
Amine oxide	6 wt%	3 wt% MGDA	57	11.4	31.6	61.9	26.6
	6 wt%	3 wt% GLDA	55	11.2	33.3	52.7	26.8
	5 wt%	0.5 wt% Ammonium citrate	56	11.9	20.7	44.1	26.3
Quat	1.3 wt%	3 wt% MGDA	44	11.8	9.06	10.7	26.5
	1.5 wt%	0.5 wt% GLDA	47	11.8	4.20	10.3	27.0
	1.3 wt%	2 wt% Ammonium citrate	46	11.8	6.72	9.55	26.7

Table 4.4: Concentration and physicochemical properties of the cleaning systems with fixed chelating agent and varying secondary surfactant.

Cleaning system	[Chelating agent]	Secondary surfactant	Clouding temperature [°C]	pH	Viscosity [mPas]	Foam height [mm]	Surface tension [mN/m]
MGDA	3 wt%	1.9 wt% Amphoteric	56	11.7	2.40	55.0	27.2
	3 wt%	6 wt% Amine oxide	57	11.4	31.6	61.9	26.8
	2 wt%	1.3 wt% Quat	53	11.7	6.49	17.1	26.8
GLDA	1 wt%	2 wt% Amphoteric	46	11.7	2.22	51.8	27.4
	5 wt%	6 wt% Amine oxide	45	12.0	41.6	57.4	26.9
	1 wt%	1.5 wt% Quat	45	12.1	4.94	10.3	26.5
Ammonium citrate	2 wt%	2.6 wt% Amphoteric	48	10.5	4.26	51.6	27.1
	2 wt%	5 wt% Amine oxide	49	10.4	26.8	55.9	26.4
	1 wt%	1.3 wt% Quat	49	10.7	5.49	20.4	26.7

4.2.1 Macroscopic observation of the cleaning

The results from the black box tests are shown in Figure 4.8 and the first three rows correspond to the three cleaning systems in Table 4.3 and the last three rows correspond to the systems in Table 4.4. In these cleaning tests the formulations have been diluted to be able to compare the cleaning ability, as a highly concentrated cleaning formulation might be able to clean well for all three systems being compared while a diluted system might not. Most systems were diluted to contain between 2.5 and 10 wt% cleaning formulation but the quat system with varying chelating agent stands out with approximately 20 wt% for the glass and metal plates. The reason these systems were not as diluted as the others is because the formulation with quat and GLDA became cloudy when diluted below ∼17 wt%. This is the reason why only MGDA and ammonium citrate are compared on the ceramic plate and why all the pictures under GLDA only compares GLDA with amphoteric and amine oxide.

None of the formulations cleaned the metal plate.

Figure 4.8: Pictures of the performed black box tests on the formulations presented in Tables 4.3 and 4.4. Left: ceramic surface; Middle: glass surface; Right: vehicle finished metal surface.

Another observation that can be done from the figure is that most of the cleaning formulations are less effective when used on a metal plate with engine soil. However, they seem to present the same order of efficiency as for ceramic and glass. The amine oxide combined with GLDA and MGDA is best at cleaning the metal plate but amphoteric with GLDA and MGDA is also good. The quat does not clean the metal plate well with any chelating agent, which is interesting as it was quite effective on glass. Ammonium citrate is very ineffective as it does not clean the metal plate with any secondary surfactant. That is also the reason why the picture from the test with ammonium citrate and the different secondary surfactants wasn't included as none of the formulations managed to clean the plate even at very little dilution. Actually, the ammonium citrate cleans quite poorly on all surfaces.

Ammonium citrate is the most different in molecular structure from GLDA and MGDA which could be negatively impacting the cleaning efficiency. Ammonium citrate seems to clean best in combination with quat. When 0.5 wt% ammonium citrate is used with amine oxide at 5 wt% dilution it doesn't clean either the ceramic or the glass, while it does clean both when 2 wt% ammonium citrate is used at 10 wt% dilution. The reason for this might be because of the lower dilution.

GLDA and MGDA have a similar structure and have had quite similar physicochemical properties. They also show similar cleaning efficiency, at least in combination with amphoteric and amine oxide. Interestingly, amphoteric with 7 wt% GLDA cleans really well while with 1 wt% it does not. Amphoteric with both 3 and 7 wt% MGDA cleans well on ceramic. In Figure 4.9 formulations with amphoteric and 1 and 3 wt% of GLDA and MGDA were tested on the same ceramic plate and a similar observation was made, suggesting there is a critical lower limit of chelating agent.

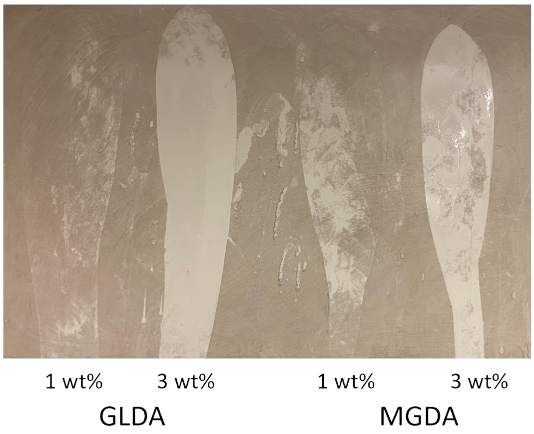


Figure 4.9: Performed black box test for formulations containing 2 wt% amphoteric with 1 and 3 wt% GLDA and 1.9 wt% amphoteric with 1 and 3 wt% MGDA. The formulations were diluted to 5 wt%.

In Figure 4.6 it can be seen that the contact angle for 1 wt% GLDA against time on glass is a lot higher than for the other concentrations. This means it has a lower wettability than the other concentrations which might be a reason to why this formulation does not clean efficiently. This is however not the case for 1 wt% MGDA as can be seen in Figure B.6. Therefore differences in cleaning between these two systems cannot solely be explained considering the contact angle differences.

When MGDA was compared with the different secondary surfactants in Figure 4.8 it is clear that both amphoteric and amine oxide clean well. This shows that the cleaning efficiency is not affected by the interaction between the chelating agents and the amphoterics' head group. It might, however, be affected by the concentration of the secondary surfactant. Amine oxide is more concentrated than amphoteric and therefore it might be better to use the formulation with amphoteric as it cleans equally efficiently but uses less surfactant.

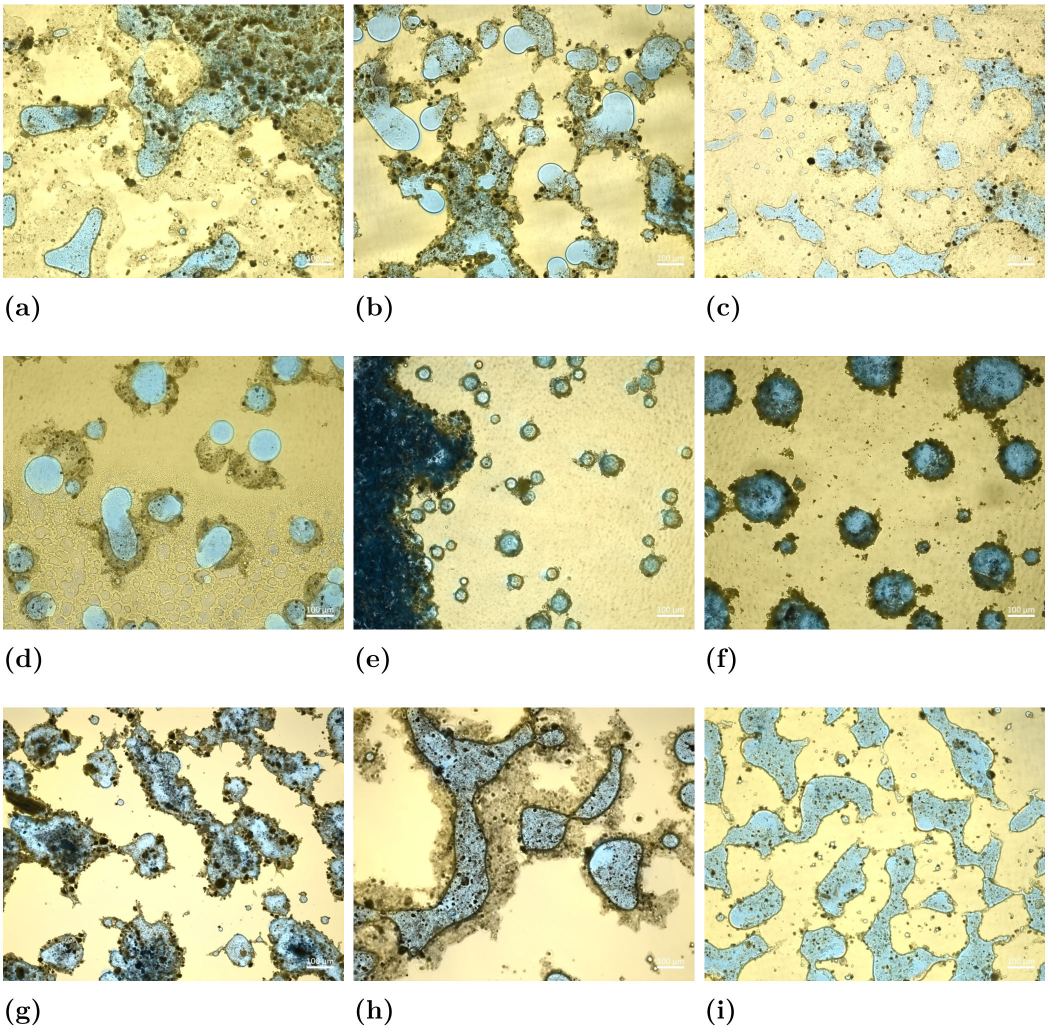
4.2.2 Microscopy observation of the cleaning

In Figure 4.10 pictures from the cleaning under microscope are presented. The first row presents the formulations with amphoteric, the second presents the ones with amine oxide and the third with the quat. The left column of pictures all consist of GLDA, the middle has MGDA and the right one consist of ammonium citrate. The blue regions indicate the oil of the soil and the yellow is the cleaning formulation. The black is the solid particles of the soil.

It was observed that the dirt assembled differently depending on which secondary surfactant was used in the cleaning formulation. Amine oxide formed small round droplets of dirt as seen in Figures 4.10d, 4.10e and 4.10f. For amphoteric and quat the dirt assembled into bigger more non-uniform and elongated droplets which in some cases were connected and formed a network. The oil droplets in the amine oxide-based formulations are believed to be spherical partly because of higher viscosity which creates a bigger resistance for soil droplets to flow in the medium. It is also clear that the solid particles of the soil help stabilize the spherical droplets of amine oxide. The pictures suggest that the most relevant cleaning mechanisms taking place are probably emulsification and the roll-up mechanism, considering the spherical, stabilized drops.

For the quat, it was also seen that the soil particles are good at stabilizing the soil regions. This could correlate to the quat being cationic and the solid particles most likely being negatively charged. The quat would then be more effective on more particulate soils, containing a lot of solid particles.

The pictures with the formulations containing both amphoteric and quat show a more bicontinuous network of soil. This suggests that the most relevant cleaning mechanism taking place for these formulations is via solubilization. Solubilization tends to give more of a continuous network because the oil more directly dissolves into the cleaning formulation.



(a) **(b)** **(c)**

(d) **(e)** **(f)**

(g) **(h)** **(i)**

Figure 4.10: Pictures of microscopy observations of the cleaning for cleaning formulations containing (a) 2 wt% Amphoteric and 7 wt% GLDA (b) 1.9 wt% Ampoteric and 7 wt% MGDA (c) 2.6 wt% Amphoteric and 2 wt% Ammonium citrate (d) 6 wt% Amine oxide and 5 wt% GLDA (e) 6 wt% Amine oxide and 3 wt% MGDA (f) 5 wt% Amine oxide and 2 wt% Ammonium citrate (g) 1.5 wt% quat and 1 wt% GLDA (h) 1.3 wt% Quat and 3 wt% MGDA (i) 1.3 wt% Quat and 1 wt% Ammonium citrate.

When looked at the cleaning through microscopy, the type of chelating agent does not seem to affect the cleaning mechanisms. The determining component is more likely to be the secondary surfactant. Chelating agents are not surface active in nature and do not interact with the surface on their own, so this result is very reasonable.

5

Conclusion

The aim of the study was to evaluate the influence of different secondary surfactants and chelating agents on the physicochemical properties and the cleaning ability of cleaning formulations. The dependence between the chelating agent and the secondary surfactant was also investigated.

Of the physicochemical properties evaluated, clouding temperature , viscosity, foaming and wettability were influenced by the choice of secondary surfactant and/or chelating agent. Surface tension was not influenced.

Amphoteric was the only secondary surfactant able to disrupt the typical salting out behaviour that occurs when having chelating agents in a cleaning formulation. This was observed with a rise in clouding temperature to some degree of added chelating agent, for the chelating agents (MGDA and GLDA) with great similarities to the amphoteric surfactants head groups in molecular structure. This behaviour is believed to depend on an interaction between the amphoteric surfactant and MGDA/GLDA, decreasing the CPP. Citric acid showed a different behaviour in comparison to the other chelating agents. It was able to increase the solubility of the nonionic surfactant, acting as a cosurfactant. The rise in clouding temperature when using an amphoteric secondary surfactant and a chelating agent with great similarities in their molecular structure makes it possible to formulate more concentrated products. This is also likely to be possible by using citric acid as both solubilizer and chelating agent.

Both foaming and viscosity further indicated that there was an interaction between the amphoteric surfactant and MGDA/GLDA. Low CPP favours formation of smaller and more spherical micelles which gives lower viscosity and higher foaming, which was observed for the above mentioned systems. There was also an indication that the initial contact angle was decreased by the interaction.

The conclusion from the cleaning tests is that formulations with amphoteric, as well as amine oxide, in combination with GLDA and MGDA are the most effective at cleaning all surfaces and with both soils. Especially when the concentration of chelating agent is higher. This means that the amphoteric and GLDA/MGDA cleaning formulations is a great choice for making more concentrated products.

Bibliography

[1] Nouryon. “Cleaning solutions.” (n.d), [Online]. Available: `https://www.nouryon.com/markets/cleaning/` (visited on 03/13/2024).

[2] S. Muresan, J. A. Velásquez Cano, and O. Forsberg, “Chelate-amphoteric surfactant liquid concentrates and use thereof in cleaning applications,” WO2023275269, 2023. [Online]. Available: `https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2023275269`.

[3] N. Suzuki, “Interaction parameters for the formation of mixed micelles and partitioning of solutes in them: A review,” *AppliedChem*, vol. 4, no. 1, pp. 1–14, 2024. DOI: `10.3390/appliedchem4010001`. [Online]. Available: `https://www.mdpi.com/2673-9623/4/1/1`.

[4] Nouryon, *Cleaning applications*, Brochure, North America, 2023. [Online]. Available: `https://www.nouryon.com/globalassets/inriver/resources/brochure-cleaning-na-product-catalog-en.pdf` (visited on 01/24/2024).

[5] T. I. Yunusov, L. F. Davletshina, L. A. Magadova, and M. A. Silin, “Study of chelating agent-surfactant interactions on the interphase as possibly useful for the well stimulation,” *Energies*, vol. 16, no. 4, 2023. DOI: `10.3390/en16041679`.

[6] K. S. Birdi, *Surface and Colloid Chemistry: Principles and Applications.* Baton Rouge, UNITED STATES: Taylor & Francis Group, 2009, ISBN: 978-1-4200-9504-3. [Online]. Available: `http://ebookcentral.proquest.com/lib/chalmers/detail.action?docID=533629` (visited on 03/13/2024).

[7] “Detergent,” *International Union of Pure and Applied Chemistry (IUPAC)*, 2019. [Online]. Available: `https://doi.org/10.1351/goldbook.D01643` (visited on 03/13/2024).

[8] B. Kronberg, K. Holmberg, and B. Lindman, *Surface Chemistry of Surfactants and Polymers*, 1st ed. John Wiley & Sons, Incorporated, Dec. 2014, ISBN: 978-1-118-69600-2. [Online]. Available: `https://ebookcentral.proquest.com/lib/chalmers/reader.action?docID=1791862#` (visited on 03/14/2024).

[9] E. H. Crook, G. F. Trebbi, and D. B. Fordyce, “Thermodynamic Properties of Solutions of Homogeneous p,t-Octylphenoxyethoxyethanols (OPE $_{1\text{-}10}$),” en, *The Journal of Physical Chemistry*, vol. 68, no. 12, pp. 3592–3599, Dec. 1964, ISSN: 0022-3654, 1541-5740. DOI: `10.1021/j100794a026`. [Online]. Available: `https://pubs.acs.org/doi/abs/10.1021/j100794a026` (visited on 05/17/2024).

[10] *Encyclopedia of Separation Science*, en. [Online]. Available: `http://www.sciencedirect.com:5070/referencework/9780122267703/encyclopedia-of-separation-science` (visited on 04/15/2024).

[11] "Front Matter," in *Handbook for Cleaning/Decontamination of Surfaces*, I. Johansson and P. Somasundaran, Eds., Amsterdam: Elsevier Science B.V., Jan. 2007, p. iii, ISBN: 9780444516640. DOI: `10.1016/B978-0-444-51664-0.50029-2`. [Online]. Available: `https://www.sciencedirect.com/science/article/pii/B9780444516640500292` (visited on 04/15/2024).

[12] Y. Nakama, "Chapter 15 - Surfactants," in *Cosmetic Science and Technology*, K. Sakamoto, R. Y. Lochhead, H. I. Maibach, and Y. Yamashita, Eds., Amsterdam: Elsevier, Jan. 2017, pp. 231–244, ISBN: 978-0-12-802005-0. DOI: `10.1016/B978-0-12-802005-0.00015-X`. [Online]. Available: `https://www.sciencedirect.com/science/article/pii/B978012802005000015X` (visited on 04/04/2024).

[13] A. Honciuc, "Chapter 4 - Surfactants and amphiphiles," in *Chemistry of Functional Materials Surfaces and Interfaces*, A. Honciuc, Ed., Elsevier, Jan. 2021, pp. 43–77, ISBN: 9780128210598. DOI: `10.1016/B978-0-12-821059-8.00011-9`. [Online]. Available: `https://www.sciencedirect.com/science/article/pii/B9780128210598000119` (visited on 04/15/2024).

[14] S. M. S. Hussain, A. Mahboob, and M. S. Kamal, "Synthesis and Evaluation of Zwitterionic Surfactants Bearing Benzene Ring in the Hydrophobic Tail," *Materials*, vol. 13, no. 8, p. 1858, Apr. 2020, ISSN: 1996-1944. DOI: `10.3390/ma13081858`. [Online]. Available: `https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7215865/` (visited on 05/17/2024).

[15] J. J. Williams, "B.1.II - Formulation of Carpet Cleaners," in *Handbook for Cleaning/Decontamination of Surfaces*, I. Johansson and P. Somasundaran, Eds., Amsterdam: Elsevier Science B.V., Jan. 2007, pp. 103–123, ISBN: 9780444516640. DOI: `10.1016/B978-044451664-0/50004-8`. [Online]. Available: `https://www.sciencedirect.com/science/article/pii/B9780444516640500048` (visited on 04/15/2024).

[16] S. R. Sumpter, "ENVIRONMENTAL APPLICATIONS | Pressurized Fluid Extraction," in *Encyclopedia of Separation Science*, I. D. Wilson, Ed., Oxford: Academic Press, Jan. 2000, pp. 2687–2695, ISBN: 9780122267703. DOI: `10.1016/B0-12-226770-2/02131-1`. [Online]. Available: `https://www.sciencedirect.com/science/article/pii/B0122267702021311` (visited on 04/15/2024).

[17] *Comprehensive Heterocyclic Chemistry*, en. [Online]. Available: `http://www.sciencedirect.com:5070/referencework/9780080965192/comprehensive-heterocyclic-chemistry` (visited on 04/15/2024).

[18] "Front Matter," in *Biobased Surfactants (Second Edition)*, D. G. Hayes, D. K. Y. Solaiman, and R. D. Ashby, Eds., AOCS Press, Jan. 2019, pp. i–ii, ISBN: 9780128127056. DOI: `10.1016/B978-0-12-812705-6.09991-3`. [Online]. Available: `https:`

//www.sciencedirect.com/science/article/pii/B9780128127056099913 (visited on 04/15/2024).

[19] B. Thalhamer, A. S. Guntner, and W. Buchberger, “Simultaneous analysis of quaternary ammonium cations and corresponding halide counterions by pyrolysis gas chromatography / mass spectrometry,” *Journal of Analytical and Applied Pyrolysis*, vol. 162, p. 105 447, Mar. 2022, ISSN: 0165-2370. DOI: `10.1016/j.jaap.2022.105447`. [Online]. Available: `https://www.ncbi.nlm.nih.gov/pmc/articles/PMC8763416/` (visited on 04/15/2024).

[20] R. Sarkar, A. Pal, A. Rakshit, and B. Saha, “Properties and applications of amphoteric surfactant: A concise review,” en, *Journal of Surfactants and Detergents*, vol. 24, no. 5, pp. 709–730, Sep. 2021, ISSN: 1097-3958, 1558-9293. DOI: `10.1002/jsde.12542`. [Online]. Available: `https://aocs.onlinelibrary.wiley.com/doi/10.1002/jsde.12542` (visited on 04/04/2024).

[21] B. Folmer, K. Holmberg, and M. Svensson, “Interaction of *Rhizomucor miehei* Lipase with an Amphoteric Surfactant at Different pH Values,” en, *Langmuir*, vol. 13, no. 22, pp. 5864–5869, Oct. 1997, ISSN: 0743-7463, 1520-5827. DOI: `10.1021/la962094p`. [Online]. Available: `https://pubs.acs.org/doi/10.1021/la962094p` (visited on 04/10/2024).

[22] “12 - USE IN INDUSTRIAL PRODUCTS,” in *Handbook of Antiblocking, Release, and Slip Additives (Third Edition)*, G. Wypych, Ed., William Andrew Publishing, Jan. 2014, pp. 201–247, ISBN: 9781895198836. DOI: `10.1016/B978-1-895198-83-6.50014-3`. [Online]. Available: `https://www.sciencedirect.com/science/article/pii/B9781895198836500143` (visited on 04/17/2024).

[23] S. K. Singh, M. Bajpai, and V. Tyagi, “Amine Oxides: A Review,” *Journal of Oleo Science*, vol. 55, no. 3, pp. 99–119, 2006. DOI: `10.5650/jos.55.99`.

[24] M. Baglioni, Y. Jàidar Benavides, D. Berti, R. Giorgi, U. Keiderling, and P. Baglioni, “An amine-oxide surfactant-based microemulsion for the cleaning of works of art,” *Journal of Colloid and Interface Science*, vol. 440, pp. 204–210, Feb. 2015, ISSN: 0021-9797. DOI: `10.1016/j.jcis.2014.10.003`. [Online]. Available: `https://www.sciencedirect.com/science/article/pii/S0021979714007474` (visited on 04/15/2024).

[25] *Berol 260 Narrow range non-ionic surfactant*, en. [Online]. Available: `https://www.nouryon.com/product/berol-260-narrow-range-non-ionic-surfactant/` (visited on 05/23/2024).

[26] *Aromox MCD-W Cocodimethyl amine oxide (fractionated cocoalkyl) INCI Name: Cocamine Oxide*, en. [Online]. Available: `https://www.nouryon.com/product/aromox-mcd-w-cocodimethyl-amine-oxide-fractionated-cocoalkyl-inci-name-cocamine-oxide/` (visited on 05/23/2024).

[27] *Ampholak YCE Sodium cocopropylenediamine propionates*, en. [Online]. Available: `https://www.nouryon.com/product/ampholak-yce-sodium-cocopropylenediamine-propionates/` (visited on 05/23/2024).

[28] *Dodecyltrimethylammonium chloride | 112-00-5*, en. [Online]. Available: `https://www.chemicalbook.com/ChemicalProductProperty_EN_CB0461278.htm` (visited on 05/23/2024).

[29] N. C. Solutions, *Dodecyl Trimethyl Ammonium Chloride 112-00-5 specialty chemical supplier distributor*. [Online]. Available: `https://www.parchem.com/chemical-supplier-distributor/dodecyl-trimethyl-ammonium-chloride-021024` (visited on 05/23/2024).

[30] S. Shafaei, "Composites of lyotropic lamellar systems and micro-particles," [Online]. Available: `https://www.researchgate.net/figure/Schematic-representation-of-some-physical-properties-which-exhibit-a-sudden-change-or_fig3_30010699` (visited on 05/23/2024).

[31] N. A. N. Hanafy, M. El-Kemary, and S. Leporatti, "Micelles Structure Development as a Strategy to Improve Smart Cancer Therapy," *Cancers*, vol. 10, no. 7, p. 238, Jul. 2018, ISSN: 2072-6694. DOI: `10.3390/cancers10070238`. [Online]. Available: `https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6071246/` (visited on 04/17/2024).

[32] K. Holmberg, *Yt- och kolloidkemi*, Aug. 2007.

[33] R. G. Alargova, I. I. Kochijashky, M. L. Sierra, and R. Zana, "Micelle Aggregation Numbers of Surfactants in Aqueous Solutions: A Comparison between the Results from Steady-State and Time-Resolved Fluorescence Quenching," en, *Langmuir*, vol. 14, no. 19, pp. 5412–5418, Sep. 1998, ISSN: 0743-7463, 1520-5827. DOI: `10.1021/la980565x`. [Online]. Available: `https://pubs.acs.org/doi/10.1021/la980565x` (visited on 04/17/2024).

[34] S. Shafaei, "Composites of lyotropic lamellar systems and micro-particles," Jul. 2007. [Online]. Available: `https://www.researchgate.net/publication/30010699_Composites_of_lyotropic_lamellar_systems_and_micro-particles` (visited on 04/17/2024).

[35] S. Chatterjee, P. K. Sen, K. Das, S. C. Bhattacharya, and R. Palepu, "Mixed Micellization of Ionic and Nonionic Surfactants in Aqueous Solution," en, *Journal of Dispersion Science and Technology*, vol. 27, no. 5, pp. 751–759, Aug. 2006, ISSN: 0193-2691, 1532-2351. DOI: `10.1080/01932690600662695`. [Online]. Available: `http://www.tandfonline.com/doi/abs/10.1080/01932690600662695` (visited on 05/19/2024).

[36] M. Ludwig, R. Geisler, S. Prévost, and R. von Klitzing, "Shape and Structure Formation of Mixed Nonionic–Anionic Surfactant Micelles," *Molecules*, vol. 26, no. 14, p. 4136, Jul. 2021, ISSN: 1420-3049. DOI: `10.3390/molecules26144136`. [Online]. Available: `https://www.ncbi.nlm.nih.gov/pmc/articles/PMC8307929/` (visited on 05/19/2024).

[37] N. Ferlin, D. Grassi, C. Ojeda, *et al.*, "Calcium Chelating Sugar-Based Surfactants for Hard-Water Detergency," en, *Journal of Surfactants and Detergents*, vol. 15, no. 3, pp. 259–264, May 2012, ISSN: 1097-3958, 1558-9293. DOI: `10.1007/s11743-011-1310-3`. [Online]. Available: `https:`

`//aocs.onlinelibrary.wiley.com/doi/10.1007/s11743-011-1310-3` (visited on 04/29/2024).

[38] F. Dwyer, *Chelating Agents and Metal Chelates*, en. Elsevier, Dec. 2012, Google-Books-ID: u5fGbY20mpQC, ISBN: 9780323146418.

[39] R. Y. Ning, *Expanding Issues in Desalination*, en. BoD – Books on Demand, Sep. 2011, Google-Books-ID: 7OqPDwAAQBAJ, ISBN: 9789533076249.

[40] F. Suanon, Q. Sun, B. Dimon, D. Mama, and C.-P. Yu, "Heavy metal removal from sludge with organic chelators: Comparative study of N, N-bis(carboxymethyl) glutamic acid and citric acid," *Journal of Environmental Management*, vol. 166, pp. 341–347, Jan. 2016, ISSN: 0301-4797. DOI: `10.1016/j.jenvman.2015.10.035`. [Online]. Available: `https://www.sciencedirect.com/science/article/pii/S0301479715303339` (visited on 04/17/2024).

[41] A. Phenix and A. Burnstock, "THE REMOVAL OF SURFACE DIRT ON PAINTINGS WITH CHELATING AGENTS," en, *The Conservator*, vol. 16, no. 1, pp. 28–38, Jan. 1992, ISSN: 0140-0096. DOI: `10.1080/01400096.1992.9635624`. [Online]. Available: `http://www.tandfonline.com/doi/abs/10.1080/01400096.1992.9635624` (visited on 04/17/2024).

[42] A. M. Al-Sabagh, N. M. Nasser, M. A. Migahed, and N. G. Kandil, "Effect of chemical structure on the cloud point of some new non-ionic surfactants based on bisphenol in relation to their surface active properties," *Egyptian Journal of Petroleum*, vol. 20, no. 2, pp. 59–66, Jun. 2011, ISSN: 1110-0621. DOI: `10.1016/j.ejpe.2011.06.006`. [Online]. Available: `https://www.sciencedirect.com/science/article/pii/S1110062111000079` (visited on 03/14/2024).

[43] K. P. Gregory, G. R. Elliott, H. Robertson, *et al.*, "Understanding specific ion effects and the Hofmeister series," en, *Physical Chemistry Chemical Physics*, vol. 24, no. 21, pp. 12 682–12 718, Jun. 2022, Publisher: The Royal Society of Chemistry, ISSN: 1463-9084. DOI: `10.1039/D2CP00847E`. [Online]. Available: `https://pubs.rsc.org/en/content/articlelanding/2022/cp/d2cp00847e` (visited on 03/14/2024).

[44] *A Comprehensive Guide to Liquid Detergent Viscosity: Understanding the Importance, Factors, and Applications* -, en-US, Section: Formulation Expertise, Jun. 2023. [Online]. Available: `https://yeserchem.com/a-comprehensive-guide-to-liquid-detergent-viscosity-understanding-the-importance-factors-and-applications/` (visited on 04/17/2024).

[45] L. Chen and E. Bonaccurso, "Effects of surface wettability and liquid viscosity on the dynamic wetting of individual drops," *Physical Review E*, vol. 90, Jul. 2014. DOI: `10.1103/PhysRevE.90.022401`.

[46] D. E. Gragson, B. M. McCarty, and G. L. Richmond, "Surfactant/Water Interactions at the Air/Water Interface Probed by Vibrational Sum Frequency Generation," en, *The Journal of Physical Chemistry*, vol. 100, no. 34, pp. 14 272–14 275, Jan. 1996, ISSN: 0022-3654, 1541-5740. DOI:

10.1021/jp961034p. [Online]. Available: `https://pubs.acs.org/doi/10.1021/jp961034p` (visited on 05/06/2024).

[47] T. T. P. Nguyen, F. Raji, C. V. Nguyen, N. N. Nguyen, and A. V. Nguyen, "Effects of Charged Surfactants on Interfacial Water Structure and Macroscopic Properties of the Air-Water Interface," en, *ChemPhysChem*, vol. 24, no. 23, e202300062, Dec. 2023, ISSN: 1439-4235, 1439-7641. DOI: 10.1002/cphc.202300062. [Online]. Available: `https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/cphc.202300062` (visited on 05/06/2024).

[48] A. Bonfillon-Colin and D. Langevin, "Why Do Ethoxylated Nonionic Surfactants Not Foam at High Temperature?" *Langmuir*, vol. 13, no. 4, pp. 599–601, Feb. 1997, Publisher: American Chemical Society, ISSN: 0743-7463. DOI: 10.1021/la950439i. [Online]. Available: `https://doi.org/10.1021/la950439i` (visited on 04/10/2024).

[49] L. Quintero and N. F. Carnahan, "Chapter 2 - Microemulsions for Cleaning Applications," in *Developments in Surface Contamination and Cleaning*, R. Kohli and K. L. Mittal, Eds., Oxford: William Andrew Publishing, Jan. 2013, pp. 65–106, ISBN: 978-1-4377-7879-3. DOI: 10.1016/B978-1-4377-7879-3.00002-9. [Online]. Available: `https://www.sciencedirect.com/science/article/pii/B9781437778793000029` (visited on 04/11/2024).

[50] C. A. Miller and K. H. Raney, "Solubilization—emulsification mechanisms of detergency," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 74, no. 2, pp. 169–215, Jul. 1993, ISSN: 0927-7757. DOI: 10.1016/0927-7757(93)80263-E. [Online]. Available: `https://www.sciencedirect.com/science/article/pii/092777579380263E` (visited on 04/15/2024).

[51] N. Miyazaki, Y. Sugai, K. Sasaki, Y. Okamoto, and C. Ouyang, "Dual Role of Citric Acid as a Binding Inhibitor of Anionic Surfactant with Bivalent Cations and Co-Surfactant on Bio-Surfactant EOR," en, OnePetro, Nov. 2018. DOI: 10.2118/193277-MS. [Online]. Available: `https://dx.doi.org/10.2118/193277-MS` (visited on 05/14/2024).

[52] Q. Song, W. Guan, W. Liu, L. Liu, C. Wei, and L. Cai, "Preparation and physicochemical stability of tomato seed oil microemulsions," en, *Journal of Food Science*, vol. 86, no. 12, pp. 5385–5396, 2021, _eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1111/1750-3841.15961, ISSN: 1750-3841. DOI: 10.1111/1750-3841.15961. [Online]. Available: `https://onlinelibrary.wiley.com/doi/abs/10.1111/1750-3841.15961` (visited on 05/14/2024).

[53] M. R. Behera, S. R. Varade, P. Ghosh, P. Paul, and A. S. Negi, "Foaming in Micellar Solutions: Effects of Surfactant, Salt, and Oil Concentrations," en, *Industrial & Engineering Chemistry Research*, vol. 53, no. 48, pp. 18 497–18 507, Dec. 2014, ISSN: 0888-5885, 1520-5045. DOI: 10.1021/ie503591v. [Online]. Available: `https://pubs.acs.org/doi/10.1021/ie503591v` (visited on 05/14/2024).

[54] B. Petkova, S. Tcholakova, M. Chenkova, *et al.*, "Foamability of aqueous solutions: Role of surfactant type and concentration," en, *Advances in Colloid and Interface Science*, vol. 276, p. 102 084, Feb. 2020, ISSN: 00018686.

DOI: 10.1016/j.cis.2019.102084. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/S0001868619303021 (visited on 05/23/2024).

[55] B. Petkova, S. Tcholakova, and N. Denkov, “Foamability of surfactant solutions: Interplay between adsorption and hydrodynamic conditions,” *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 626, p. 127 009, Oct. 2021, ISSN: 0927-7757. DOI: 10.1016/j.colsurfa.2021.127009. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0927775721008785 (visited on 05/23/2024).

A

Appendix 1

A.1 Microscopy pictures

In Appendix A.1 micrographs are presented for the cleaning formulations selected in Tables 4.3 and 4.4.

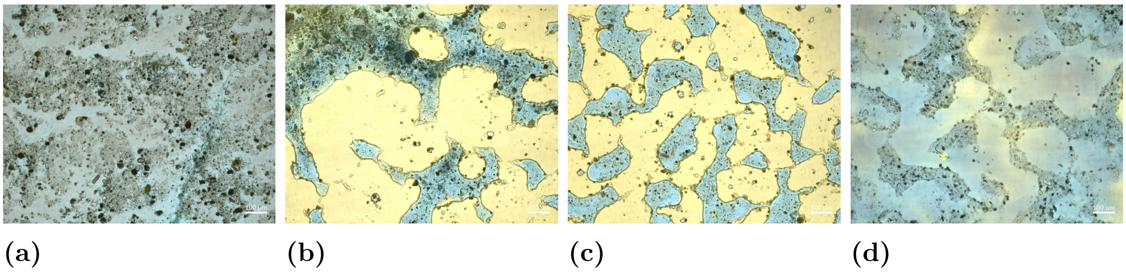

(a) (b) (c) (d)

Figure A.1: Micrographs of cleaning formulations containing 1.3 wt% quat and 1 wt% ammonium citrate.

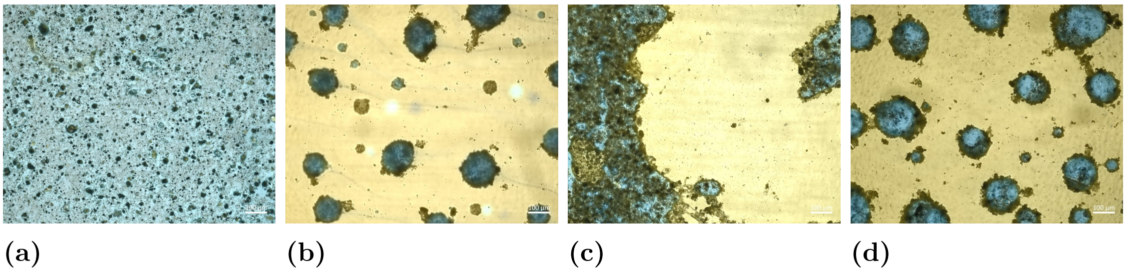
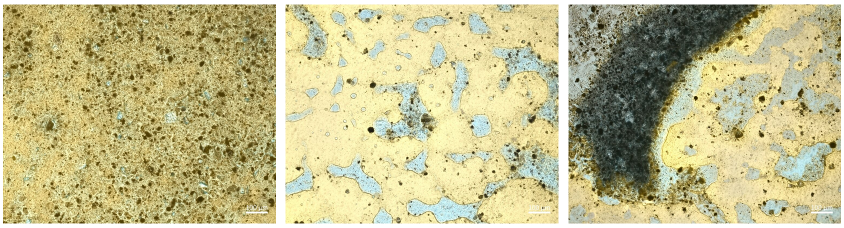
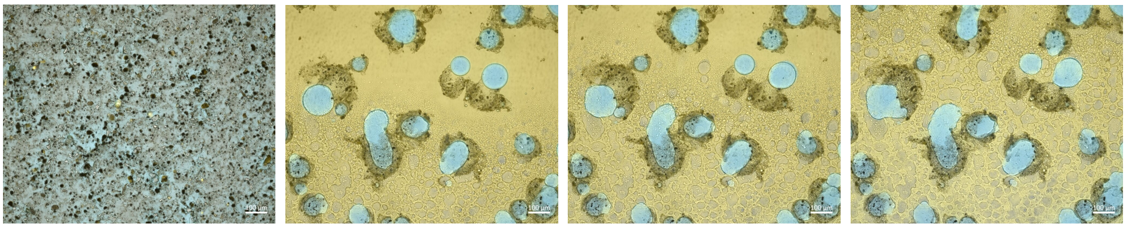

(a) (b) (c) (d)

Figure A.2: micrographs of cleaning formulations containing 5 wt% amine oxide and 2 wt% ammonium citrate.



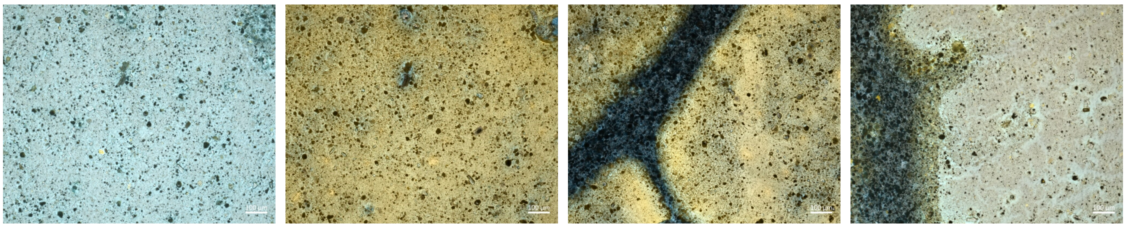
(a) (b) (c)

Figure A.3: micrographs of cleaning formulations containing 2.6 wt% amphoteric and 2 wt% ammonium citrate.



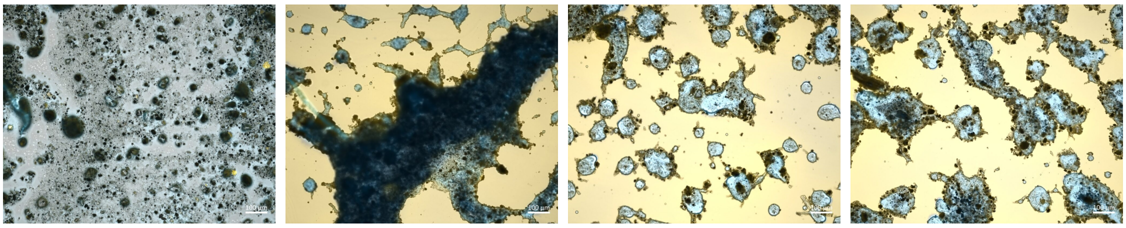
(a) (b) (c) (d)

Figure A.4: micrographs of cleaning formulations containing 6 wt% amine oxide and 5 wt% GLDA.



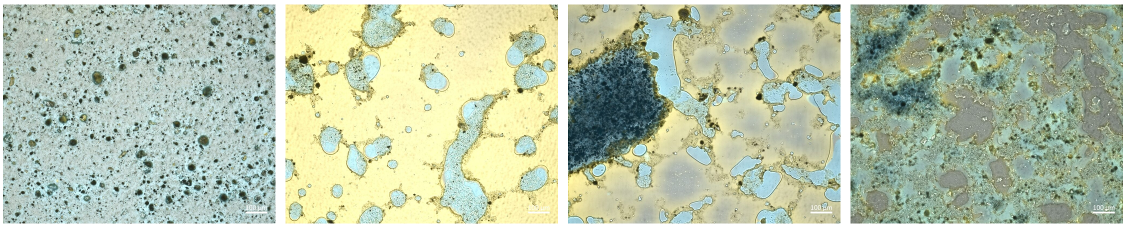
(a) (b) (c) (d)

Figure A.5: micrographs of cleaning formulations containing 2 wt% amphoteric and 1 wt% GLDA.



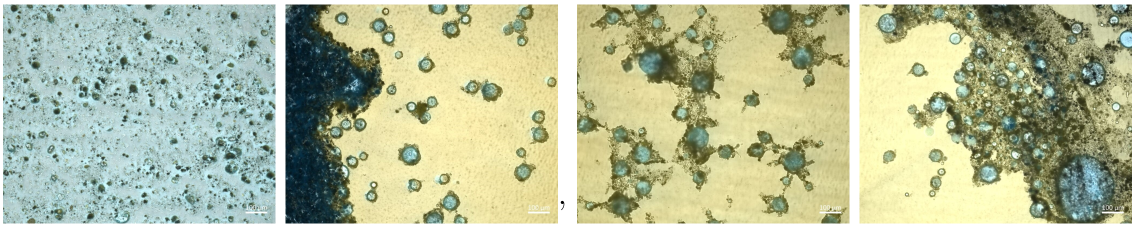
(a) (b) (c) (d)

Figure A.6: micrographs of cleaning formulations containing 1.5 wt% quat and 1 wt% GLDA.



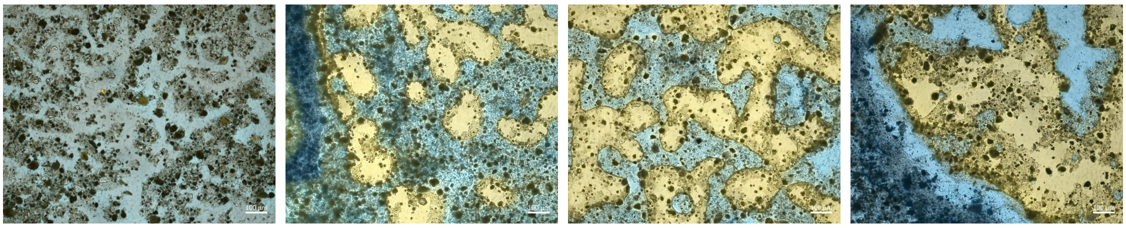
(a) (b) (c) (d)

Figure A.7: micrographs of cleaning formulations containing 1.9 wt% amphoteric and 3 wt% MGDA.



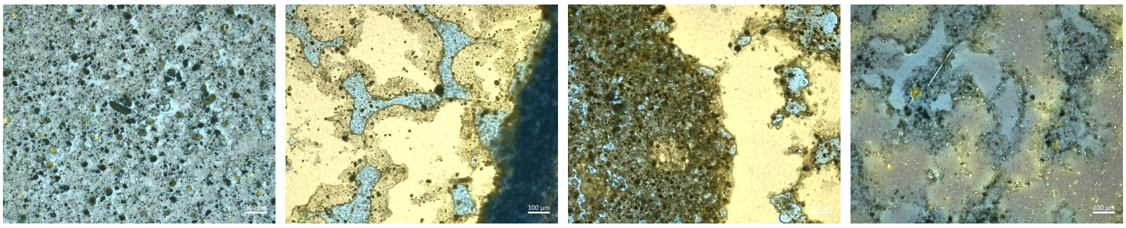
(a) (b) (c) (d)

Figure A.8: micrographs of cleaning formulations containing 6 wt% amine oxide and 3 wt% MGDA.



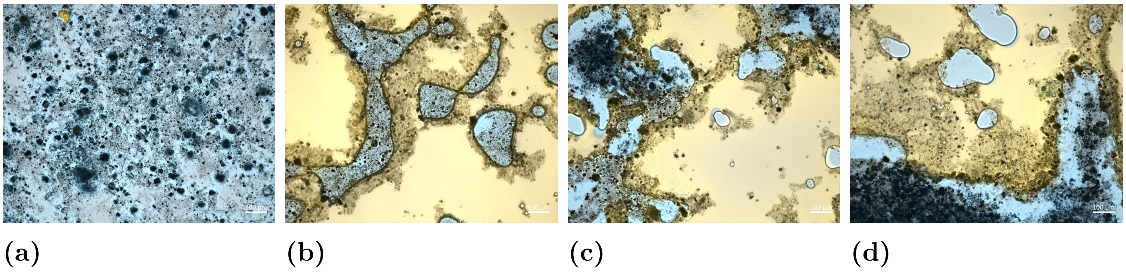
(a) (b) (c) (d)

Figure A.9: micrographs of cleaning formulations containing 1.3 wt% quat and 2 wt% MGDA.



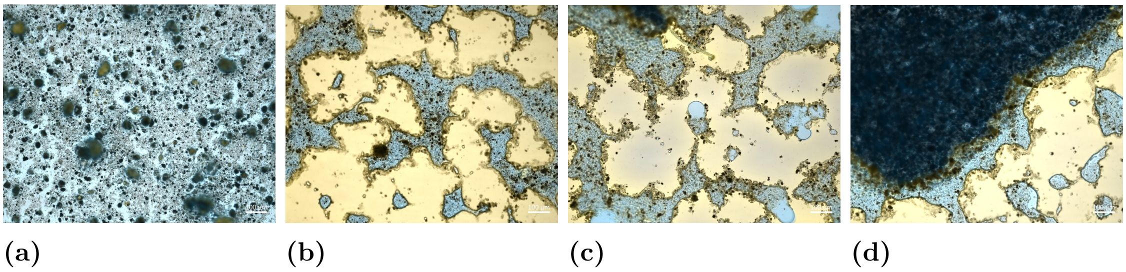
(a) (b) (c) (d)

Figure A.10: micrographs of cleaning formulations containing 1.3 wt% quat and 2 wt% ammonium citrate.



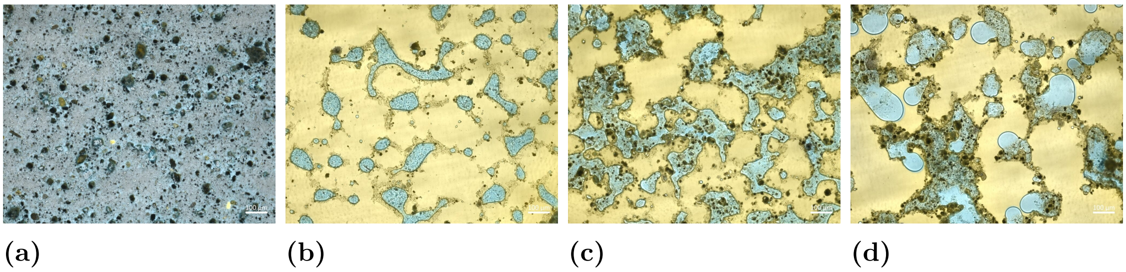
(a) **(b)** **(c)** **(d)**

Figure A.11: micrographs of cleaning formulations containing 1.3 wt% quat and 3 wt% MGDA.



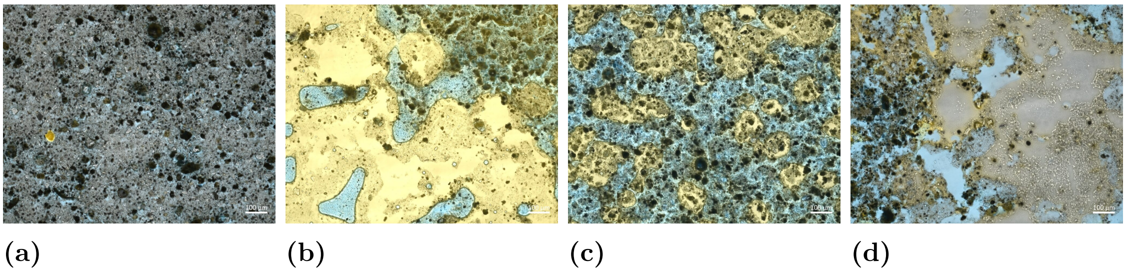
(a) **(b)** **(c)** **(d)**

Figure A.12: micrographs of cleaning formulations containing 1.5 wt% quat and 0.5 wt% GLDA.



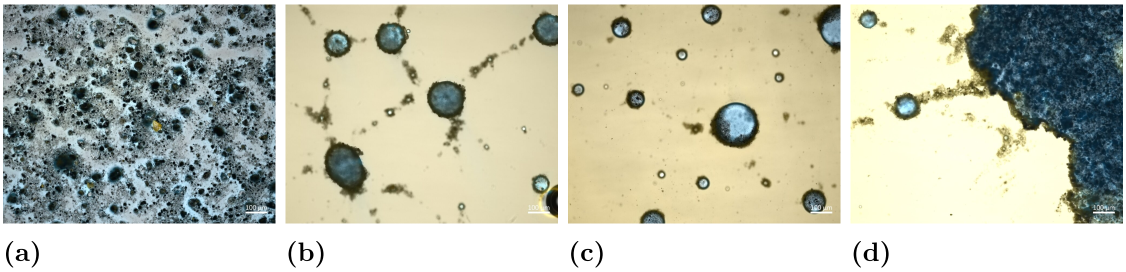
(a) **(b)** **(c)** **(d)**

Figure A.13: micrographs of cleaning formulations containing 1.9 wt% amphoteric and 7 wt% MGDA.



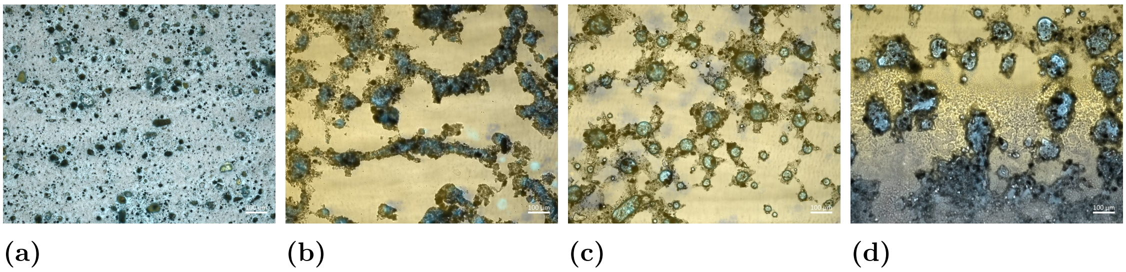
(a) **(b)** **(c)** **(d)**

Figure A.14: micrographs of cleaning formulations containing 2 wt% amphoteric and 7 wt% GLDA.



(a) **(b)** **(c)** **(d)**

Figure A.15: micrographs of cleaning formulations containing 5 wt% amine oxide and 0.5 wt% ammonium citrate.



(a) **(b)** **(c)** **(d)**

Figure A.16: micrographs of cleaning formulations containing 6 wt% amine oxide and 3 wt% GLDA.

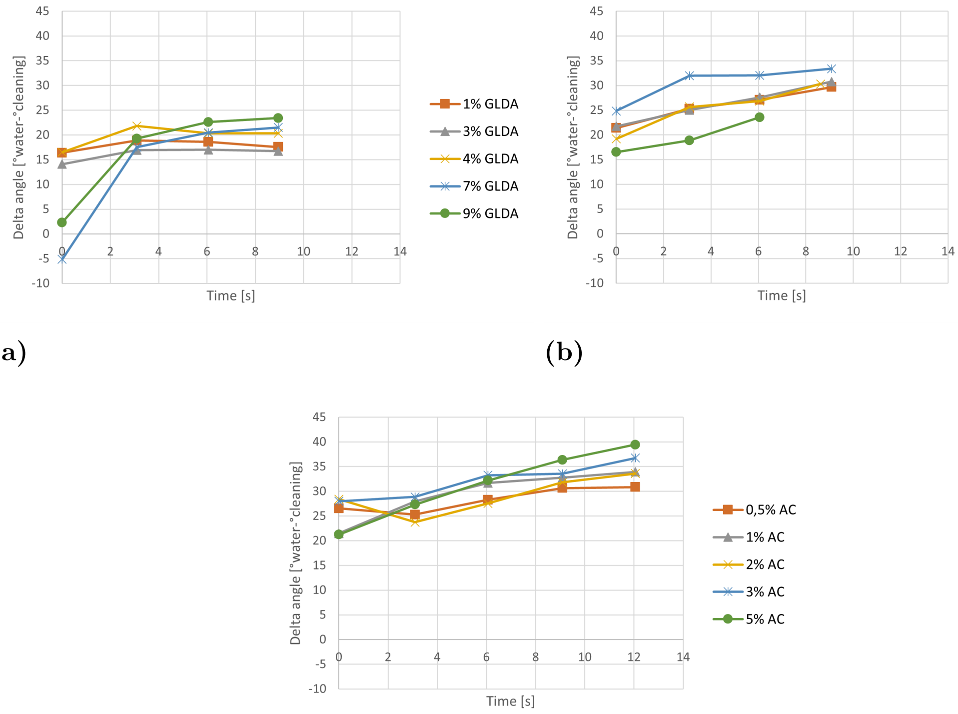
B

Appendix 2

B.1 Contact angle

In Appendix B.1 more quantitative and detailed results from all contact angle measurements are presented.

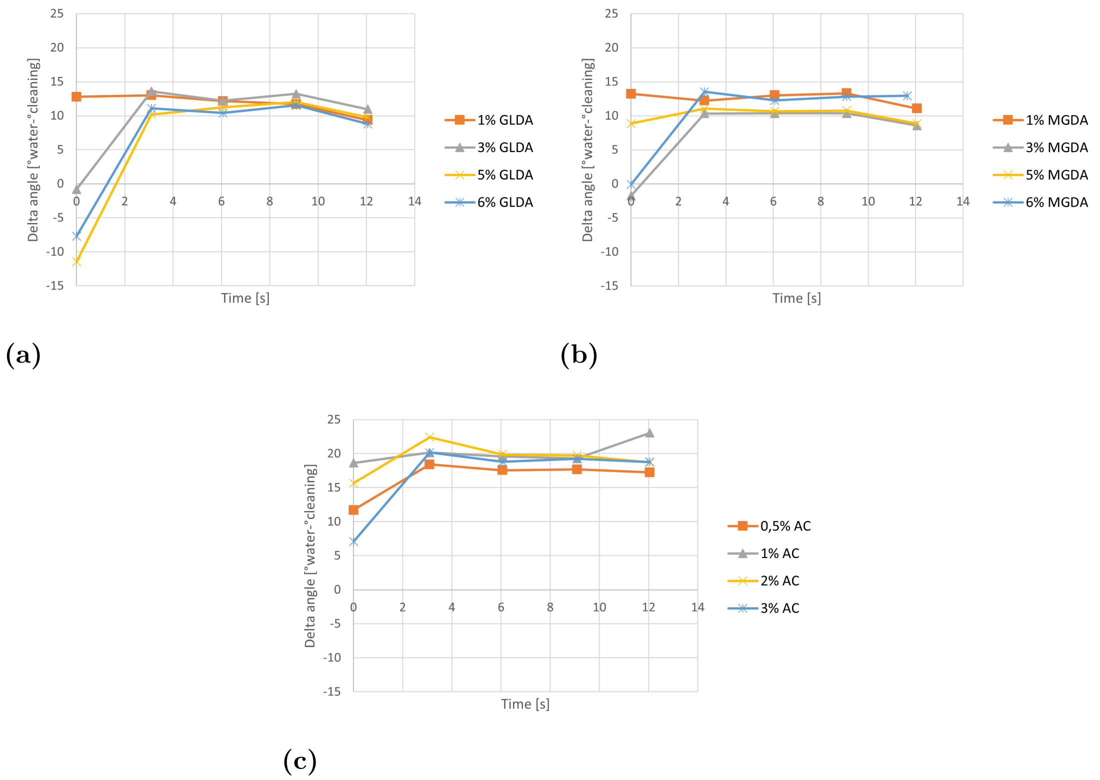
B.1.1 Ceramic with kitchen soil



(a) **(b)**

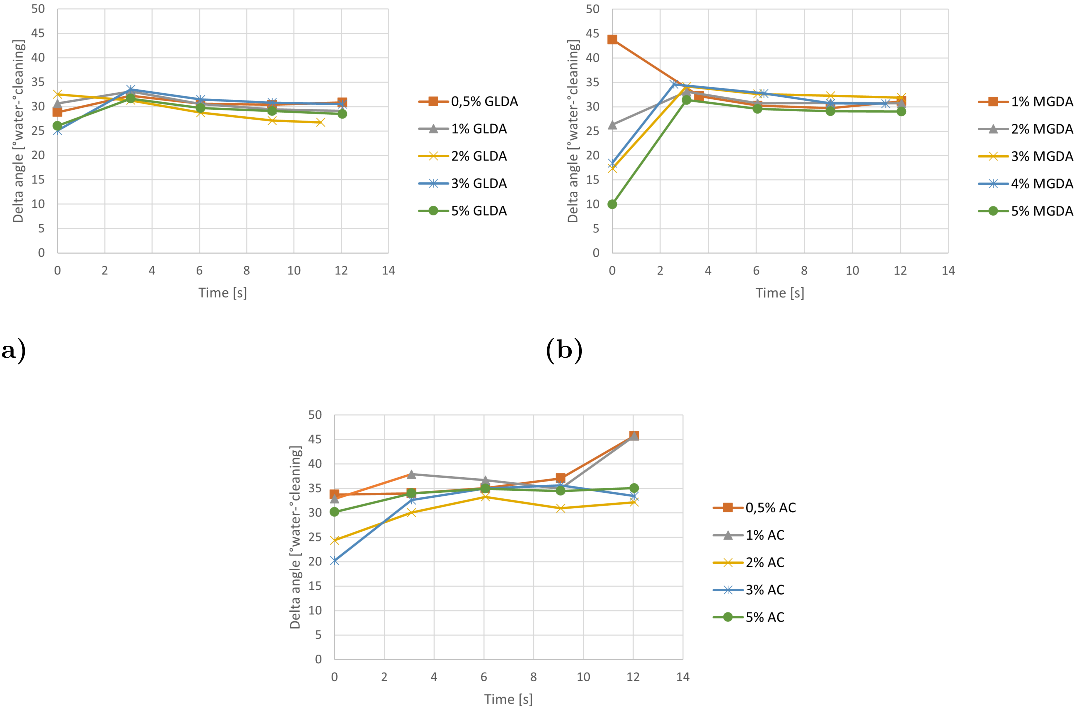
(c)

Figure B.1: Impact on contact angle for formulations containing an amphoteric secondary surfactant when increasing chelating agent concentration (a) GLDA (b) MGDA and (c) ammonium citrate on ceramic surface with kitchen soil.



(a) **(b)** **(c)**

Figure B.2: Impact on contact angle for formulations containing an amine oxide secondary surfactant when increasing chelating agent concentration (a) GLDA (b) MGDA and (c) ammonium citrate on ceramic surface with kitchen soil.

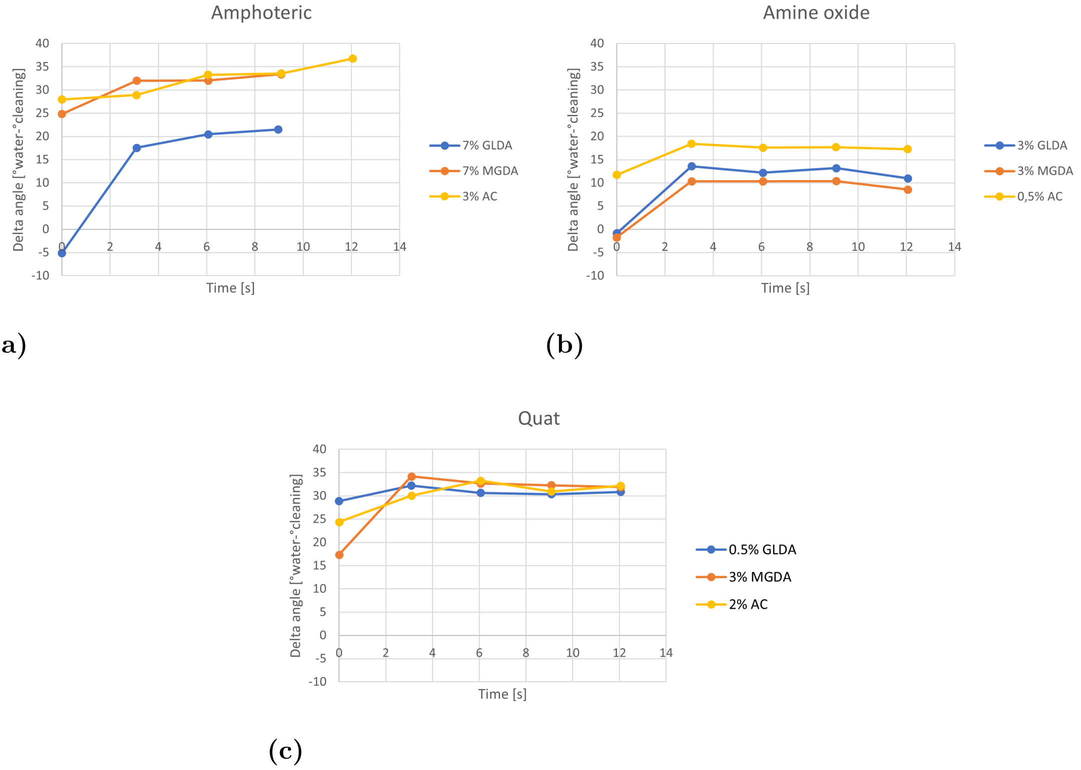


(a) **(b)**

(c)

Figure B.3: Impact on contact angle for formulations containing a quat secondary surfactant when increasing chelating agent concentration (a) GLDA (b) MGDA and (c) ammonium citrate on ceramic surface with kitchen soil.

In Figures B.4 and B.5 the contact angles for the formulations chosen for the cleaning tests, that can be seen in Tables 4.3 and 4.4 respectively, are presented.

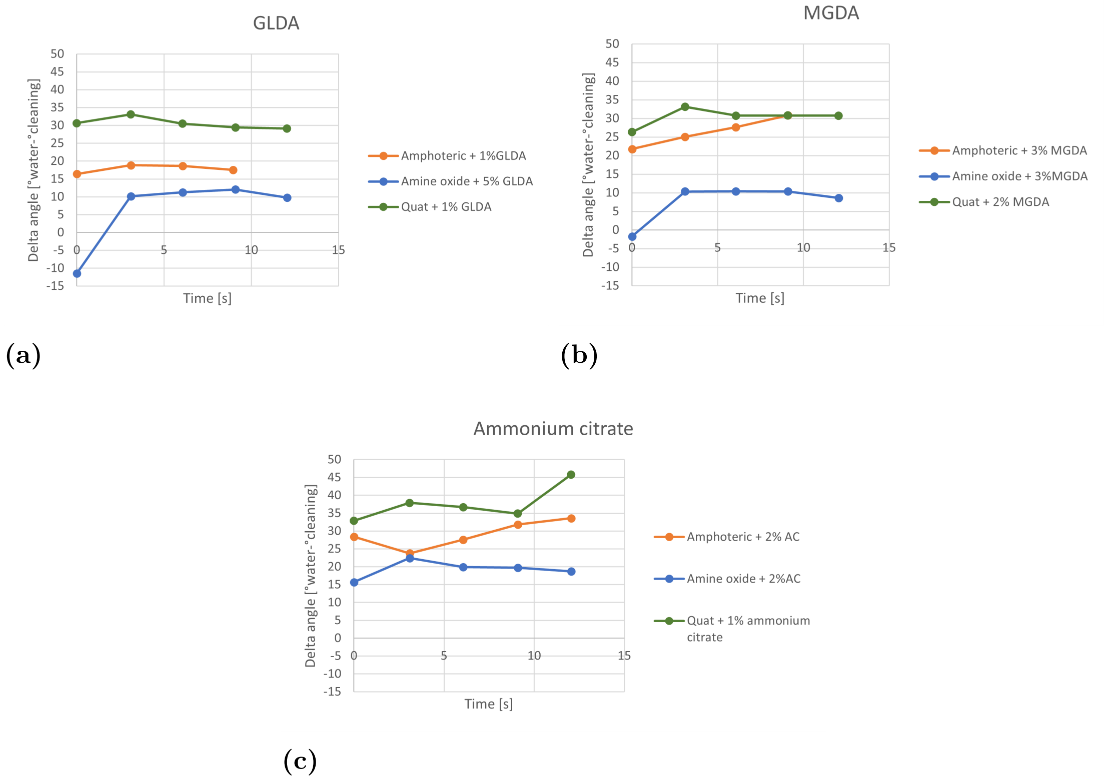


(a)

(b)

(c)

Figure B.4: Difference in contact angle between water and the cleaning formulation on ceramic surface with kitchen soil. The formulations contained (a) amphoteric (b) amine oxide and (c) quat and the chelating agent was varied

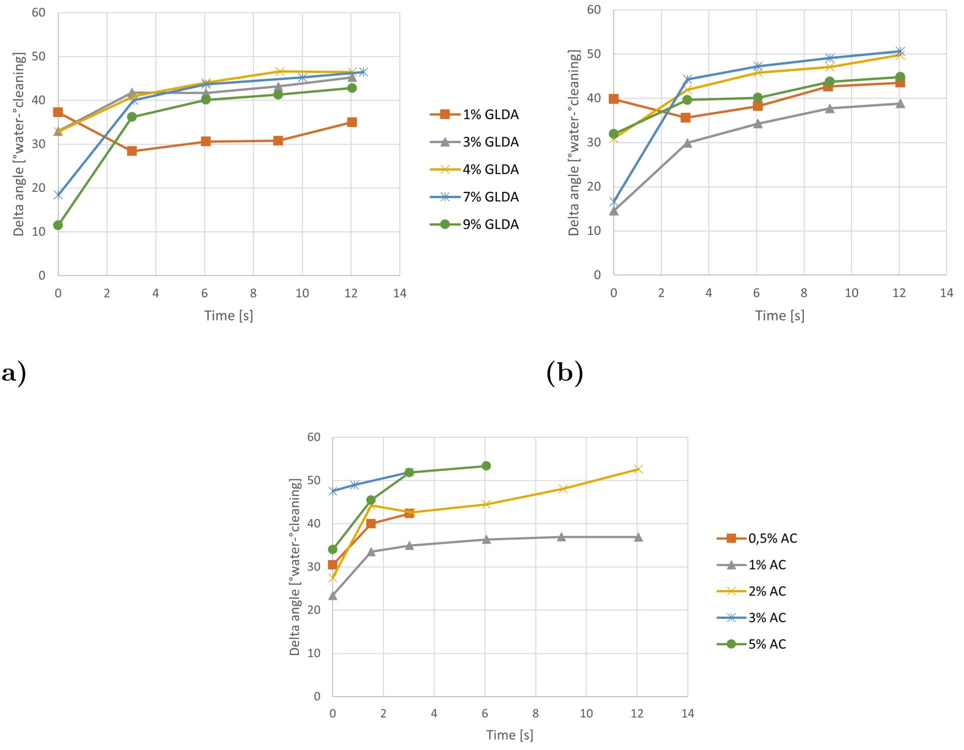


(a) (b)

(c)

Figure B.5: Difference in contact angle between water and the cleaning formulation on ceramic surface with kitchen soil. The formulations contained (a) GLDA (b) MGDA and (c) ammonium citrate and the secondary surfactant was varied

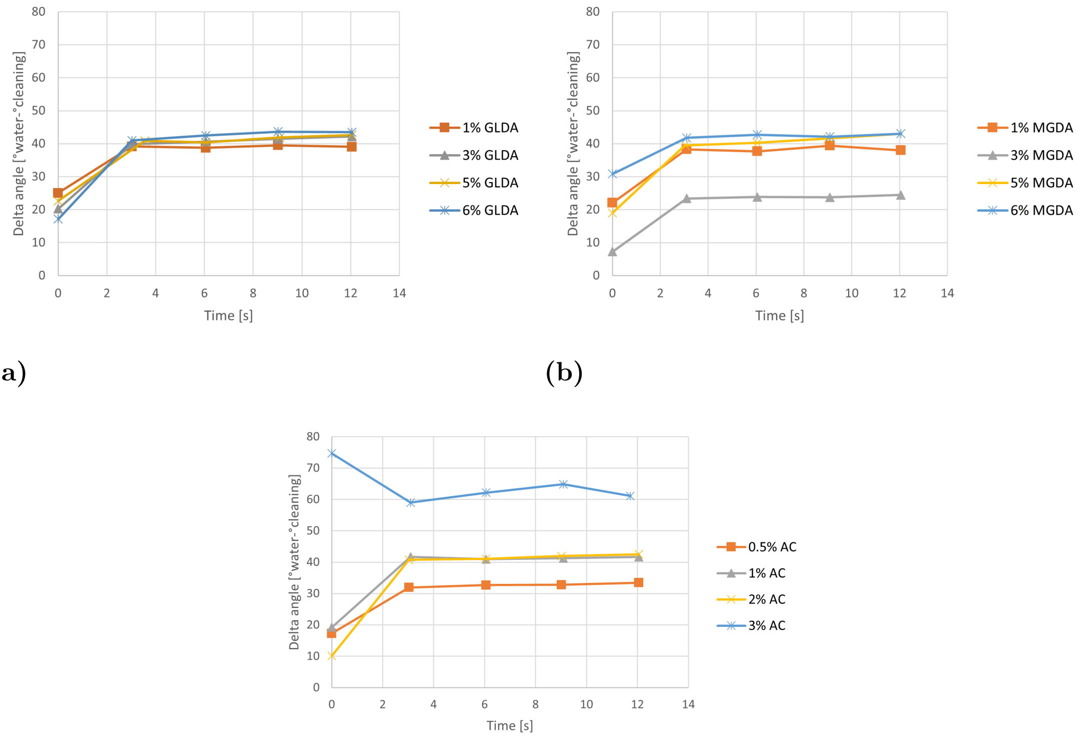
B.1.2 Glass with kitchen soil



(a) **(b)**

(c)

Figure B.6: Impact on contact angle for formulations containing an amphoteric secondary surfactant when increasing chelating agent concentration (a) GLDA (b) MGDA and (c) ammonium citrate on glass surface with kitchen soil.

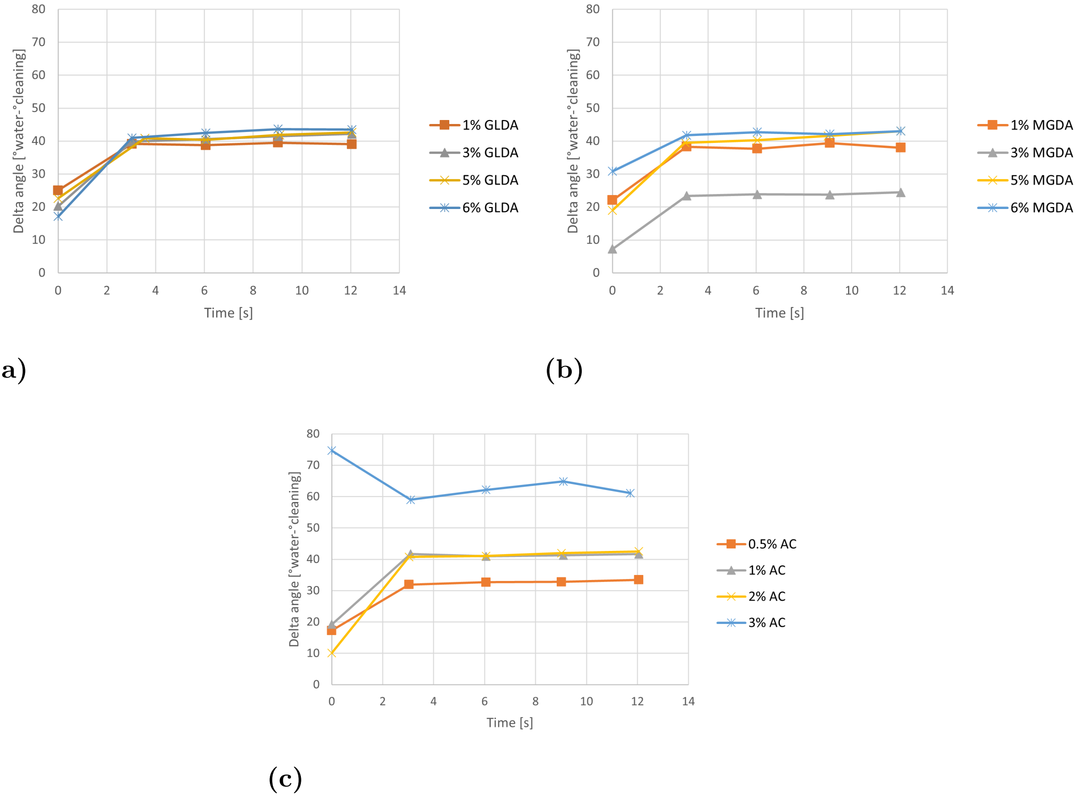


(a)

(b)

(c)

Figure B.7: Impact on contact angle for formulations containing an amine oxide secondary surfactant when increasing chelating agent concentration (a) GLDA (b) MGDA and (c) ammonium citrate on glass surface with kitchen soil.

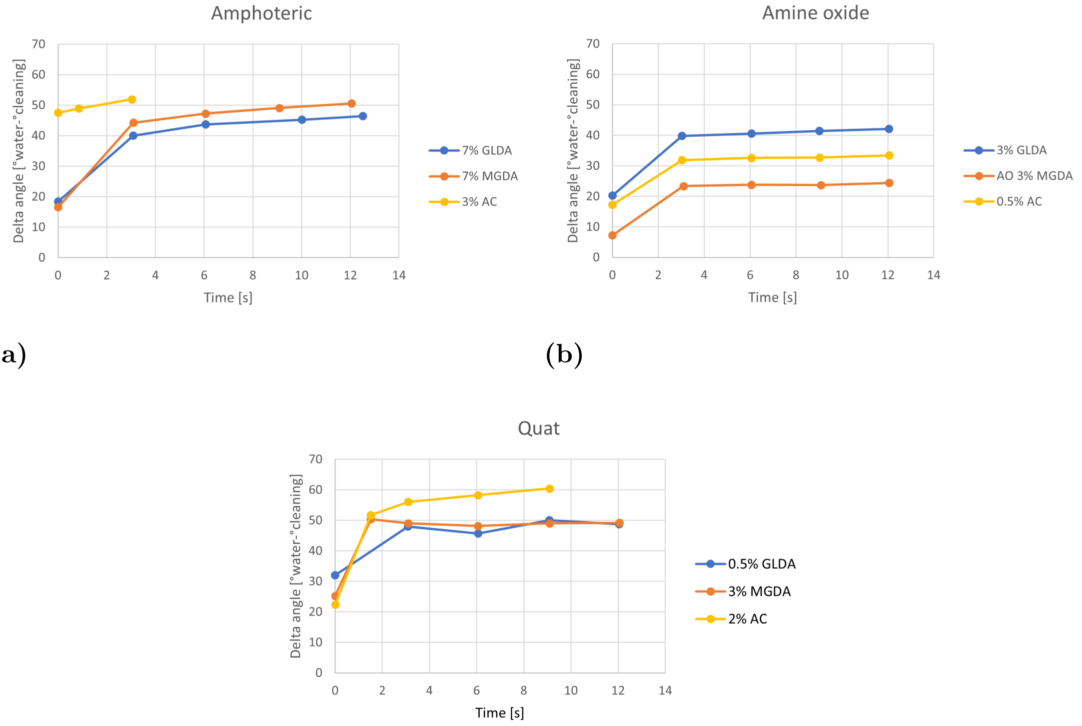


(a) **(b)**

(c)

Figure B.8: Impact on contact angle for formulations containing a quat secondary surfactant when increasing chelating agent concentration (a) GLDA (b) MGDA and (c) ammonium citrate on glass surface with kitchen soil.

In Figures B.9 and B.10 the contact angles for the formulations chosen for the cleaning tests, that can be seen in Tables 4.3 and 4.4 respectively, are presented.

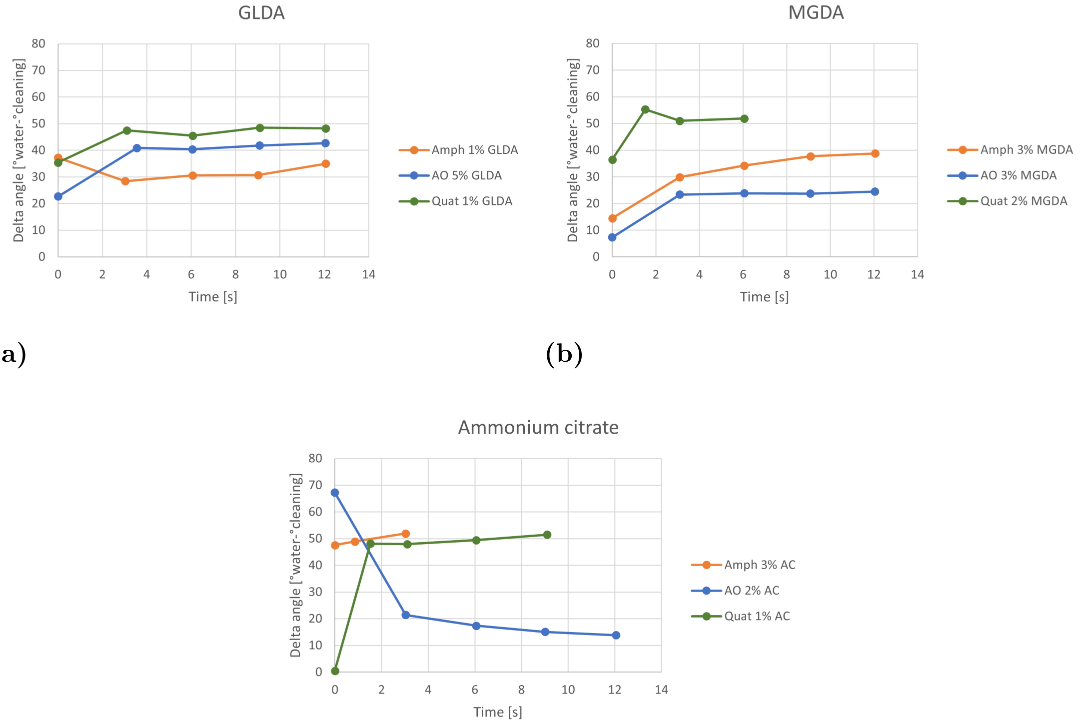


(a)

(b)

(c)

Figure B.9: Difference in contact angle between water and the cleaning formulation on glass surface with kitchen soil. The formulations contained (a) amphoteric (b) amine oxide and (c) quat and the chelating agent was varied.

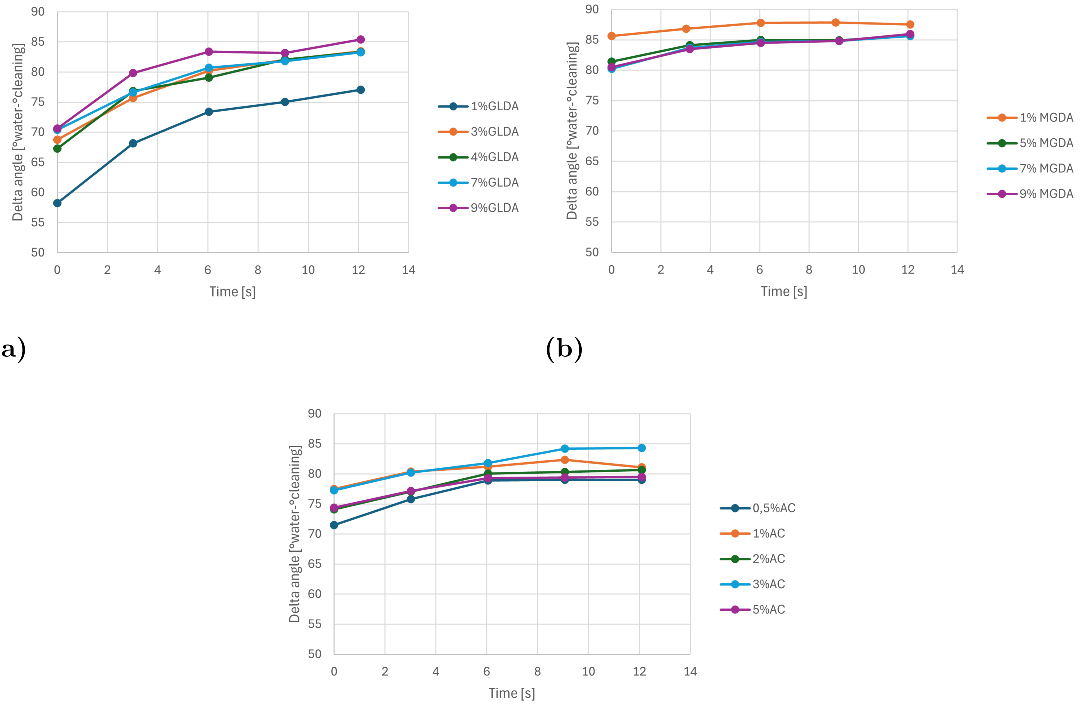


(a) **(b)**

(c)

Figure B.10: Difference in contact angle between water and the cleaning formulation on glass surface with kitchen soil. The formulations contained (a) GLDA (b) MGDA and (c) ammonium citrate and the secondary surfactant was varied.

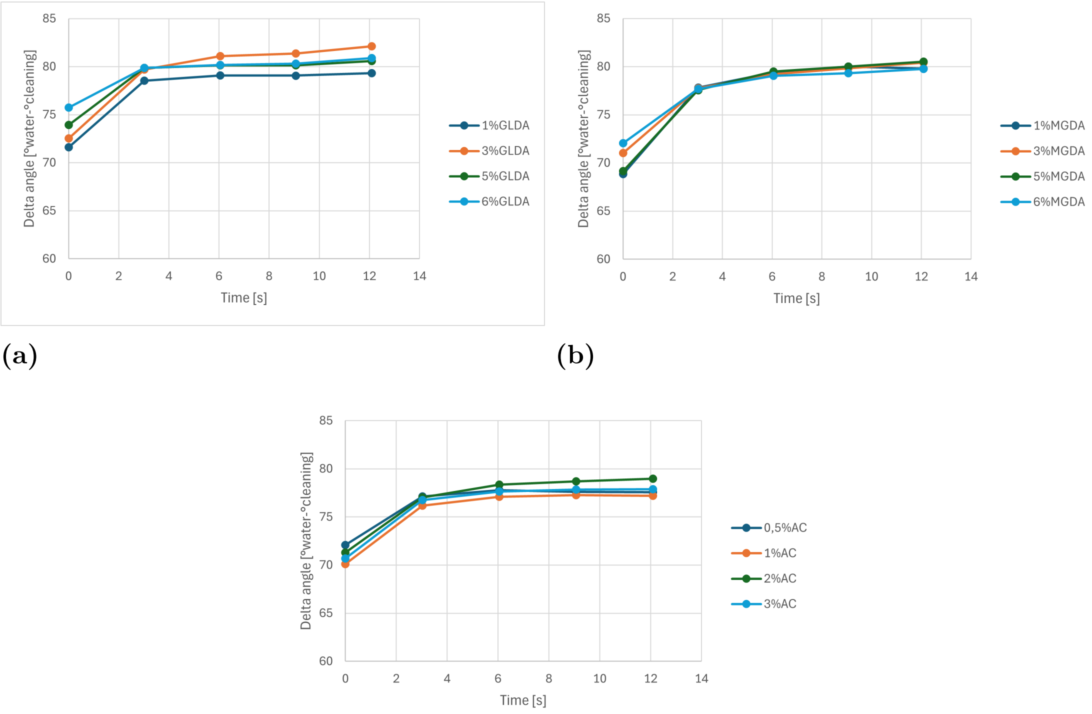
B.1.3 Metal with vehicle finish and engine soil



(a) **(b)**

(c)

Figure B.11: Impact on contact angle for formulations containing an amphoteric secondary surfactant when increasing chelating agent concentration (a) GLDA (b) MGDA and (c) ammonium citrate on metal surface with engine soil.

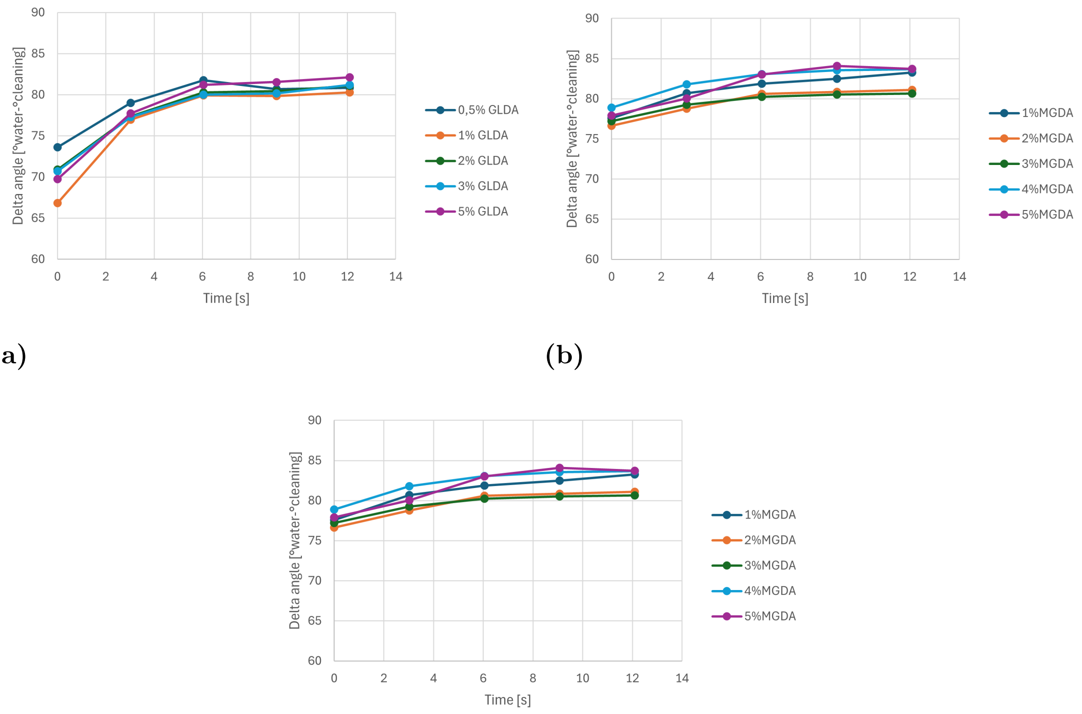


(a)

(b)

(c)

Figure B.12: Impact on contact angle for formulations containing an amine oxide secondary surfactant when increasing chelating agent concentration (a) GLDA (b) MGDA and (c) ammonium citrate on metal surface with engine soil.



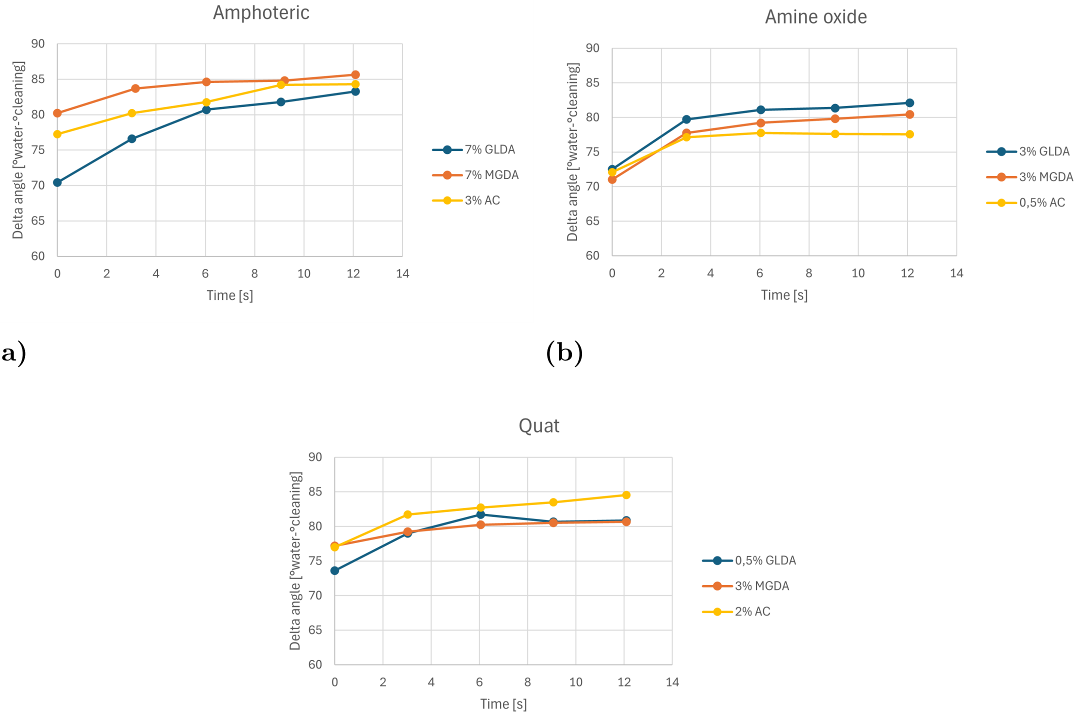
(a)

(b)

(c)

Figure B.13: Impact on contact angle for formulations containing a quat secondary surfactant when increasing chelating agent concentration (a) GLDA (b) MGDA and (c) ammonium citrate on metal surface with engine soil.

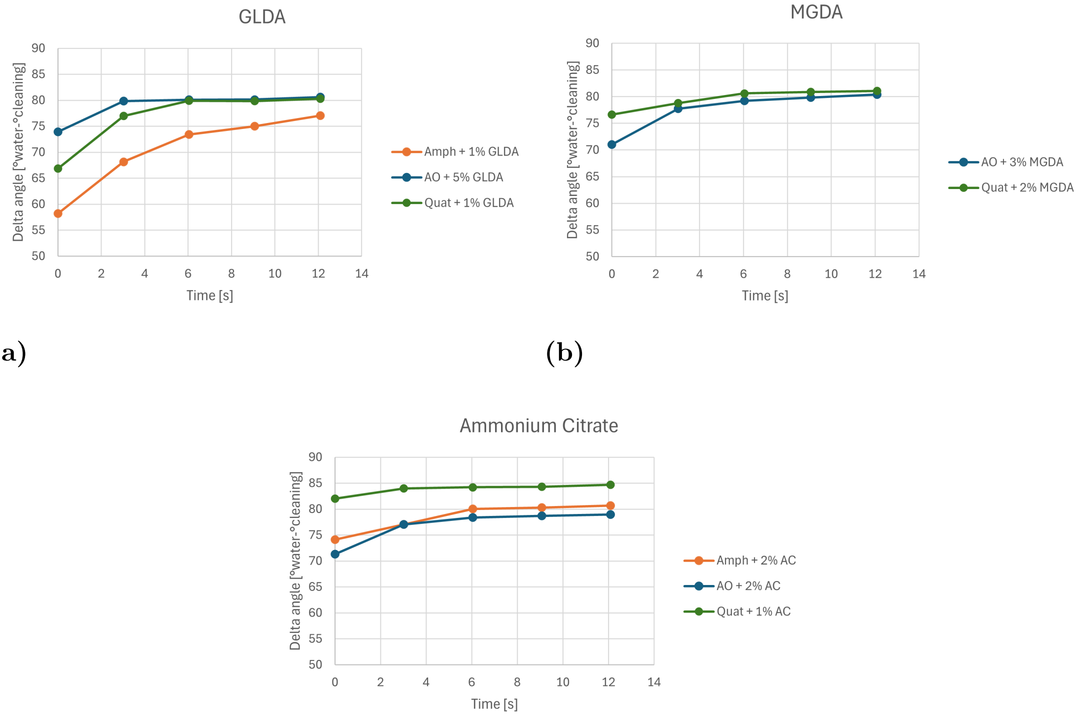
In Figures B.14 and B.15 the contact angles for the formulations chosen for the cleaning tests, that can be seen in Tables 4.3 and 4.4 respectively, are presented. In Figure B.15b the formulation with amphoteric is missing as this test result was not valid and a new test has not been carried out.



(a) **(b)**

(c)

Figure B.14: Difference in contact angle between water and the cleaning formulation on metal surface with engine soil. The formulations contained (a) amphoteric (b) amine oxide and (c) quat and the chelating agent was varied.



(a) **(b)**

(c)

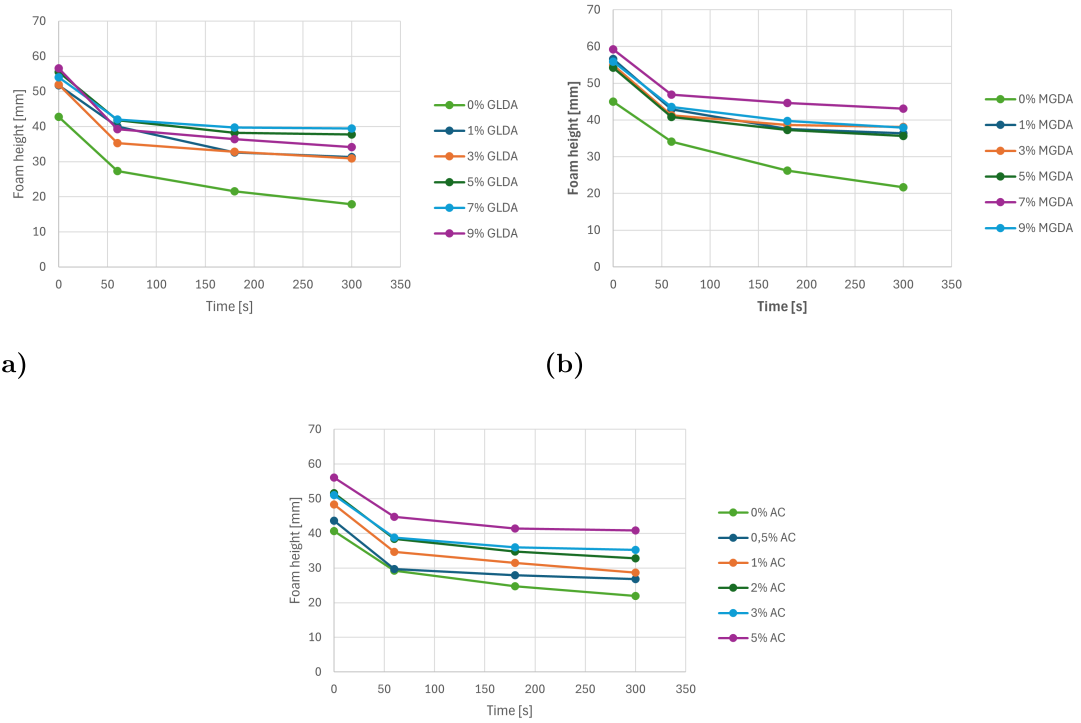
Figure B.15: Difference in contact angle between water and the cleaning formulation on metal surface with engine soil. The formulations contained (a) GLDA (b) MGDA and (c) ammonium citrate and the secondary surfactant was varied.

C

Appendix 3

C.1 Foaming

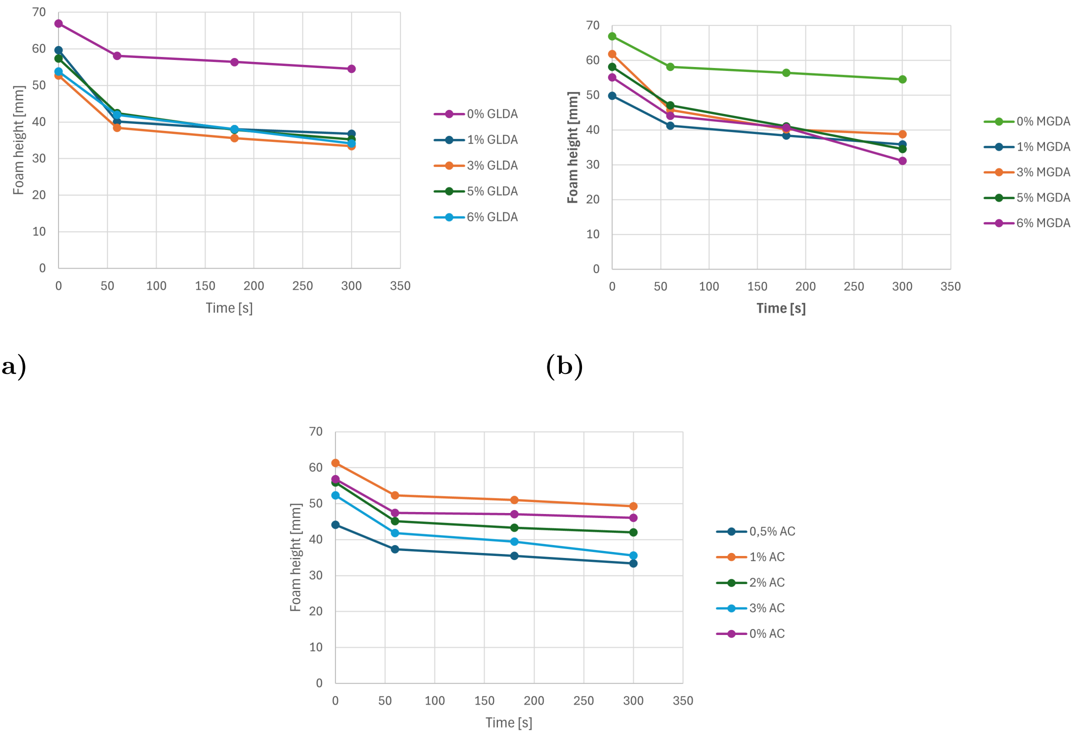
Appendix C.1 presents the result of the foam test.



(a) (b)

(c)

Figure C.1: Foam height for formulations containing an amphoteric secondary surfactant when increasing chelating agent concentration (a) GLDA (b) MGDA and (c) ammonium citrate.

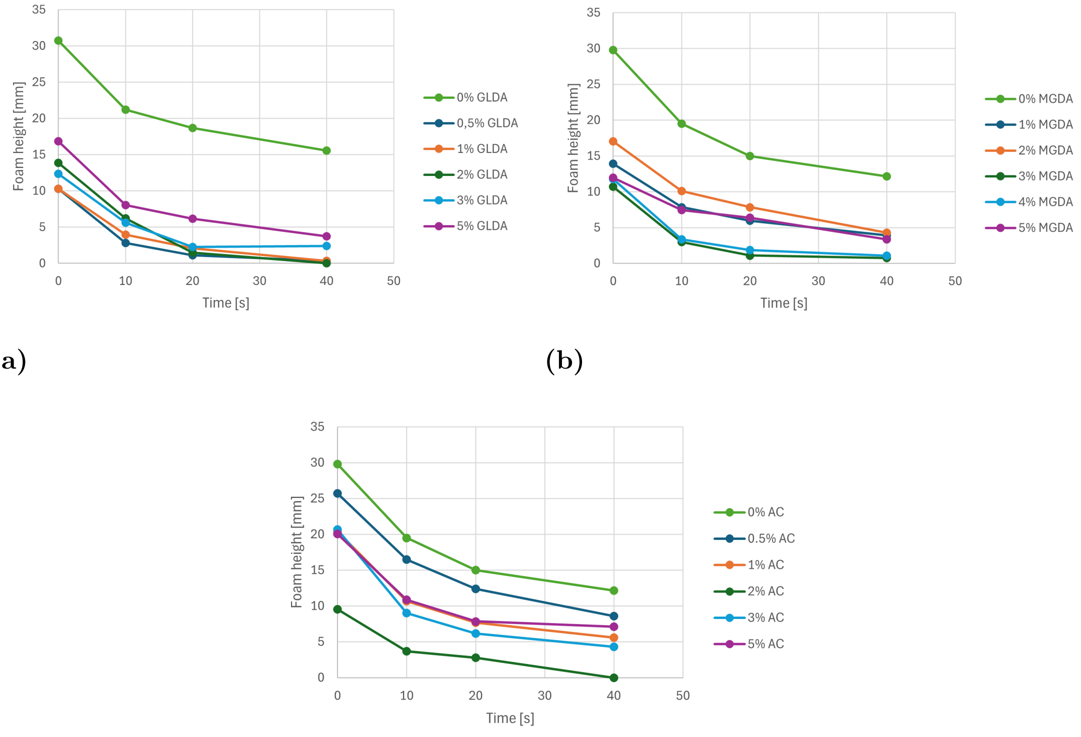


(a)

(b)

(c)

Figure C.2: Foam height for formulations containing an amine oxide secondary surfactant when increasing chelating agent concentration (a) GLDA (b) MGDA and (c) ammonium citrate.

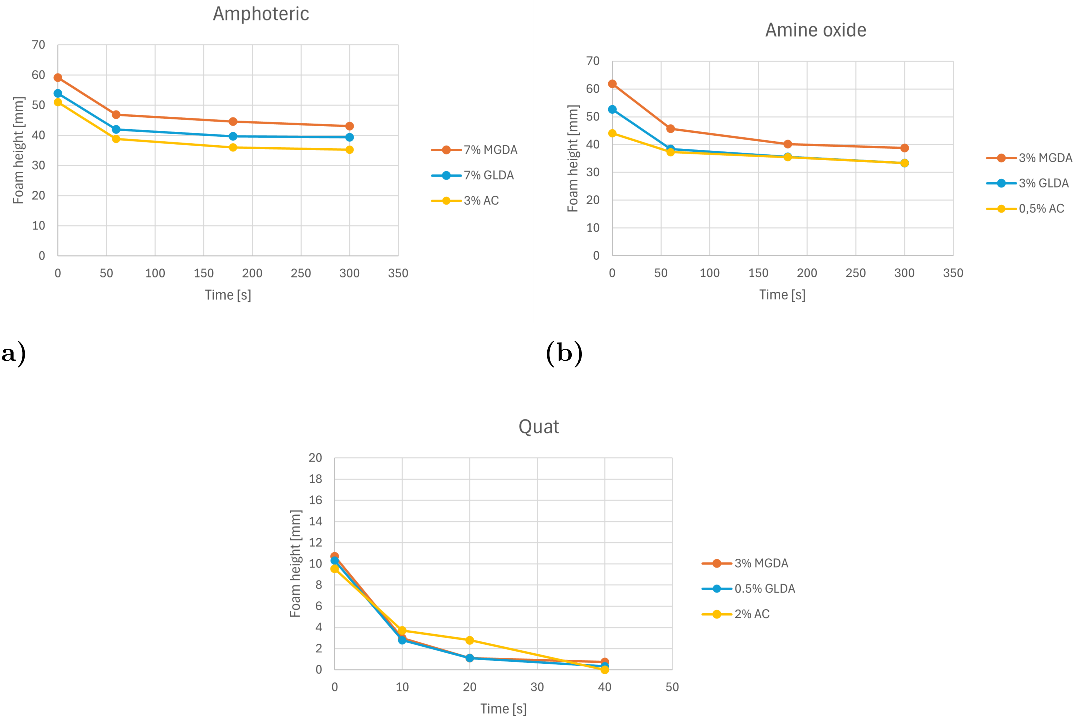


(a) **(b)**

(c)

Figure C.3: Foam height for formulations containing a quat secondary surfactant when increasing chelating agent concentration (a) GLDA (b) MGDA and (c) ammonium citrate.

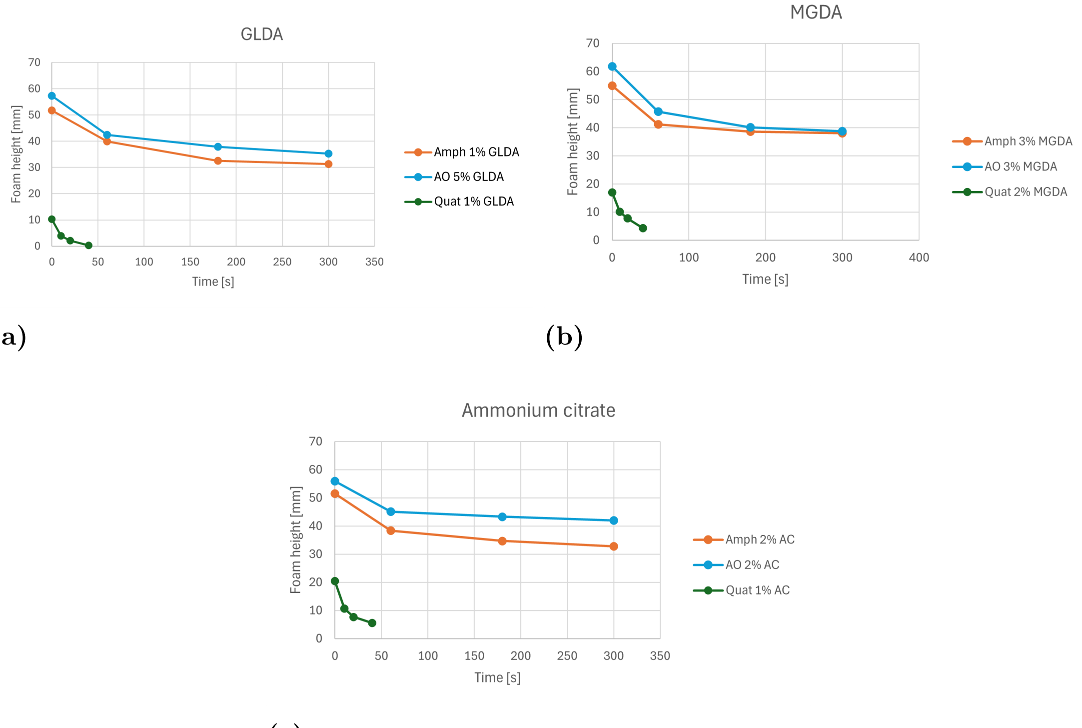
In Figures C.4 and C.5 the foam height for the formulations chosen for the cleaning tests, which can be seen in Tables 4.3 and 4.4 respectively, are presented.



(a) (b)

(c)

Figure C.4: Foam height for the cleaning formulation that contained (a) amphoteric (b) amine oxide and (c) quat, where the chelating agent was varied.



(a) **(b)**

(c)

Figure C.5: Foam height for the cleaning formulations that contained (a) GLDA (b) MGDA and (c) ammonium citrate, where the secondary surfactant was varied.

In Figure C.6 the foam height for the formulations in Table 4.4, where the secondary surfactant is varied and the chelating agent is fixed, is presented.

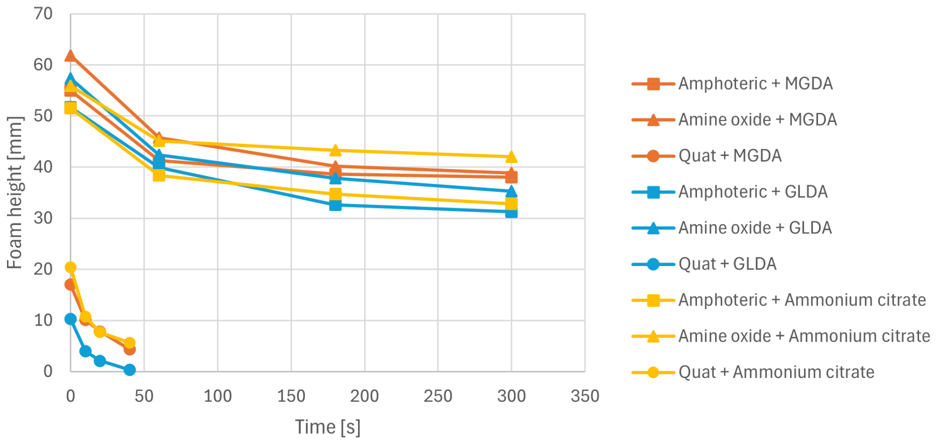


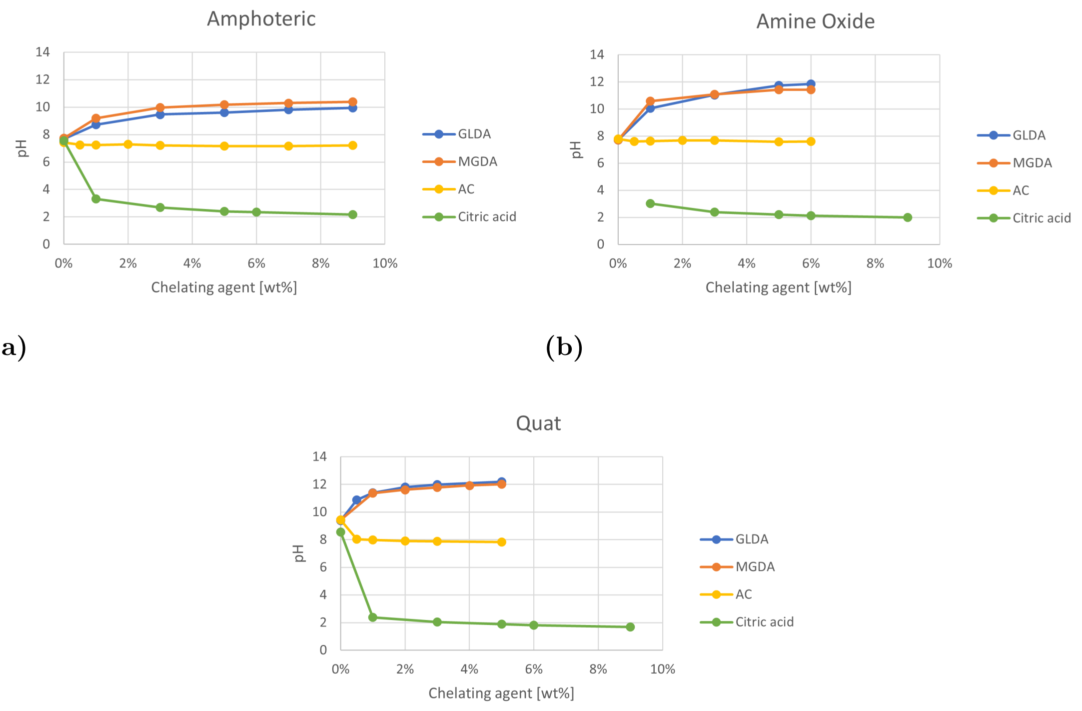
Figure C.6: Foam height for the cleaning systems with fixed chelating agent and varied secondary surfactant presented in Table 4.4.

D

Appendix 4

D.1 pH

In Appendix D.1 pH values for all cleaning formulations are presented.



(a)

(b)

(c)

Figure D.1: pH for cleaning formulations containing (a) amphoteric (b) amine oxide and (c) quat as secondary surfactant and were the chelating agent was varied.

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