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**FUNDAMENTAL CHARACTERIZATION AND TECHNICAL
ASPECTS OF A CHELATING SURFACTANT**

Ida Svanedal

Supervisors:
Professor Håkan Edlund
Professor Magnus Norgren

Chemistry
Faculty of Science, Technology and Media
Mid Sweden University, SE-851 70 Sundsvall, Sweden

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Ida Svanedal

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Chemistry
Faculty of Science, Technology and Media
Mid Sweden University, SE-851 70 Sundsvall, Sweden

Telephone: +46 (0)771-975 000

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Ida Svanedal

FSCN - Fibre Science and Communication Network, Department of Chemical Engineering, Mid Sweden University, SE-851 70 Sundsvall, Sweden. ISSN 1652-893X, Mid Sweden University Doctoral Thesis 179; ISBN 978-91-87557-39-2

Abstract

The purpose of this study was to investigate the fundamental characteristics of a chelating surfactant in terms of solution behaviour, chelation of divalent metal ions, and interaction in mixtures with different foaming agents and divalent metal ion, as well as examining its prospects in some practical applications. Chelating surfactants are functional molecules, with both surface active and chelating properties, which are water soluble and therefore suitable for chelation in many aqueous environments. The dual functionality offers the possibility to recover the chelating surfactant as well as the metals.

The DTPA (diethylenetriaminepentaacetic acid)-based chelating surfactant 4-C₁₂-DTPA (2-dodecyldiethylenetriaminepentaacetic acid) was synthesized at Mid Sweden University. In the absence of metal ions, all eight donor atoms in the headgroup of 4-C₁₂-DTPA are titrating and the headgroup charge can be tuned from +3 to -5 by altering the pH. The solution properties, studied by surface tension measurements and NMR diffusometry, were consequently found strongly pH dependent. pH measurements of chelating surfactant solutions as a function of concentration was used to extract information regarding the interaction between surfactants in the aggregation process.

Small differences in the conditional stability constants ($\log K$) between coordination complexes of DTPA and 4-C₁₂-DTPA, determined by competition measurements utilizing electrospray ionization mass spectrometry (ESI-MS), indicated that the hydrocarbon tail only affected the chelating ability of the headgroup to a limited extent. This was further confirmed in hydrogen peroxide bleaching of thermomechanical pulp (TMP) treated with 4-C₁₂-DTPA.

Interaction parameters for mixed systems of 4-C₁₂-DTPA and different foaming agents were calculated following the approach of Rubingh's regular solution theory. The mixtures were also examined with addition of divalent metal ions in equimolar ratio to the chelating surfactant. Strong correlation was found between the interaction parameter and the phase transfer efficiency of Ni²⁺ ions during

flotations. Furthermore, a significant difference in $\log K$ between different metal complexes with 4-C₁₂-DTPA enabled selective recovery of the metal ion with the highest $\log K$.

The findings in this study contribute to the understanding of the fundamental characteristics of chelating surfactants, which can be further utilized in practical applications.

Keywords: chelating surfactant, DTPA based surfactant, pH-responsive, characterization, surface tension, NMR diffusometry, conditional stability constants, interaction parameter, ion flotation

Sammandrag

Syftet med den här studien var att undersöka de fundamentala egenskaperna hos en kelerande surfaktant med avseende på lösningsbeteende, komplexbindning av tvåvärda metalljoner och interaktioner i blandningar med olika skumbildare och tvåvärda joner, samt att undersöka dess framtidsutsikter inom några praktiska tillämpningar. Kelerande surfaktanter är funktionella molekyler, med både komplexbindande och ytaktiva egenskaper, som är vattenlösliga och därför passar för komplexbindning i många olika vattenmiljöer. Den dubbla funktionaliteten gör det möjligt att separera och återvinna både den kelerande surfaktanten och metallerna.

Den DTPA (dietylentriamin pentaättiksyra)-baserade kelerande surfaktanten 4-C₁₂-DTPA (2-dodecyldietylentriamin pentaättiksyra) syntetiserades på Mittuniversitetet. Utan tillsats av metalljoner är alla donatoratomer i huvudgruppen hos 4-C₁₂-DTPA titrerande, och huvudgruppens laddning kan justeras från +3 till -5 genom att ändra pH. Lösningsbeteendet, som studerades med hjälp av ytspänningsmätningar och diffusions NMR, visade följaktligen starkt pH beroende. Mätningar av pH som funktion av koncentration på lösningar av den kelerande surfaktanten gav information om interaktionen mellan surfaktanter under aggregeringsprocessen.

Små skillnader i den relativa styrkan mellan komplex av DTPA och 4-C₁₂-DTPA, som bestämdes med hjälp av konkurrensmätningar och elektropray-jonisation-masspektrometri (ESI-MS), tydde på att de komplexbindande egenskaperna hos huvudgruppen endast påverkades i liten utsträckning av kolvätekedjan. Detta kunde även bekräftas i experiment med väteperoxidblekning av termomekanisk massa (TMP) som behandlats med 4-C₁₂-DTPA.

Interaktionsparametrar beräknades för blandningar av 4-C₁₂-DTPA och olika skumbildare, samt för system med tillsats av tvåvärda metalljoner i ekvimolärt förhållande till den kelerande surfaktanten. Stark korrelation mellan interaktionsparametern och avskiljning av Ni²⁺ joner genom flotation kunde konstateras. En signifikant skillnad mellan styrkan hos två metallkomplex med den kelerande surfaktanten möjliggjorde dessutom selektiv avskiljning av det starkaste metallkomplexet.

Resultaten från denna studie bidrar till förståelsen av de fundamentala egenskaperna hos kelerande surfaktanter, vilka kan utnyttjas i praktiska tillämpningar.

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List of papers

This thesis is mainly based on the following five papers, herein referred to by their Roman numerals:

- Paper I Anomalies in solution behavior of an alkyl aminopolycarboxylic chelating surfactant
Svanedal, I.; Persson, G.; Norgren, M.; Edlund, H.
Langmuir **2013**, 29, 13708-13716.
- Paper II Metal ion coordination, conditional stability constants and solution behavior of chelating surfactant metal complexes
Svanedal, I.; Boija, S.; Almesåker, A.; Persson, G.; Andersson, F.; Hedenström, E.; Bylund, D.; Norgren, M.; Edlund, H.
Submitted to *Langmuir*
- Paper III Interactions in mixed micellar systems of an amphoteric chelating surfactant and ionic surfactants
Svanedal, I.; Persson, G.; Norgren, M.; Edlund, H.
Langmuir **2014**, 30, 1250-1256.
- Paper IV Headgroup interactions and ion flotation efficiency in mixtures of a chelating surfactant, different foaming agents and divalent metal ions
Svanedal, I.; Boija, S.; Norgren, M.; Edlund, H.
Submitted to *Langmuir*
- Paper V Brightness development of a hydrogen peroxide bleached spruce TMP. Comparisons of pre-treatments with DTPA and a separable chelating surfactant
Högberg, I.; Zasadowski, D.; Karlsson, A.; Wikman, B.; Andersson, F.; Hedenström, E.; Edlund, H.; Norgren, M.
Nord. Pulp Pap. Res. J. **2012**, 27, 50-55.

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Related papers and patents

The interaction parameter in binary surfactant mixtures of a chelating surfactant and a foaming agent

Högberg, I.; Andersson, F.; Hedenström, E.; Norgren, M.; Edlund, H.
Prog. Colloid Polym. Sci. **2011**, 138, 17-20.

Use of chelating surfactants as complexing agents for removal of manganese from mechanical pulp fibres prior to hydrogen peroxide bleaching

Högberg, I.; Karlsson, A.; Wikman, B.; Zasadowski, D.; Andersson, F.; Hedenström, E.; Edlund, H.; Norgren, M.
Proceedings of the 16th ISWFPC Conference 2011.

Chemical and method for chelating metal ions included in water and separating/recovering of formed chelate

Norgren, M.; Hedenström, E.; Edlund, H.; Andersson, F.; Högberg, I.
Patents: SE533165, 2010 (Sweden); CN102119247, 2013 (China)
Patent applications: WO2009151366, 2009 (PCT); EP2297397, 2011 (Europe); CA2739217, 2009 (Canada); US2011124898, 2011 (USA)

Methods for complex binding of metal ions

Norgren, M.; Hedenström, E.; Edlund, H.; Andersson, F.; Högberg, I.
Patent applications: WO2011070160, 2011 (PCT); EP2509922, 2012 (Europe); CN102652116, 2012 (China); CA2782463, 2011 (Canada); US2012318750, 2012 (USA)

1. Introduction

A chelating agent is a polydentate ligand, capable of forming strong coordination complexes with metal ions, while a surfactant is a molecule that adsorbs at interfaces and reduces the interfacial tension. The combination of these two functionalities in a single molecule results in a chelating surfactant. Surfactants are utilized as cleansers, emulsifiers, dispersants, and so on in a variety of consumer products and industrial processes. They are found for instance in the oil industry, in detergents, and in pharmaceuticals, just to mention a few. A mix of surfactants is often used to improve the performance. In living materials, surface active polar lipids act as solubilizers and as structural components of cell membranes.

By the formation of strong coordination complexes with chelating agents, metal ions are rendered harmless with respect to further chemical reactions. Chelating agents are used in a wide range of applications where metal ions must be controlled. Examples include industrial applications within pulp and paper industry, photo industry, textile industry, and metal finishing as well as in consumer products such as toothpaste, shampoo, detergents and many more. In all of the mentioned consumer products, a combination of chelating agents and surfactants are used. In nature, siderophores, which are among the strongest chelating agents known for Fe^{3+} , are produced by many microorganisms to enhance the mineral nutrient availability.

There are unfortunately environmental impacts of using synthetic chelating agents, which should not be overlooked considering the ever increasing demand for sustainable developments. Large amounts of chelating agents are released from household and industrial waste waters to the aquatic environment, which may have detrimental consequences on wild life due to for example increased bioavailability of heavy metals.^{1,2} Chelating surfactants could be of great interest from these perspectives.

Chelating surfactants are relatively small and water soluble molecules, which penetrate easily in porous media, making them suitable for chelation in most aqueous environments. The metal complexes can easily be separated from the water phase, e.g. by foam flotation, and the collected foam can be further treated by electrolysis to regenerate the chelating surfactant and metals separately. Besides the traditional areas where chelating agents are used, the dual functionality opens up new application areas.

Furthermore, chelating surfactants are interesting from a scientific point of view.^{3,4} As surfactants they are rather extreme with their large amphoteric headgroups containing numerous titrating groups, or in the presence of metal ions where strong coordination complexes are formed, sometimes referred to as metallosurfactants.^{5,6} Although these substances have gained quite a lot of

attention in the past few decades due to their application prospects, chelating surfactants is a group of surfactants that is sparsely studied, especially those with very strong metal ion binding capacity.

On this basis, a chelating surfactant was designed. The aim of this thesis is to investigate the fundamental characteristics of the chelating surfactant 4-C₁₂-DTPA (2-dodecyldiethylenetriaminepentaacetic acid) in terms of solution behaviour, chelation of divalent metal ions, and interactions in mixtures with different foaming agents and divalent metal ion, which are all of great importance in practical applications for chelating surfactants.

1.1. Outline of the thesis

In this first chapter the background to the study is explained, along with practical application prospects for chelating surfactants. In chapter 2, the properties characterising chelating surfactants in general, and 4-C₁₂-DTPA in particular, is described. Rubingh's regular solution theory for calculating interaction parameters in surfactant mixtures is presented in chapter 3, as well as a discussion about amphoteric surfactant interactions. The most important applied experimental methods are introduced in chapter 4, more detailed experimental descriptions are found in the appended papers. Thereafter, the most important results from paper I-V are discussed, divided into four areas rather than the five papers. Chapter 5 describes the solution behaviour of 4-C₁₂-DTPA (paper I) and the studied divalent metal complexes of 4-C₁₂-DTPA (paper II). The chelating ability is discussed in chapter 6, with respect to determination of conditional stability constants (paper II) and the application in hydrogen peroxide bleaching of paper pulp (paper V). In chapter 7, the use of pH curves as an analytical tool for detecting the cmc (paper I) and gather information about coordination behaviour (paper II) as well as interactions in mixed micelles (paper III) is described. The correlation between the interaction parameter for mixed monolayer formation at the air-water interface and the ion flotation efficiency in mixtures of 4-C₁₂-DTPA, different foaming agents, and divalent metal ions is examined in chapter 8 (paper IV). Lastly, general conclusions are presented in chapter 9, along with a discussion regarding future research opportunities.

1.2. Environmental aspects of using conventional chelating agents

The first industrially manufactured chelating agents appeared during the 1930s,¹ with the purpose to capture solvated metal ions and prevent them from interfering with the industrial process. The coordinated metal ions remain in solution, but are restrained from participating in chemical reactions. The presence of metal ions may have detrimental effects on many industrial processes; they can form insoluble precipitates, trigger corrosion, catalyze undesired chemical reactions and cause

colour changes in the products. Adding chelating agents with high affinity to metal ions is therefore often vital for optimal process conditions. Chelating agents are utilized in a variety of consumer products and industrial applications, including household products, detergents, pulp and paper industry, photo industry, metal finishing and textile industry.

However, substantial amounts of chelating agents end up in the aquatic environment via waste waters and chelating agents are frequently accused of remobilizing heavy metals from sewage sludge and sediments.¹ The persistence to biodegradation of the chelating agents brings enduring harm to animals and plants.⁷ Once released to the environment, the chelating agents can sequester heavy metals that may be present, buried in the ground sediment, thereby markedly increasing the mobility of heavy metals and risk of exposure to living organisms.²

More recently, biodegradable chelating agents have become an alternative to the conventional chelating agents. The long-term environmental effects are considerably reduced by the biological degradation.^{8,9} The conventional chelating agents are however still the most widely used.¹⁰ An explanation to this may be that it is difficult to design sufficiently strong, and yet, biodegradable chelating agents.

In order to put a permanent end to the vast discharge of chelating agents to the recipient, a separable unit could be incorporated with the chelating structure. By this approach, the separated metals can be recovered and the chelating agent can be regenerated and reused. A number of materials could be of interest as separable carriers for the chelating groups. The chelators can for instance be attached to macromolecules^{11,12} or immobilized to micro particles, such as silica gel.¹³ Hydrocarbon chains can also be used, whereby a chelating surfactant is created.¹⁴⁻¹⁶ There are several fundamental separation techniques available, which may be more or less suitable for the various modified materials. The most widely applicable techniques are flocculation, flotation, adsorption, sedimentation, and filtration. Some conceivable routes are shown in Figure 1. The choice of modification depends on the area of application, as well as the accompanying separation method. The chelating part can also be designed from strategic choices to make the ligand more suitable for specific metal ions, thereby producing a metal selective chelating agent.

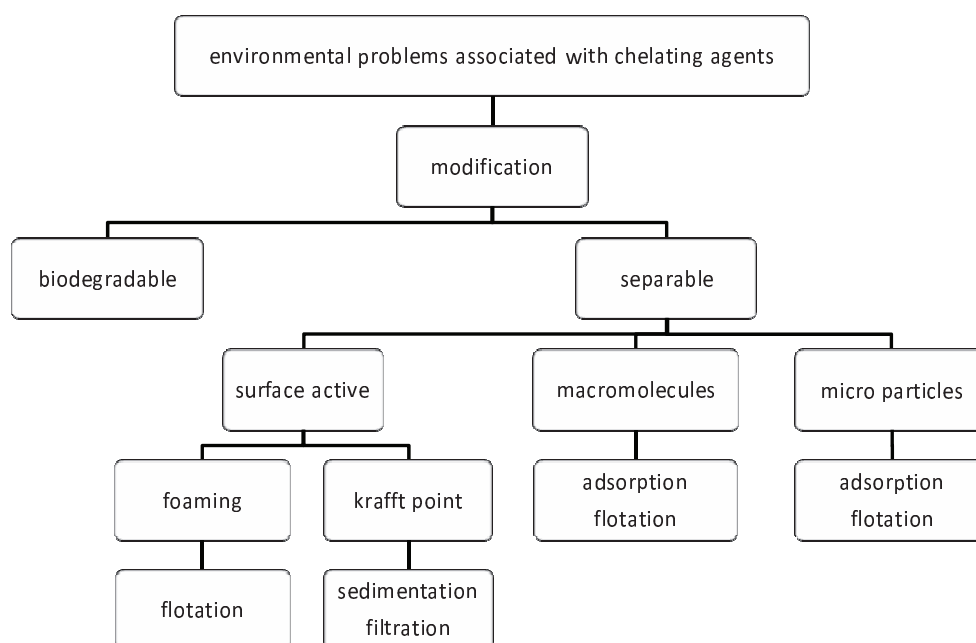


Figure 1. Possible routes for modification of chelating agents to reduce the environmental impact.

In this study, surface activity was utilized as separable functionality. DTPA (diethylenetriaminepentaacetic acid) one of the strongest synthetic chelating agents available, was chosen as the headgroup and a hydrocarbon chain was added to this headgroup. The resulting chelating surfactant 4-C₁₂-DTPA was synthesized at Mid Sweden University.

1.3. Practical applications for chelating surfactants

Practical applications for chelating surfactants and metallosurfactants are found within magnetic resonance imaging,¹⁷⁻¹⁹ templating of mesoporous materials²⁰ and catalysis of carboxylic and phosphate ester hydrolysis.²¹ Chelating surfactants may be utilized in many consumer products where a combination of chelating agents and surfactants are traditionally used. The nonpolar part makes the structure suitable in a hydrophobic matrix, such as cosmetic creams and lotions. Their amphiphilic character offers the possibility of separation, and the use of chelating surfactants to remove metal ions from aqueous solutions by foam flotation²² or micellar-enhanced ultrafiltration¹⁴ has been studied, although quite sparsely. By separating the metal complexes from industrial water, release of chelating agents as well as metal ions could be prevented. This can also be utilized to recover

valuable metal ions, e.g. from waste waters from metal finishing industry. Additionally, this technique can be used to purify metal contaminated water or oil.

1.3.1. Hydrogen peroxide bleaching of paper pulp

Totally chlorine free bleaching became a well-known concept in the pulp and paper industry during the 1980s, when the environmental issues of chlorine bleaching were recognized,^{23,24} and chlorine was replaced by hydrogen peroxide in many paper mills. Bleaching with hydrogen peroxide requires that the concentrations of certain transition metal ions are kept extremely low, in order to utilize the peroxide efficiently.^{25,26} Different metal ions are bound to acidic groups, e.g. carboxylic and phenolic groups, in the fibre walls of wood, and metal ions may also derive from process equipment. During bleaching of paper pulp with hydrogen peroxide, transition metal ions such as iron, manganese, and copper have been found catalysing the decomposition of the bleaching chemicals, resulting in increased consumption of the bleaching chemicals and brightness reduction of the pulp.²⁷ For successful bleaching, these metal ions need to be taken care of before the bleaching operation takes place. The most common way to do this is by washing the pulp fibres with chelating agents before the bleaching operation. Synthesized chelating agents, e.g. NTA (nitrilotriacetic acid), EDTA (ethylenediaminetetraacetic acid), and DTPA (diethylenetriaminepentaacetic acid), are among the most commonly used,¹⁰ with logarithmic stability constants ($\log K$) in the range of 5 to 30.²⁸ The pulp suspension is however a complex matrix of a number of components and the efficiency of the chelating agents depend on the overall conditions in the system, such as the presence of other electrolytes, the pH value, and the temperature.

The prospect for the chelating surfactant 4-C₁₂-DTPA in this application was examined by treating thermomechanical pulp (TMP) with the chelating surfactant, followed by hydrogen peroxide bleaching (paper V).

2. Description of chelating surfactants

The term chelating surfactant, which was introduced in the previous chapter, refers to a merging of the concept surface active chelating agent. As the name suggests, chelating surfactants possess dual functionalities. The headgroup can coordinate metal ions, and the combination of a hydrophilic headgroup and a hydrophobic tail provides surface activity to the structure. These two functionalities are discussed in this chapter, along with the complex dissociation behaviour resulting from the numerous donor atoms.

2.1. Surfactants

Surface active agents, or surfactants, have the tendency to adsorb at the interface between two immiscible phases, like for instance the surface between water and air. Surfactants are amphiphilic molecules, meaning that they contain both lyophilic and lyophobic groups, referred to as the headgroup and the tail, respectively (see Figure 2). In aqueous solutions, which will be solely discussed here, the two parts are called hydrophilic and hydrophobic. When surfactants are dissolved in water, the hydrophobic tails distort the water structure. The system responds to this increase in free energy by minimizing the contact between the hydrophobic groups and the water molecules. By the orientation of the surfactants at the water surface, the hydrophilic headgroups are surrounded by water while the hydrophobic tails are expelled from the water. This reduces the surface tension of the water, which is further discussed in section 4.1. The maximum packing at the surface, and consequently the maximum surface tension reduction, varies between different surfactants. The hydrophilic headgroups on the other hand, prevents the surfactants from complete phase separation from the water, since this would require dehydration of the hydrophilic groups.

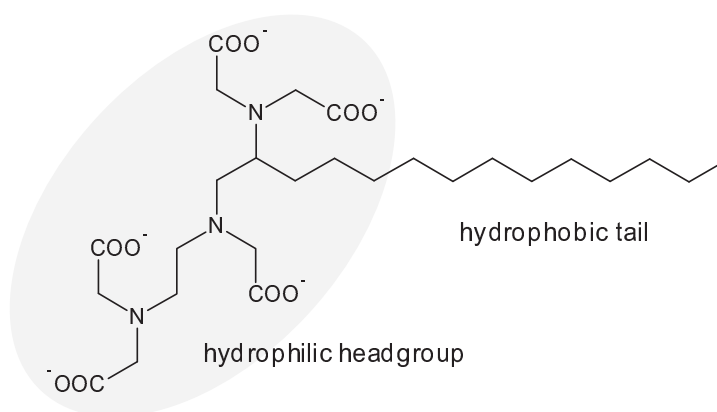


Figure 2. Molecular structure of 4-C₁₂-DTPA at high pH, with eight potential donor atoms, i.e., the five carboxylate oxygen atoms and the three nitrogen atoms.

Surfactants are usually classified according to the charge of their headgroup, such as anionic, cationic, non-ionic, and zwitterionic. A zwitterionic surfactant carries both positive and negative charge at the same time. The terms amphoteric and pH-responsive, or pH-sensitive, can sometimes be used interchangeably. An important note is however that amphoteric surfactants are transforming from cationic at low pH, over zwitterionic and finally to anionic at high pH,²⁹⁻³¹ whereas the denomination pH-responsive can be used in a broader sense.³²⁻³⁴

Chelating surfactants are pH-responsive due to the titrating properties of the donor atoms. When the structure contains both acidic and basic groups, such as the carboxylic and tertiary amine groups in 4-C₁₂-DTPA shown in Figure 2, it is an amphoteric surfactant.

2.1.1. Surfactant micellization

An important feature of surfactants is the micelle formation (see Figure 3), first suggested by McBain in 1913.³⁵ The concentration at which the surfactant monomers start to aggregate and form micelles is known as the critical micelle concentration, cmc. After this point, the concentration of monomers in the solution remains approximately constant or decreases. In an aqueous solution, the hydrophobic tails are directed towards the centre of the aggregate, while the headgroups are directed outwards. The micelles have high solubility in water due to the hydrophilic headgroups at the micellar surface, and consequently low surface activity. The formation of micelles is another way of excluding the hydrophobic parts from the water and reducing the free energy of the system. The hydrophobic effect is however opposed by the repulsion between the headgroups, and the cmc therefore depends on a number of possible variations in the chemical structure of the surfactant, as well as some properties of the surrounding solution. Factors that either increase the hydrophobicity of the surfactants or reduce the repulsion between the headgroups will lower the cmc, and vice versa. Some of these are worth mentioning here. Non-ionic surfactants generally have lower cmc than ionic ones, and multiply charged surfactants typically have even higher cmc. The hydrophobic tail has a large impact on the cmc; increasing the alkyl chain length decreases the cmc. For ionic surfactants, increasing the valency of the counterions strongly reduces the cmc. Furthermore, salt addition leads to a remarkable lowering of the cmc, especially if the counterions are multiply charged.

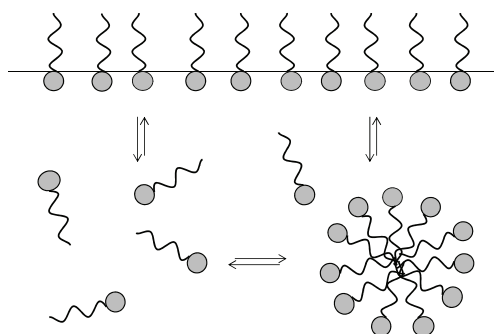


Figure 3. Illustration of the dynamic equilibria in surfactant solutions between free monomers, adsorbed monomers at the air-water interface, and micelles.

Different surfactants may form aggregates of different geometrical shape and size. The critical packing parameter, cpp , describing the geometry of a surfactant, is often useful to explain the type of aggregate formed.³⁶ The cpp is the ratio between the cross-sectional area of the hydrophobic and the hydrophilic parts:

$$cpp = \frac{v_t}{l_{c,t}a_h} \quad (1)$$

where v_t is the volume of the tail, the critical length of the tail $l_{c,t}$ is the effective length of the tail in the liquid state, and a_h is the optimal headgroup area at the micellar surface. The size of a_h is balanced between the attractive forces from the hydrocarbon chains and the repulsive forces between the headgroups. Ionic surfactants typically have cpp values less than 1/3 in the absence of electrolytes, and are known to form spherical micelles. The large headgroups of chelating surfactants lead to unusually low cpp , and spherical micelles are therefore expected. The headgroup area of a chelating surfactant, and consequently the cpp , can be tuned by changing the pH. Coordination of a metal ion is also expected to reduce the headgroup area as a result of the reduced repulsion within and between surfactant headgroups.

Alternatively, aggregate structures can be discussed in terms of spontaneous curvature of the surfactant film, where the curvature is the inverse of the radius of curvature. The curvature is positive if the film is curved around the hydrophobic part, and negative if it is curved around the hydrophilic part.

2.1.2. Foaming

Another property of surfactant solutions is the ability to produce foam, where gas bubbles are dispersed in a liquid. The appearance of the foam depends on the ratio of gas in the liquid, called the foam number. Stable foams have high foam numbers. The gas bubbles in these foams are separated by thin liquid films, called the lamellae of the foam. Where three or more bubbles meet, an edge is formed between the lamellae called the plateau border.

For a liquid to foam, the liquid lamellae must possess surface elasticity, which is the force counteracting the stress that tend towards local thinning or stretching of the lamellae, and this force must increase with increased stress. The elasticity results from the local increase in surface tension due to extension of the lamella. The surface elasticity must be valid in the time during which the lamella is stretched and restored. The diffusion of surfactants to the expanded surface must therefore be sufficiently slow; otherwise the adsorption of surfactants will decrease the surface tension and result in a permanently stretched lamella with reduced strength. The cmc of the surfactant is significant in this context, since a high cmc

implies a high concentration of monomers in the liquid and thereby faster adsorption of monomers at the expanded surface.

The drainage of the liquid films in stable foams occurs from the gravitational and capillary forces acting on the liquid. The capillary forces derive from the higher hydrostatic pressure in the planar liquid lamellae compared to the plateau borders. The stability is also affected by gas transport from smaller to larger gas bubbles, through the liquid, due to higher gas pressure in smaller bubbles. When the film becomes very thin, the overlap of the electrical double layers of the surfactant headgroups causes a repulsive force that counteracts further thinning. This begins at a distance of approximately 10-100 nm, depending on the electrical charge of the system. The foaming ability and the cpp of surfactants are closely related. Close-packing increases the surface elasticity and viscosity, leading to higher foaming ability and stability due to higher cohesion in the liquid lamellae. There is, however, an optimum in the cpp value of the surfactant system, due to the opposing effect of hole-formations in the lamellae. The formation of molecular size holes in the film, which decreases the foam stability, becomes easier the higher the cpp of the surfactants. The holes require a large negative curvature of the film, thus less energy is needed to form holes in surfactant systems with high cpp values.

The poor foaming properties of 4-C₁₂-DTPA are related primarily to its low cpp that prevents close-packing in planar geometries. The relatively high cmc and hydrophilicity, at intermediate to high pH, may also reduce the foaming properties.

2.2. Chelating agents

A chelating agent is a polydentate ligand, which can form several bonds to a central atom, most commonly a metal ion, to form a coordination complex. The bond between the ligand and the metal ion can range from covalent bonding to a bonding of more ionic character, and originate from the donation of one or more electron pairs from the ligand to the metal ion. Chelating agents generally form more stable complexes than monodentate ligands, with $\log K$ values sometimes well above 20.¹ This is mainly an entropic consequence of the formation of multiple bonds from one single ligand, as compared to complexes involving several monodentate ligands. Generally, the more donor atoms that are present in the molecular structure of the chelating agent, the stronger is the complex. The surrounding solution may however affect the stability of the complexes. A lower pH decreases the strength due to protonation of the functional groups, while at to high pH on the other hand, the strength may be reduced by formation of metal hydroxides.

The strength of the complex also depends on the radius of the metal ion, and varies therefore between different metals. Smaller ions are generally coordinated stronger due to stronger electrostatic interactions. For the transition metal ions, there are additional contributions from the crystal field stabilization energy, as well as Jahn-Teller distortion in the case of Cu^{2+} , that increases the stability.³⁷

The concept of hard and soft acids and bases (HSAB), which implies that hard bases preferably coordinate hard acids and soft bases prefer soft acids, is useful when discussing coordination of metal ions.³⁸ The relative strength between the coordination of different metal ions with a specific chelating agent often correlates to the classification of the metal ions on the scale from hard to soft acids. A typical hard acid is a small metal ion with high charge density and low polarizability, whereas soft acids are larger, have lower charge density and are more polarizable. Among the metal ions examined in this study, the divalent alkaline earth metals are classified as harder acids than the divalent transition metals. Donor atoms are described as hard or soft bases in a similar manner. When it comes to the two different donor atoms in the headgroup of 4- C_{12} -DTPA, the negatively charged carboxylate oxygen atoms are harder bases than the neutral nitrogen atoms. The examined divalent alkaline earth metals, being hard acids, are consequently coordinated stronger by the carboxylate groups than by the amine groups. The divalent transition metal ions on the other hand, are coordinated strongly by both types of donor atoms.

2.3. Dissociation behaviour of chelating surfactants

As briefly discussed in section 2.1, the titrating donor atoms in the headgroups of chelating surfactants make them pH-responsive. The more donor atoms the stronger is the chelating ability, and since different metal ions are coordinated preferably by different donor atoms, several donor atoms of different nature are advantageous to achieve a strong chelator for many different metal ions. This implies however a rather complex dissociation behaviour of strong chelating surfactants, since the headgroup charge varies with the pH. A number of surfactant properties are related to the headgroup charge, including solubility, self-assembling, and surface tension reduction effectiveness and efficiency. A significant feature of chelating surfactants is the numerous pK_a values, which may be overlapping, leading to a distribution of differently charged species present in the solution, rather than a single surfactant with a defined charge. Studies of DTPA have revealed the complexity in the protonation sequence and pK_a values from numerous titrating groups.³⁹⁻⁴² A chelating surfactant solution at any intermediate pH can thus be considered a mixed system, where the components and mixing ratio depend on the pH. This picture becomes even more complex as micelles start to form, since the high charge density at the micellar surface affects the dissociation

of surfactants in micelles, and the distribution of the different species may therefore differ between free monomers and surfactants in micelles.

There are two types of donor atoms in the headgroup of 4-C₁₂-DTPA (see Figure 2); five carboxylate oxygen atoms, giving rise to negative charges when they are dissociated, and three tertiary amine nitrogen atoms, generating positive charges in their protonated form. In the absence of metal ions, all donor atoms are titrating and the headgroup charge can be tuned by varying the pH, in theory from +3 at low pH to -5 at high pH. The solubility is very poor around the isoelectric point, above which a number of zwitterionic species with negative net charge are formed.

The binding of divalent or trivalent metal ions to the headgroup of chelating surfactants differs from conventional surfactants due to the formation of coordination complexes of high stability. These counterions are therefore very tightly bound and not exchanged regularly as counterions normally are. Because of this, metal complexes with chelating surfactants are sometimes referred to as metallosurfactants, and the aggregates formed consequently as metallomicelles.^{5,6} The coordination of a metal ion markedly changes the headgroup of a chelating surfactant. The net charge is affected by the coordination of the positively charged metal ion. Since the donor atoms are engaged in coordinating a metal ion, the titrating ability is reduced and there is less steric flexibility in the configuration as well as in the allocation of protons in the headgroup. The pH-response may persist however, if the number of donor atoms exceeds the coordination number of the metal ion. This is the case for the divalent metal complexes with 4-C₁₂-DTPA in this study.

An important consequence of the amphoteric nature of chelating surfactants is that measurements of pH vs concentration can be used to detect the cmc. An amphoteric surfactant can accept or donate protons to the aqueous solution in order to adjust its electrical charge. The pK_a values of a free monomer in solution are governed by the electrostatic interaction between titrating groups within the molecule. At the micellization, the dissociation of the aggregated surfactants is affected by the increased charge density at the micellar surface, due to the interaction between adjacent monomers. For the negatively charged 4-C₁₂-DTPA, in the examined pH region between 3 and 10, surfactants in micelles will consequently become protonated to a higher degree than the free monomers, with increasing pH at cmc as a result.

3. Surfactant mixtures

In mixtures of two or more surfactants, synergism often appears due to favourable interactions between the different surfactants.⁴³⁻⁴⁵ This may result in reduced surface tension or cmc for the mixed system. Surfactant mixtures are used in many

practical applications due to the improved properties of the mixture compared to those of the individual surfactants.

3.1. Rubingh's regular solution theory

The interaction parameter β^M for mixed micelle formation is commonly calculated using Rubingh's regular solution theory.⁴⁶ Although there are some limitations in this approximation, it provides a robust description of the nonideal behaviour of surfactant mixtures. Investigations of the limiting assumption of zero entropy of mixing can be found in the literature.^{47,48} The interaction parameter reflects the nature of the interaction in the mixed system relative to the self-interaction for the two individual surfactants. The value of the interaction parameter is proportional to the free energy of mixing, and the stronger the attraction and/or the weaker the repulsion in the mixture relative to the self-interaction for the individual surfactants, the more negative is the interaction parameter.

The critical micelle concentration of a mixture of two surfactants, cmc_{12} , at the mole fraction α of surfactant 1 (on a surfactant-only basis) is calculated from the cmc 's of the individual surfactants 1 and 2 (cmc_1 and cmc_2) and the activity coefficients of surfactant 1 and 2 in the mixed micelle (f_1^M and f_2^M):

$$\frac{1}{\text{cmc}_{12}} = \frac{\alpha}{f_1^M \text{cmc}_1} + \frac{1-\alpha}{f_2^M \text{cmc}_2} \quad (2)$$

The cmc 's were determined by NMR diffusometry in this study if not otherwise stated (see Figure 4). When there is no net interaction between the two surfactants, i.e., in the ideal case, $f_1^M = f_2^M = 1$. In the nonideal case, the activity coefficients of the surfactants in the mixed micelle can be calculated from the regular solution theory:

$$\ln f_1^M = (1 - X_1^M)^2 \beta^M \quad \text{and} \quad \ln f_2^M = (X_1^M)^2 \beta^M \quad (3)$$

X_1^M , the mole fraction of surfactant 1 (on a surfactant-only basis) in the mixed micelles, and β^M is calculated from the cmc 's of the individual surfactants and their mixture at α . Eq 4 is solved numerically for X_1^M , which is then substituted into eq 5 to calculate β^M .

$$\frac{(X_1^M)^2 \ln (\alpha \text{cmc}_{12} / X_1^M \text{cmc}_1)}{(1-X_1^M)^2 \ln [(1-\alpha) \text{cmc}_{12} / (1-X_1^M) \text{cmc}_2]} = 1 \quad (4)$$

$$\beta^M = \frac{\ln (\alpha \text{cmc}_{12} / X_1^M \text{cmc}_1)}{(1-X_1^M)^2} \quad (5)$$

The interaction parameter β^σ for mixed adsorption at the air-water interface is calculated from surface tension data in a similar manner using eqs 6 and 7.⁴⁹

$$\frac{X_1^2 \ln(\alpha C_{12}/X_1 C_1^0)}{(1-X_1)^2 \ln[(1-\alpha)C_{12}/(1-X_1)C_2^0]} = 1 \quad (6)$$

$$\beta^\sigma = \frac{\ln(\alpha C_{12}/X_1 C_1^0)}{(1-X_1)^2} \quad (7)$$

where C_1^0 , C_2^0 and C_{12} are the solution phase molar concentrations of surfactants 1 and 2 and their mixture at α , respectively, required to produce a given surface tension value (see Figure 4).⁴⁶ Eq 6 is solved numerically for X_1 , the mole fraction of surfactant 1 in the mixed monolayer, which is then substituted into eq 7 to calculate β^σ .

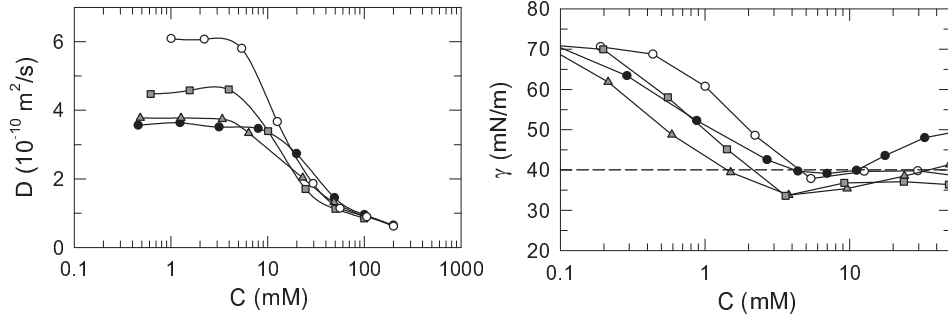


Figure 4. Left; self-diffusion coefficient vs concentration at pH 7 for Mg^{2+} -4- C_{12} -DTPA (\bullet), SDS (\circ), and their mixtures at $\alpha_{\text{Mg}^{2+}\text{-4-C}_{12}\text{-DTPA}} = 0.75$ (\blacktriangle) and $\alpha_{\text{Mg}^{2+}\text{-4-C}_{12}\text{-DTPA}} = 0.25$ (\blacksquare). Right; surface tension vs concentration at pH 5 for Ni^{2+} -4- C_{12} -DTPA (\bullet), SDS (\circ), and their mixtures at $\alpha_{\text{Ni}^{2+}\text{-4-C}_{12}\text{-DTPA}} = 0.75$ (\blacktriangle) and $\alpha_{\text{Ni}^{2+}\text{-4-C}_{12}\text{-DTPA}} = 0.25$ (\blacksquare). C_1^0 , C_2^0 and C_{12} were obtained at $\gamma = 40$ mN/m.

When the cmc of a mixture of two surfactants is lower than the cmc of either individual surfactant, the system exhibits synergism in mixed micelle formation. The two conditions for this type of synergism to occur is (i) the β^M parameter must be negative and (ii) $|\beta^M| > |\ln(\text{cmc}_1/\text{cmc}_2)|$.⁵⁰ The maximum synergism and minimum cmc of a mixture ($\text{cmc}_{12,\text{min}}$) is found at the point where $\alpha = X_1^M$, i.e., where the composition of the solution equals the optimum composition in the mixed micelles. Corresponding conditions, with cmc exchanged for C^0 , apply for synergism in mixed monolayer formation.

As discussed in the previous chapter, a chelating surfactant solution at any intermediate pH consists of a distribution of differently charged species, and this distribution may change with the concentration as micelles are formed. A solution of 4- C_{12} -DTPA is thus already a mixed system, where the different components and mixing ratio depend on the pH. Therefore, when treating a mixed system of 4- C_{12} -DTPA and a foaming agent as a binary mixture, the following limitations are

assumed; (i) the pure 4-C₁₂-DTPA is defined as the distribution of differently charged species at the specific pH, (ii) the dissociation of 4-C₁₂-DTPA surfactants in mixed micelles and monolayers will be affected by the presence of the foaming agent, thus may the mixed micelles and monolayers consist of a distribution of 4-C₁₂-DTPA species that differs from the distribution in the pure 4-C₁₂-DTPA micelles and monolayers, and (iii) the interaction parameters are dominated by the strongest interaction in the system, and the calculated interaction parameters primarily describe this interaction. Provided the awareness of these limitations, the calculations of the interaction parameters give useful information for the understanding of interactions in mixtures containing amphoteric surfactants. This applies also to the metal complexes with 4-C₁₂-DTPA, even though the number of dissociation states is markedly reduced by the coordination of a metal ion. The same limitations as for the pure 4-C₁₂-DTPA are therefore assumed when treating mixtures of 4-C₁₂-DTPA metal complexes and foaming agents as binary mixtures.

3.2. Interactions in mixtures with amphoteric surfactants

Amphoteric surfactants can interact with ionic surfactants by accepting or donating protons to the aqueous solution in order to adjust its electrical charge and increase the attractive interaction, or reduce the repulsive interaction, with the neighbouring surfactants.^{51,52} In the derivation of the equations for calculating the interaction parameters, electrical effects are ignored. The ionic strength should therefore be kept constant, by adding a swamping electrolyte when dealing with ionic surfactants, in order to obtain interaction parameters that correctly describes the system over all mixing ratios.⁵³ In mixtures of chelating surfactants, a variation in the ionic strength with the mixing ratio is expected due to the numerous functional groups. In the case of 4-C₁₂-DTPA, with eight titrating groups, relatively high background electrolyte would be necessary to keep a constant ionic strength in the experiments. This would however reduce the electrostatic effects that provide information for instance regarding coordination of different metal ions, shown later in chapter 7. Furthermore, it would reduce the synergistic effects in mixtures of metal complexes and foaming agents pursued in foam flotation, discussed in chapter 8. It is therefore of great interest to examine these systems without added electrolyte, in order to achieve maximum synergism. Nevertheless, one should keep in mind that in systems with varying ionic strength over the mixing composition, the interaction parameters may also vary with the composition, especially when mixing two pH-responsive surfactants.

4. Experimental

In this chapter, the most important experimental methods in this study are presented; see the appended papers for detailed descriptions of sample preparation and additional experimental methods. As discussed in section 2.3, measurements of pH as a function of concentration were also utilized to extract information regarding the interaction between adjacent monomers at the formation of micelles.

4.1. Surface tension

The molecules at the surface of a liquid have higher potential energies than those in the interior of the liquid. This is a consequence of the molecules at the surface interacting stronger with the molecules in the interior of the liquid than with the widely spread gas molecules above the surface. Work is therefore required to bring molecules from the interior to the surface of a liquid.

When surfactants are dissolved in water, the hydrophobic groups disrupt the structure of the water by breaking hydrogen bonds between water molecules and orienting them around the hydrophobic groups. This increases the free energy of the system and as a result some of the surfactants are expelled from the interior to the surface. The water surface becomes covered with a layer of surfactants, with their hydrophobic groups oriented towards the air. Since the air molecules are essentially nonpolar, the accumulation of surfactants at the surface decreases the dissimilarity of the two phases, resulting in reduced surface tension. Surface tension reduction is one of the most fundamental phenomena of surfactant solutions. It depends directly on the replacement of water molecules by surfactants at the surface.

The surface tension of a liquid is a measure of the surface free energy per unit area of the phase boundary between the liquid and the air above it. It is the minimum amount of work required to create unit area of the surface or to bring molecules from the interior to the surface to expand it by unit area. Surface tension measurements are often performed using the du Noüy ring method, where a platinum ring is immersed in the solution, after which the force required to pull the ring through the surface is measured (see Figure 5). In the similar Wilhelmy plate method, a platinum plate is brought in contact with the surface and the force from the downward pull of the liquid due to wetting of the plate is measured. The pendant drop is another common method, where the shape of the drop relates to the surface tension of the liquid. Here, the surface tension measurements were performed with a Krüss K6 tensiometer and a platinum du Noüy ring.

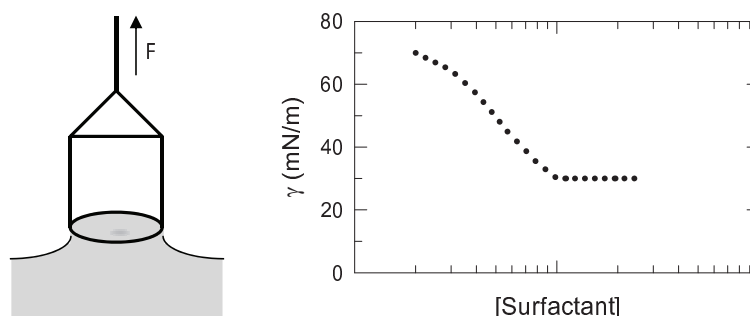


Figure 5. Schematic illustration of surface tension measurements using the du Noüy ring method (left) and the resulting surface tension vs concentration plot for a surfactant solution, where the break in the curve normally correlates to the cmc (right).

4.2. NMR diffusometry

Nuclear magnetic resonance spectroscopy, NMR, is a non destructive analytical technique, frequently used for structure determination in all disciplines of chemistry. The technique utilizes the magnetic moment, or nuclear spin, that many isotopes possess. When placed in an external magnetic field, such a nucleus interacts with the field and the nuclear spin will orient in the field in a number of ways proportional to the spin quantum number. The different spin states will have different energies, and low-energy states will be more populated than high-energy states. The difference in the distribution of nuclei between the spin states is however very small and NMR spectroscopy is therefore a relatively insensitive technique. The difference depends on the applied magnetic field strength; the higher the field strength the greater is the difference between the states. An applied radio frequency signal, which matches the resonance frequency of the nuclei, will disturb the system. The amount of energy released when the system returns to equilibrium is detected and processed to result in a resonance signal in the spectrum. Nuclei in different magnetic and electric environments show different resonance signals, which makes chemical structure analyses possible from NMR spectra.

NMR diffusometry is a very powerful technique when studying surfactant systems. By this technique, the self-diffusion coefficients of different species can be obtained. ^1H is the most commonly studied nucleus in these experiments. The translational diffusion of different components in a complex system gives information regarding size and shape of the aggregates. In this study, pulsed field gradients (PFG) were used. This technique is well established, and a detailed description can be found elsewhere.⁵⁴⁻⁵⁶ The decay of proton signals after a stimulated echo pulsed field gradient (STE-PFG) experiment is recorded for a

number of gradient strengths, and the self-diffusion coefficient D is obtained by fitting the data to eq 8

$$I = I_0 e^{\{-D(2\pi\gamma G\delta)^2(\Delta-\delta/3)\cdot 10^4\}} \quad (8)$$

where I denotes the observed echo intensity, I_0 is the echo intensity in the absence of field gradient pulses, γ is the magnetogyric ratio, G is the field gradient strength, δ is the duration of the gradient pulse, and Δ is the time between the leading edges of the gradient pulses. The NMR diffusometry experiments were performed on a Bruker Avance DPX 250 MHz NMR spectrometer equipped with a Bruker self-diffusion probe capable of providing magnetic field strengths up to 1200 G/cm.

4.3. ESI-MS

When using electrospray ionization mass spectrometry (ESI-MS) liquid phase analytes are transformed into gas phase ions in the ESI interface before continuing into the MS. The sample enters the interface through a needle and by applying a potential difference between that needle and the entrance to the mass separator, opposite to the needle, analytes are charged by addition (positive ion mode) or removal (negative ion mode) of ions, usually protons, through electrochemical reactions. When the potential is sufficiently high, a Taylor cone is formed, that bursts into a fine aerosol when the coulombic repulsion exceeds the surface tension. While the droplets travel towards the counter electrode plate the solvent evaporates, generating an increasing concentration of charges in the droplets. The resulting repulsive force causes the droplets to explode into a mist of smaller droplets with even higher charge density. This process is repeated until only gas phase molecular ions remain. ESI is referred to as a soft ionization technique due to low fragmentation of the analytes.

The ions enter into the vacuum region of the MS where they are separated according to their mass to charge ratio (m/z). With a quadrupole mass analyzer, a combination of alternating current (AC) and direct current (DC) is applied over four metal rods where the electricity is tuned so that only ions with a selected m/z ratio can pass the rods and hit the detector; alternatively a range of m/z ratios is scanned.

Determinations of conditional stability constants for the different 4-C₁₂-DTPA metal complexes were performed on an API 3000 mass spectrometer (AB SCIEX).

4.4. Foam flotation

In foam flotation of surfactant systems, the hydrophobic interactions between the nonpolar part of the surfactants and the gas bubbles are utilized. Since metal ions are floated here, or rather metal complexes of 4-C₁₂-DTPA, the species to be

recovered are water soluble and surface active. A foaming agent is however necessary in order to improve the foaming ability and stability and there need to be a strong interaction between the metal complex and the foaming agent for the complex to be transferred from the bulk to the foam phase. Efficient recovery of metal ions, i.e., high depletion of metal ions while retaining as much as possible of the bulk liquid, is sought. Good draining of the foam is therefore important. The pH must be controlled since the interactions between metal complexes and foaming agents depend on the pH.

The flotation experiments were performed in a customized flotation cell with a volume of 1.6 l, consisting of a plexiglass cylinder and a sintered glass frit mounted at the bottom of the cell (see Figure 6). A nitrogen flow is applied through the frit to induce the bubbles and the valve on the top of the cylinder is used to control the rate of the foam transport out of the flotation unit. Samples can be taken from the bulk during the flotation.

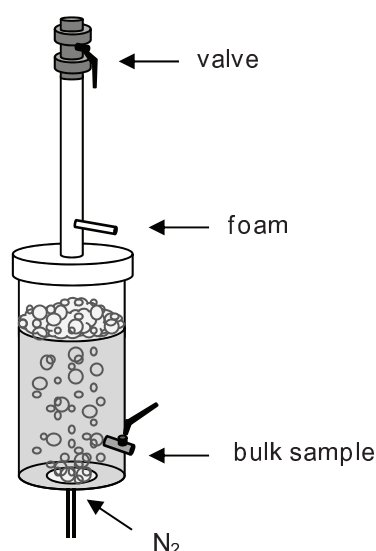


Figure 6. Customized flotation cell.

5. Solution behaviour of 4-C₁₂-DTPA

The headgroup charge of 4-C₁₂-DTPA (see Figure 2) can be tuned by varying the pH, in theory from +3 at low pH to -5 at high pH. The solution properties are therefore expected to be pH dependent. Because of the poor solubility around the isoelectric point, 4-C₁₂-DTPA was studied above the solubility gap, where it is zwitterionic with a negative net charge. The negative net charge increases with increasing pH due to enhanced dissociation of the functional groups.

5.1. Determination of cmc; anomalies between surface tension and NMR diffusometry

The solution properties of 4-C₁₂-DTPA were studied at different pH between 3 and 10 by surface tension measurements, pH measurements, and NMR diffusometry (paper I). Thorough comparisons between the results from the three different techniques revealed a more complex relationship between surface tension, surface coverage, and cmc than usually considered. As seen in Figure 7, the break in the self-diffusion coefficient vs concentration plot matches the increase in surface tension at increasing concentration. It also matches the pH curve, which will be discussed in chapter 7. This was the case also for the divalent metal complexes with 4-C₁₂-DTPA (paper II), Ni²⁺-4-C₁₂-DTPA is shown as an example in Figure 7. The interpretation of the results from NMR diffusometry is considered unambiguous, while there may be more reasons for speculations about surface tension data. The cmc must therefore be located at this point.

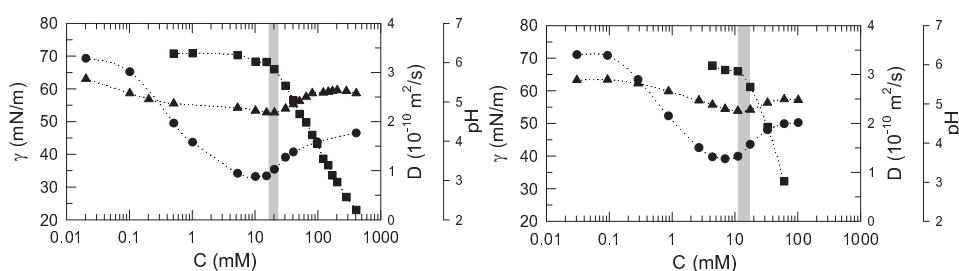


Figure 7. Correlations between NMR diffusometry (■), surface tension (●), and pH (▲) vs concentration for 4-C₁₂-DTPA (left) and Ni²⁺-4-C₁₂-DTPA (right). The determined cmc's are highlighted by the grey zones.

Naturally, the question arises as to what is detected at the point in the surface tension plot usually assigned as the onset of micellization. A hypothesis is proposed, where the first break in the surface tension plot is interpreted as the point of surface saturation, and the surface consequently saturated throughout the plateau (paper I). This hypothesis is however not in line with the common interpretation of Gibbs adsorption equation, i.e., that the surface is saturated with surfactants throughout the linear part of the declining surface tension plot. There has been some debate around Gibbs adsorption equation, where attention has been paid specifically to the concept of surface saturation preceding the cmc.^{57,58} It should be stressed though, that surface saturation is not explicitly stated by Gibbs adsorption equation, as pointed out by Laven and de With,⁵⁹ but rather a frequent interpretation. The relation between adsorption and micellization has been thoroughly examined and discussed in two articles where Gibbs adsorption

equation applied to surface tension data was compared with neutron reflectivity measurements for nonionic surfactants, where the authors found saturation of the surface before cmc,⁶⁰ as well as anionic surfactants, where the authors found that the adsorption was cut off by the micellization.⁶¹ Based on these two studies, it seems like saturation of the surface prior to cmc cannot be assumed as a general rule since the adsorption will level off if micelles start to form before the adsorption has reached saturation. This is quite reasonable, considering that adsorption and micellization are two different equilibrium processes, even though the equilibria are connected. The hypothesis that is proposed here is a situation where the adsorption reaches saturation, and the surface tension levels off, at a concentration significantly lower than the cmc.

When the cmc is reached, the surface tension of 4-C₁₂-DTPA starts to increase, this is interpreted as monomers favouring the micelles over the saturated surface. The origin of this is most likely electrostatic repulsion between the negatively charged headgroups in the adsorbed layer, which will cause desorption once the micelles have started to form. Generally, electrostatic repulsion tends to disfavour the adsorption more than the micellization.⁶² This may be particularly prominent in this system due to the large headgroup that makes the chelating surfactant wedge shaped and therefore more favourably packed in micelles. In mixed systems of 4-C₁₂-DTPA with SDS and DoTAC, respectively, this behaviour becomes less pronounced with decreasing mole fraction of 4-C₁₂-DTPA and finally extinguishes as the mole fraction of 4-C₁₂-DTPA ($\alpha_{4-C_{12}-DTPA}$) is reduced to 0.25 (see Figure 8 for the 4-C₁₂-DTPA/SDS mixture) (paper III).

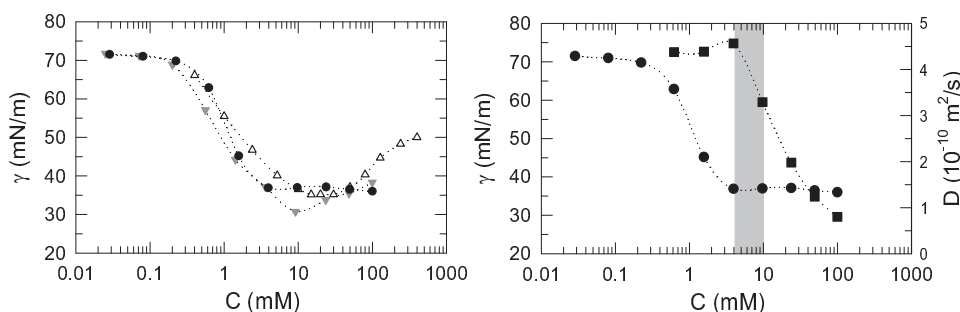


Figure 8. Left; surface tension vs concentration for 4-C₁₂-DTPA (Δ), 4-C₁₂-DTPA/SDS at $\alpha_{4-C_{12}-DTPA} = 0.75$ (∇), and 4-C₁₂-DTPA/SDS at $\alpha_{4-C_{12}-DTPA} = 0.25$ (\bullet). Right; correlation between NMR diffusometry (\blacksquare) and surface tension (\bullet) vs concentration for 4-C₁₂-DTPA/SDS at $\alpha_{4-C_{12}-DTPA} = 0.25$, the determined cmc is highlighted by the grey zone.

This can be explained when considering the difference in geometry between the two surfactants. The critical packing parameter, cpp , is useful in this context. For

ionic surfactants, like SDS and DoTAC, $\text{cpp} \leq 1/3$ is usually found. It is clear that 4-C₁₂-DTPA must have a cpp significantly lower than SDS and DoTAC due to its large headgroup. The size of the headgroup is most likely the reason why 4-C₁₂-DTPA saturates the surface at a concentration lower than the cmc, and with its low cpp, 4-C₁₂-DTPA is geometrically more suited in micelles than at the air-water interface and consequently favours the micelles once the cmc is reached. Conventional behaviour is attained when SDS or DoTAC is present in excess due to the smaller headgroups and larger cpp of these surfactants; the surface does not necessarily reach saturation,⁶¹ or it becomes saturated approximately at the cmc, and consequently the break in the surface tension plot is consistent with the cmc determined from NMR diffusometry, as seen in Figure 8. Furthermore, there is no significant change in the surface tension above the cmc.

5.2. pH dependent solution behaviour

As a consequence of the numerous titrating groups in the 4-C₁₂-DTPA headgroup, the solution behaviour of 4-C₁₂-DTPA was strongly pH dependent (paper I). The variations in cmc and adsorption efficiency with varying pH between 3 and 10 were straightforward. The adsorption efficiency is expressed by the parameter C₂₀, which is the surfactant concentration required to reduce the surface tension of the solvent by 20 mN/m. Both cmc and C₂₀ increases with the pH as 4-C₁₂-DTPA becomes more hydrophilic and the electrostatic repulsion increases (see Table 1 and Figure 9). The relative effects of pH on micellization and adsorption was evaluated by the cmc/C₂₀ ratio. The decreasing cmc/C₂₀ values with increasing pH indicate that the adsorption is inhibited more than the micellization by the increased electrostatic repulsion at higher pH. This seems reasonable when compared with the effects of ionic strength, which reduces the electrostatic repulsion for ionic surfactants and thereby increases the cmc/C₂₀.⁶²

Table 1. Effects of bulk pH on cmc, C₂₀, cmc/C₂₀, and γ_{cmc} for 4-C₁₂-DTPA

pH	cmc ^a (mM)	C ₂₀ ^b (mM)	cmc/C ₂₀	γ_{cmc} ^b (mN/m)
10	37 ± 12	2.9	13	41.2
8.5	38 ± 12	1.2	32	38.2
6.5	35 ± 10	2.3	15	35.5
5	20 ± 3	0.39	51	33.2
4	12.5 ± 5	0.27	46	39.6
3	4.8 ± 2	0.057	84	40.2

^aDetermined by NMR diffusometry. ^bDetermined by surface tension.

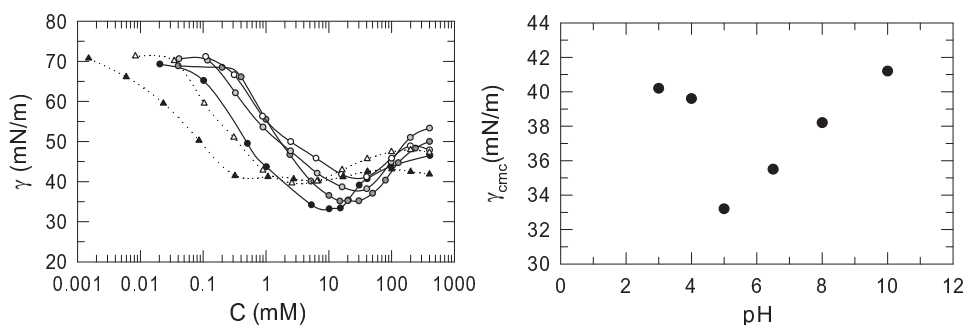


Figure 9. Left; surface tension vs 4-C₁₂-DTPA concentration at pH 3 (▲), pH 4 (Δ), pH 5 (●), pH 6.5 (●), pH 8.5 (●), and pH 10 (○). Right; pH dependence of γ_{cmc} at the different investigated pH levels. The optimum balance between hydrophilic and hydrophobic character for surface tension reduction effectiveness is found at pH 5.

The large dependence of γ_{cmc} , i.e., the surface tension of the plateau at cmc, on the pH of the solution is shown to the right in Figure 9 and it is clear that there is a maximum in surface tension reduction at pH 5. One should keep in mind that in the examined pH region, 4-C₁₂-DTPA is zwitterionic and that the number of negative charges relative to positive charges increases with the pH. This means that there is an attractive interaction between the headgroups at pH 3, which is associated with the formation of precipitate, and a repulsive interaction at pH 10. The surface tension reduction is limited by the low solubility at pH 3, and the surface tension levels off when the solution starts to precipitate. No precipitation was seen in the solution at pH 4, although the high γ_{cmc} indicates that there may be some form of microcrystallites present in the solution, which are not visible for the eye. When increasing the pH, the hydrophilic character of 4-C₁₂-DTPA increases, and the optimum balance between its hydrophilic and hydrophobic character, in terms of surface tension reduction effectiveness, appears at pH 5. At pH above 5, the high solubility and the electrostatic repulsion reduce the surface activity, since the monomers are less attracted to the surface, which is also evident from the increasing C_{20} with pH. A similar pH-dependence have been reported for *N*-acyl ED3A.⁶³ Plausible explanations to the strong adsorption at pH 5 could be both electrostatic attraction and hydrogen bonding between headgroups at the surface, due to a proper balance between protonated and dissociated groups. This may result in the formation of dimers which enables a closer packing at the surface.

5.3. Solution behaviour of metal complexes

The coordination of a metal ion markedly changes the headgroup of the chelating surfactant. Generally, the investigated divalent metal ions affected the solution

behaviour of 4-C₁₂-DTPA similarly, and the effects could be linked to the neutralization of the negative net charge of the headgroup as a result of the coordination of the positively charged metal ion (paper II). The addition of the respective metal salt also increases the ionic strength, which may contribute to the observed results. This can however be expected to have a minor effect compared to the effect of metal ion coordination. When the donor atoms are engaged in coordinating a metal ion, the titrating ability is reduced and there is less flexibility in the configuration and allocation of protons in the headgroup. Because of this, the pH dependence of the solution behaviour was reduced by the coordination of a metal ion. At both investigated pH levels, all metal complexes exhibited lower cmc than the pure 4-C₁₂-DTPA, a natural consequence of the reduced electrostatic repulsion due to the reduced headgroup charge. Cu²⁺-4-C₁₂-DTPA and Ni²⁺-4-C₁₂-DTPA are shown as examples in Figure 10.

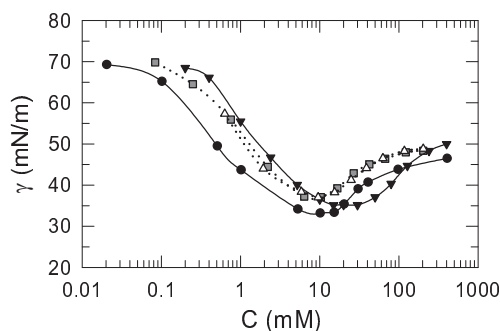


Figure 10. Surface tension vs concentration for 4-C₁₂-DTPA at pH 5 (●), Cu²⁺-4-C₁₂-DTPA at pH 5 (■), Ni²⁺-4-C₁₂-DTPA at pH 7 (Δ), and 4-C₁₂-DTPA at pH 7 (▼).

Generally, reduced charge will reduce the electrostatic repulsion at the air-water interface, which is often associated with reduced γ_{cmc} as a consequence of the increased adsorption of surfactants at the surface. The increased γ_{cmc} by the coordination of metal ions may therefore seem unexpected at first. This effect can however be explained when considering the pH dependence of γ_{cmc} for the pure 4-C₁₂-DTPA, where a minimum in γ_{cmc} was found at pH 5, as shown in Figure 9 (paper I). This minimum indicates an optimum in the attractive interaction between the headgroups at the surface, i.e., an optimal charge distribution for maximum surface tension reduction, at this pH. With this in mind, it is not surprising that the γ_{cmc} increases since the interaction between surfactants at the surface in fact become less attractive by the chelation of metal ions, even though the net charge is lower. C₂₀ is also affected by the coordination of metal ions. The effect is however different for the two investigated pH levels, when the metal complexes are compared to the pure chelating surfactant at the respective pH. In

fact, the C_{20} of the metal complexes at both pH fall in between the C_{20} of the pure 4- C_{12} -DTPA at the two pH levels (see Figure 10). Thus, when the metal complexes are compared to each other, there is no significant difference in C_{20} between the two pH levels.

5.4. Time dependence of monomer adsorption

Studies of the surface tension during equilibration further illustrate the complex adsorption behaviour of 4- C_{12} -DTPA. Normally, the adsorption of surfactants to the air-water interface is fast, with equilibrium reached within seconds,⁶⁴ and relaxation times up to one min is considered slow.⁶⁵ In the case of 4- C_{12} -DTPA (paper I) and its metal complexes (paper II) the surface tension was slowly decreasing for several hours and 24 h equilibration was allowed to ensure equilibrium surface tension. The decreasing surface tension strongly indicates increased adsorption of monomers to the surface for relatively long time, due to a slow equilibrium process. The adsorbed monomers will create a surface potential, which acts as a repulsive barrier that must be overcome for further adsorption. The balance between adsorbed and free monomers must be notably governed by this electrostatics. The high charge density in the headgroups may slow down the equilibrium process by metastable configurations in the headgroups. The surface potential is however opposed by a strong driving force to obtain dense packing of monomers at the surface, to lower the free energy of the phase boundary. The continuously increasing adsorption is most probably due to changes in configuration and rearrangements at the surface. There are possibilities for both electrostatic interaction and hydrogen bonding within and between adjacent headgroups, which can reduce the headgroup area and increase the packing parameter, and consequently lead to further adsorption of monomers.

The surface tension plots at different states in the adsorption process are shown in Figure 11 for the Mg^{2+} -4- C_{12} -DTPA complex, as an example. The surface tension was first measured during subsequent dilution of the stock solution. A portion of the sample was removed and the remaining was diluted to obtain the next sample. Each removed portion was then measured twice; once directly after pouring the sample into the measuring cup (the t_0 set) and then after 24 h equilibration (the t_{24h} set).

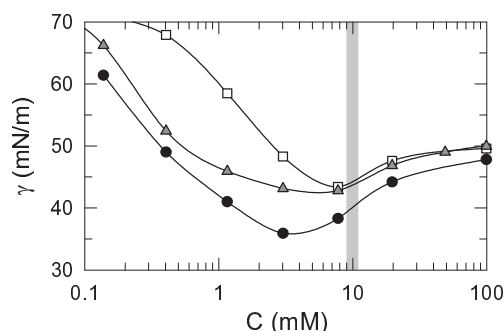


Figure 11. Surface tension vs concentration at different aging times of the air-water interface; t_0 (□), subsequent dilution (▲), and t_{24h} (●) for Mg^{2+} -4- C_{12} -DTPA. The determined cmc is highlighted by the grey zone.

An important note here is that the surface is only partially destroyed and recreated during the subsequent dilution, in contrast to the t_0 set which is measured shortly after the surface was created. The subsequent dilution set is thus a state further into the adsorption process than the t_0 set. The large difference between the t_0 set and the subsequent dilution set is seen in Figure 11. Since the du Noüy ring method does not measure dynamic surface tension, the value at t_0 is by no means equal to the initiation of the adsorption, but rather the surface tension at a state well into the adsorption process. This approach thus serves only to study slow equilibria, while fast processes would have reached equilibrium already at t_0 . As seen in the figure, the time dependence of the relaxation process is different at different concentrations. At low concentrations, and consequently low surface coverage, the effect emerges already on the short timescale from t_0 to the subsequent dilution set, which in turn is rather close to the t_{24h} set. As the surface becomes increasingly populated, when approaching the cmc, the relaxation time seems to increase and the effect becomes more pronounced on the longer timescale. At concentrations above the cmc, no significant effect is seen during the short time equilibration, but it emerges after the 24 h equilibration. Even though the overall effect of equilibration on the surface tension, in the studied time interval, is most pronounced at concentrations up to cmc, the relaxation is actually slower at concentrations above the cmc. As shown here, the procedure of establishing equilibrium surface tension plots for the investigated chelating surfactant and its metal complexes is very time consuming. Therefore, surface tension measurements during subsequent dilution of the stock solutions are reported in all other experiments.

6. Metal ion chelation

The binding of divalent or trivalent metal ions to the headgroup of chelating surfactants differs from conventional surfactants due to the formation of coordination complexes of high stability, where all donor atoms may contribute to the coordination of the metal ion. These counterions are therefore very tightly bound to the chelating surfactant and not exchanged regularly as counterions normally are. Properties of the coordinated ion affect the strength of the complex and the strength vary therefore substantially even between ions of the same valence.

6.1. Conditional stability constants

Conditional stability constants ($\log K$) for five divalent metal complexes with 4-C₁₂-DTPA were determined by competition measurements where 4-C₁₂-DTPA and DTPA competed for the metal ion (paper II). The molar ratios of uncomplexed chelating agents ($[DTPA]_u/[4-C_{12}-DTPA]_u$) were determined using ESI-MS. Conditional stability constants for 4-C₁₂-DTPA were calculated through the following expression:

$$\log K_{M-4-C_{12}-DTPA} = \log \left(K_{M-DTPA} \frac{[DTPA]_u([4-C_{12}-DTPA]_{tot} - [4-C_{12}-DTPA]_u)}{[4-C_{12}-DTPA]_u([DTPA]_{tot} - [DTPA]_u)} \right) \quad (9)$$

where $[DTPA]_{tot}$ and $[4-C_{12}-DTPA]_{tot}$ are the total concentrations of the respective chelating agent, and the K_{M-DTPA} values are known from literature.²⁸

Competition measurements utilizing ESI-MS have been reported before, for crown ethers and metal ions.⁶⁶ This analytical method proved to be very useful for determining conditional stability constants in high precision in the studied systems. When compared with the conventional chelating agent DTPA, it is clear that the hydrocarbon tail of 4-C₁₂-DTPA only affects the coordination chemistry of the headgroup to a limited extent, as shown in Table 2.

Table 2. Ionic radii and conditional stability constants

Me ²⁺	ionic radius ^a (Å)	pH	[DTPA] _u / [4-C ₁₂ -DTPA] _u	log K	
				4-C ₁₂ -DTPA	DTPA ^b
Mn ²⁺	0.97	5	0.89±0.00	6.2	6.3
		7	0.76±0.01	10.0	10.2
Zn ²⁺	0.88	5	1.05±0.01	9.9	9.8
		7	0.86±0.02	13.0	13.1
Co ²⁺	0.88	5	1.09±0.00	10.0	9.9
		7	0.82±0.01	13.5	13.7
Ni ²⁺	0.83	5	0.83±0.02	11.4	11.6
		7	0.70±0.01	14.5	14.9
Cu ²⁺	0.87	5	0.84±0.01	11.9	12.1
		7	0.74±0.00	15.5	15.8

^aFrom ref 67. ^bFrom ref 28.

At pH 7, DTPA is the stronger chelating agent for all the studied metal ions, which may be a consequence of the hydrocarbon tail of 4-C₁₂-DTPA supporting neighbouring donor atoms with electrons and thereby reducing the acidity of those donor atoms. At pH 5 on the other hand, 4-C₁₂-DTPA is the stronger chelating agent for Zn²⁺ and Co²⁺, indicating that the strength of the complexes is not solely dependent on the pK_a values of the chelating agents. It might also be affected by small differences in the 3-D structure of the respective chelating agent, which probably has a larger effect when the chelating agents have the same degree of protonation. The order of selectivity between the five examined transition metal ions; Mn²⁺ < Zn²⁺ < Co²⁺ < Ni²⁺ < Cu²⁺, was however not affected by the addition of the hydrocarbon tail to the structure of DTPA.

6.2. Coordination of Cu²⁺

Cu²⁺ complexes with 4-C₁₂-DTPA were examined in solution by UV-visible spectroscopy in order to study the coordination behaviour of the chelating headgroup (paper II). Absorptions due to d-d transitions of Cu²⁺ complexes can be seen in the visible region and give information about the coordination environment.⁶⁸ The UV-visible spectra of Cu²⁺ complexes of 4-C₁₂-DTPA were compared to those of DTPA, which is known to be able to coordinate up to two Cu²⁺ ions.⁶⁹ DTPA coordinates one Cu²⁺ ion at first, i.e., Cu²⁺-DTPA is formed, and a change in the UV-visible absorption to longer wavelengths is seen for solutions containing more than one equivalent of Cu²⁺ ions due to formation of (Cu²⁺)₂-DTPA species. As expected, similar trends were seen for the Cu²⁺ complexes formed with 4-C₁₂-DTPA, as shown in Table 3.

Table 3. Absorption maxima, λ_{\max} , and extinction coefficients, ϵ , of Cu^{2+} complexes of DTPA and 4- C_{12} -DTPA at different pH

		$\lambda_{\max}[\text{nm}], (\epsilon [\text{M}^{-1}\text{cm}^{-1}])$		
		pH 5	pH 6	pH 8
DTPA	1:1	684 (64)	666 (76)	660 (81)
DTPA	1:2	740	740 (118)	740 (117)
4- C_{12} -DTPA	1:1	700 (66)	664 (85)	660 (91)
4- C_{12} -DTPA	1:2	725	721 (146)	721 (146)

The coordination ratios were also examined by Job's plots, shown for pH 6 in Figure 12. From these results, it is clearly seen that a 1:1 complex is formed for solutions with less and exactly one equivalent of Cu^{2+} ions present and that 2:1 complexes are formed for both DTPA and 4- C_{12} -DTPA. No more than two Cu^{2+} ions could be coordinated to the chelating agents in the studied solutions. This has been shown previously for the DTPA complexes.⁶⁹ It is worth noticing here that EDTA, which is one of the most commonly used chelating agents, is known to only coordinate one metal ion.⁷⁰ The similar absorption spectra of the Cu^{2+} complexes of DTPA and 4- C_{12} -DTPA clearly indicate that the hydrocarbon tail of 4- C_{12} -DTPA has little effect on the coordination behaviour of the chelating headgroup.

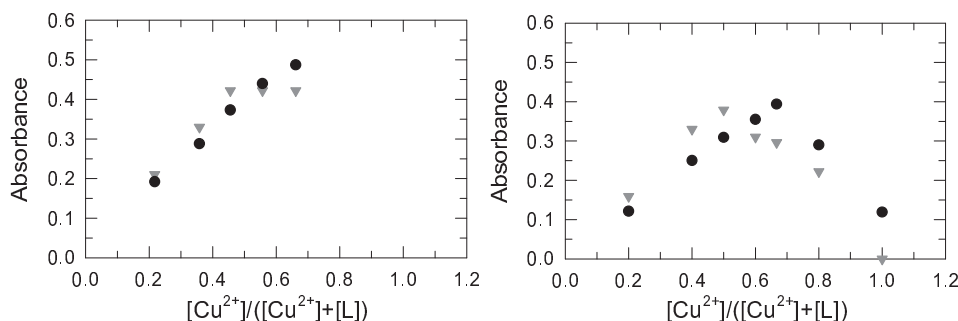


Figure 12. Job's plots for the Cu^{2+} complexes of 4- C_{12} -DTPA (left) and DTPA (right) at pH 6; Cu^{2+} -L (∇) and $(\text{Cu}^{2+})_2$ -L (\bullet).

6.3. Hydrogen peroxide bleaching of TMP

Transition metal ions such as iron, manganese and copper have been found catalysing the decomposition of hydrogen peroxide during bleaching of paper pulp. Thus, for successful bleaching these metal ions need to be taken care of before the bleaching operation takes place. 4- C_{12} -DTPA was compared with DTPA in metal ion chelation and subsequent hydrogen peroxide bleaching of

thermomechanical pulp (TMP) (paper V). The pulp was treated with the two different chelating agents, in two different molar ratios to the manganese content in the untreated pulp, as shown in Table 4. For the carry-over experiments, the pulp was then centrifuged to a consistency of 34 wt%. In the other experiments, the pulp was washed additionally with Milli-Q water before centrifugation to 34 wt%.

Table 4. Metal content in TMP fibres before bleaching

treatment ^a	addition ^b	Mn ^c (ppm)	Cu ^c (ppm)	Fe ^c (ppm)
untreated	—	104	0.56	4.1
4-C ₁₂ -DTPA	1.5:1	7.0	<0.10	3.6
4-C ₁₂ -DTPA, co	1.5:1	17	<0.10	3.6
DTPA	1.5:1	5.1	<0.10	3.2
DTPA, co	1.5:1	9.1	<0.10	3.7
4-C ₁₂ -DTPA, co	1.2:1	17	<0.10	4.9
DTPA, co	1.2:1	13	<0.10	2.8

^aco indicates the carry-over experiments. ^bMolar ratio chelating agent:Mn(untreated).

^cDetermined by ICP-OES.

As seen in Table 4, the manganese content in the pulp is slightly less reduced after treatment with 4-C₁₂-DTPA, compared with DTPA treatment, especially in the carry-over experiments where the pulp is not efficiently washed after treatment. The ISO brightness for the hydrogen peroxide bleached pulps, shown in Figure 13, does however not indicate any significant difference between the efficiency of the two chelating agents. As expected, when treated with a lower ratio of chelating agent (1.2:1), and applying carry-over conditions, the bleaching curves show slightly different brightness development and the maximum brightness is obtained at a total alkali charge of 18 kg/ton. Thereafter, a decrease in brightness at higher total alkali charge is indicated.

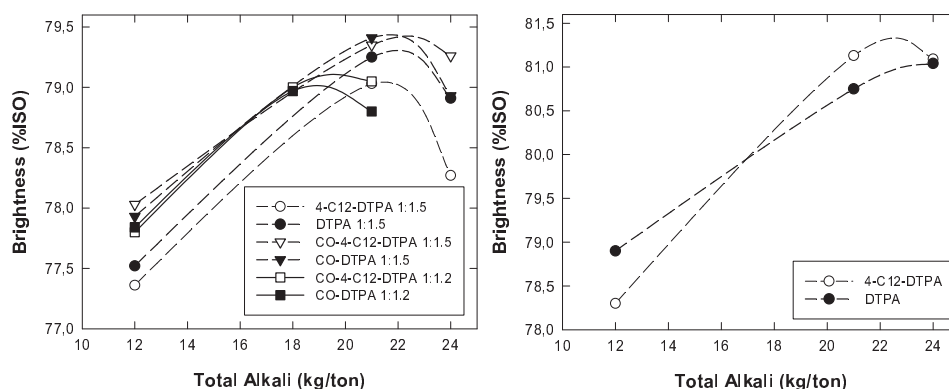


Figure 13. Brightness development of hydrogen peroxide bleached TMP vs total alkali. Left; the pulps were treated with equal charges (1.5:1 or 1.2:1) of 4-C₁₂-DTPA and DTPA, respectively, and washed to different degrees before bleaching. Right; the pulps were carefully washed with 4-C₁₂-DTPA and DTPA, respectively, at a molar ratio of 1.5:1 before bleaching at a constant charge of sodium silicate (29 kg/ton).

It is clearly seen from Figure 13 that pulps pre-treated at the same molar additions of the respective chelating agent and washed to different degrees, giving different residual metal content in the pulps, still develop very similar brightness after bleaching. This refers to the fact that even if there is a carry-over of manganese in the pulps treated with 4-C₁₂-DTPA that could be detrimental for the brightness development under bleaching conditions, the manganese is inaccessible for catalysis of hydrogen peroxide decomposition due to very strong chelation. This is consistent with the similar stability constants towards manganese for the two chelating agents, reported in section 6.1. No significant difference was found in residual hydrogen peroxide in the bleaching liquor between pulps treated with the two chelating agents. The results strongly indicate that the applied bleaching conditions do not induce any differences in hydrogen peroxide decomposition between pulps treated with DTPA and 4-C₁₂-DTPA, at equivalent molar ratios. A most likely explanation for the slightly higher manganese content in pulp treated with the chelating surfactant is that the hydrophobic complexes interact with the molecular constituents of the wood. The surface active structure facilitates interactions of hydrophobic origin between the hydrocarbon tail and wood surfaces, especially where the hydrophobic extractives are located. Hydrophobic interactions have been shown more important for the retention of surfactants than the pore size distribution of the material.⁷¹ In the present study, the hydrophobic interactions between the chelating surfactant and the wood material could induce a slower transport of the chelating surfactant through the fibre wall. However, from

a metal ion handling perspective, the transition metal ions can still be coordinated by the chelating surfactant within the fibre walls. The metal ions can thereby be prevented from taking part in the catalysis of hydrogen peroxide decomposition under bleaching, as long as the complex is not oxidised and degraded by the bleaching chemicals.⁷²

7. pH vs concentration in correlation to micellization

The pK_a values of a free monomer in solution are governed by the electrostatic interaction between titrating groups within the molecule. At the micellization, the dissociation of the aggregated surfactants is affected by the increased charge density at the micellar surface, due to the interaction between adjacent monomers. pH vs concentration plots of 4-C₁₂-DTPA, its metal complexes and mixtures with ionic surfactants can be used to detect the cmc and give valuable information about the interactions in the micelles. Because of its amphoteric nature, 4-C₁₂-DTPA accepts or donates protons to the aqueous solution in order to adjust its electrical charge. Increased protonation increases the relative amount of positive charges, whereas donation of protons increases the relative amount of negative charges.

7.1. 4-C₁₂-DTPA

For the negatively charged 4-C₁₂-DTPA, in the examined pH region between 3 and 10, surfactants in micelles will become protonated to a higher degree than the free monomers. The pH vs concentration at different start pH is shown in Figure 14 (paper I). The arrows indicate the cmc from NMR diffusometry. At pH 5 and 6.5, the increase in pH exactly matches the cmc. At pH 3 and 4 on the other hand, the rise starts at concentrations slightly below the cmc. The rise at pH 3 is consistent with the formation of a precipitate, which is protonated to a higher degree than the dissolved monomers to attain electroneutrality. The pH graphs at pH 8.5 and 10 have a different shape, and cannot be used to detect the cmc. At these pH levels, no increase is seen at the micellization, probably due to the lack of titrating groups that matches these pH levels.

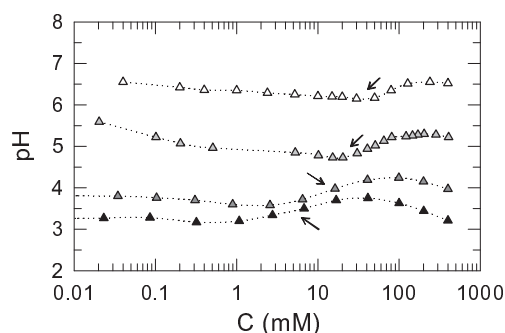


Figure 14. pH vs 4-C₁₂-DTPA concentration for starting pH 3 (▲), pH 4 (▲), pH 5 (▲), and pH 6.5 (Δ). The determined cmc's are indicated by the arrows.

7.2. Metal complexes

For the metal complexes with 4-C₁₂-DTPA, the pH vs concentration plots provide indications of different coordination chemistry between the two groups of metal ions studied; the alkaline earth metals, represented by the Mg²⁺ complex, and the transition metals, represented by the Co²⁺ complex, in Figure 15 (paper II). The pH behavior of the pure 4-C₁₂-DTPA is also shown in the figure. The general HSAB theory is useful when discussing coordination of metal ions.³⁸ The negatively charged carboxylate oxygen atoms are harder bases than the neutral nitrogen atoms. The examined divalent alkaline earth metal ions, being hard acids, are consequently coordinated stronger by the carboxylate oxygen atoms than by the nitrogen atoms. The divalent transition metal ions on the other hand, are coordinated strongly by both types of donor atoms.

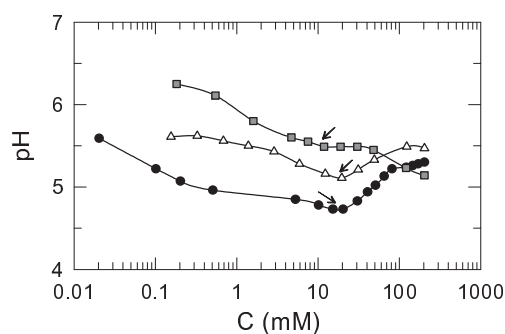


Figure 15. pH vs concentration for 4-C₁₂-DTPA (●), Co²⁺-4-C₁₂-DTPA (Δ), and Mg²⁺-4-C₁₂-DTPA (■). The determined cmc's are indicated by the arrows.

For the Co²⁺ complex, the pH behaviour is similar as for the pure chelating surfactant. The plot indicates that there is repulsion between negative charges at the formation of micelles, just as for the pure 4-C₁₂-DTPA. The increase in pH is

somewhat less pronounced due to reduced requirements to screen the electrostatic repulsion in micelles of Co^{2+} complexes compared to micelles of the pure 4- C_{12} -DTPA. For the Mg^{2+} complex, the pH is practically constant at the formation of micelles but starts to decrease at a slightly increased concentration. From this, a different coordination of Mg^{2+} compared to Co^{2+} can be assumed. The decreasing pH as a result of proton release indicates that there is repulsion between positive charges in the micellar solution of Mg^{2+} complexes, i.e., repulsion between protonated amine groups. This is a consequence of the preferred coordination to the carboxylate groups, leaving the amine groups protonated to a higher degree.

7.3. Mixed micellar systems

Effects of interactions in mixed micelles containing 4- C_{12} -DTPA can also be seen from pH measurements of the solution (paper III). This is particularly informative in a system such as the 4- C_{12} -DTPA/DoTAC, shown in Figure 16, where there is repulsion between negatively charged groups at high mole fraction of 4- C_{12} -DTPA and between positively charged groups at high mole fraction of DoTAC.

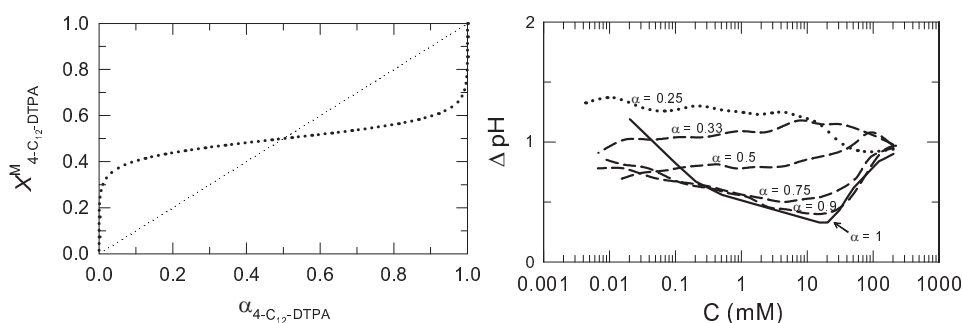


Figure 16. Left; mole fraction of 4- C_{12} -DTPA in micelles vs mole fraction of 4- C_{12} -DTPA in solution for 4- C_{12} -DTPA/DoTAC at pH 5. The optimum composition for the mixture is found where the curve crosses the diagonal. Right; pH vs total surfactant concentration for 4- C_{12} -DTPA/DoTAC mixtures at $\alpha_{4\text{-C}_{12}\text{-DTPA}}$ between 0.25 and 1, initial pH around 5.

When the mixtures are rich in 4- C_{12} -DTPA, the behaviour is similar to the pure 4- C_{12} -DTPA solution, meaning that there is still repulsion between the negative charges on 4- C_{12} -DTPA since the pH increases at the cmc. At increasing mole fraction of DoTAC, the pH curves levels off as the amount of positive charges approaches the amount of negative charges in the mixture, and the need for neutralizing electrostatic repulsions decreases. At $\alpha_{4\text{-C}_{12}\text{-DTPA}} = 0.33$ there are rather small variations in pH, but the shape of the curve differs distinctly from the mixtures at high mole fraction of 4- C_{12} -DTPA, which is an indication that the mixing ratio in the total solution has passed the point of electroneutrality. The

surfactant composition in micelles at the cmc differs from the composition in the solution, as shown in Figure 16. At increasing concentration however, the composition in the micelles must approach the composition in the total system as the monomer concentration becomes negligible. Because of this change in mixing ratio between the two types of surfactants in the micelles, the pH curve will never become perfectly flat over the examined concentration interval. At $\alpha_{4\text{-C}_{12}\text{-DTPA}} = 0.33$, the mole fraction of 4-C₁₂-DTPA in micelles is around 0.47 at the cmc (see Figure 16), and the pH increases at the formation of micelles due to the repulsion between 4-C₁₂-DTPA. As the concentration increases and the mixing ratio in the micelles approaches that of the total system ($\alpha_{4\text{-C}_{12}\text{-DTPA}} = 0.33$), the pH start to decrease at the point where the repulsion between DoTAC starts to dominate. This is because of the increased dissociation of 4-C₁₂-DTPA to increase the amount of negative charges in the micelles. At the highest mole fraction of DoTAC ($\alpha_{4\text{-C}_{12}\text{-DTPA}} = 0.25$), the mole fraction of 4-C₁₂-DTPA in micelles is around 0.45 at the cmc, and now the pH remains constant at the formation of micelles, indicating equal amounts of positive and negative charges in the micelles. The pH drops at higher concentrations when the molar ratio of DoTAC in the micelles increases as the composition in the micelles approaches the total composition.

8. Headgroup interactions and ion flotation efficiency

The synergistic effects of mixing surfactants are utilized in many practical applications, including foam flotation. In previous reports on this subject, synergism in surface tension reduction and/or mixed micelle formation in relation to foaming properties has been studied.⁷³⁻⁷⁶ In paper IV, a different approach was adopted, where the correlation between the interaction parameter and ion flotation efficiency in mixtures of a chelating surfactant metal complex and different foaming agents was investigated.

The formation of strong coordination complexes is utilized when chelating surfactants are used for recovery of metal ions from aqueous solutions by for example foam flotation.²² In such an application, a foaming agent may be necessary in order to achieve sufficient foaming. The interaction between the two surfactants plays an important role for the efficiency of the process, especially the interaction at the air-water interface, described by β^σ . Ion flotation of the systems is thus a way of studying the effects of the interactions. 4-C₁₂-DTPA has been successfully used for recovery of Cu²⁺ and Mn²⁺ ions by foam flotation in mixtures with a foaming agent.⁷⁷⁻⁷⁹

8.1. Interaction parameters

Surfactants with the same hydrophobic chain length were studied and the effects are therefore discussed in terms of headgroup interactions.⁸⁰ Amphoteric surfactants, like the studied 4-C₁₂-DTPA, can interact strongly with other ionic surfactants by accepting or donating protons to the aqueous solution in order to adjust its electrical charge and increase the attractive interaction,⁵¹ as discussed in section 7.3.

4-C₁₂-DTPA was studied in mixtures with three differently charged foaming agents; the cationic DoTAC, the anionic SDS, and the pH-responsive DDAO. DDAO is cationic at low pH and zwitterionic at high pH, with a pK_a value of 4.78 for monomers.⁸¹ 4-C₁₂-DTPA interacts with the cationic DoTAC by donating protons to the aqueous solution in order to increase its amount of negative charges, and thereby increase the attractive interaction (paper III). In mixture with the anionic SDS on the other hand, 4-C₁₂-DTPA accepts protons from the aqueous solution to increase its amount of positive charges. Because of the negative net charge of 4-C₁₂-DTPA at the investigated pH levels, the interaction was stronger with DoTAC than with SDS (see Table 5). Very strong interaction was found in the mixture with DDAO, most likely because both surfactants can adjust their headgroup charge (paper IV). The interaction parameter for the mixture with DDAO was especially sensitive to changes in pH. Increasing the pH from 5 to 7 reduced the magnitude of the β^M value from -11.6 to -6.2. The stronger interaction at pH 5 is a natural consequence of the increased protonation of both surfactants at this pH, leading to reduced repulsion in mixed micelles.

Table 5. Average calculated β parameters for mixtures at pH 5

	SDS		DDAO		DoTAC	
	β^M	β^σ	β^{Ma}	β^σ	β^M	β^σ
4-C ₁₂ -DTPA	-3.1	n/a	-11.6	-8.6	-9.3	n/a
Mg ²⁺ -4-C ₁₂ -DTPA	-4.2	-6.1	n/a	n/a	-8.2	-8.9
Ni ²⁺ -4-C ₁₂ -DTPA	-3.5	-3.6	-7.2	-6.5	-11.3	-13.7

^aDetermined from surface tension measurements.

The influence of metal ion coordination on the interaction parameter was also examined (paper IV). As seen in Table 5, the influence on the magnitude of β^M was different for the two investigated metal ions, which correlates to the difference in coordination between the two groups of metal ions (alkaline earth metals and transition metals) as discussed in section 7.2 (paper II). In the mixture with DoTAC, coordination of Ni²⁺ increased the magnitude of the β^M parameter,

whereas coordination of Mg^{2+} decreased the magnitude of the β^M parameter. Mg^{2+} is coordinated preferably by the carboxylate oxygen atoms, thereby reducing the amount of negatively charged carboxylate oxygen atoms. This reduces the attractive interaction with the cationic DoTAC, as seen from the smaller β^M value. Ni^{2+} is coordinated strongly by both types of donor atoms. Coordination of Ni^{2+} consequently reduces the amount of amine groups available for protonation, and thereby the amount of positive charges in the headgroup. This increases the attractive interaction with the cationic DoTAC, hence the increased magnitude of the β^M value. The strong attractive interaction in the Ni^{2+} -4- C_{12} -DTPA/DoTAC system was evident from the formation of precipitate at equal mixing of the surfactants or higher mole fraction of DoTAC. Generally, β^σ values are more negative than β^M , i.e., stronger interaction in mixed monolayers than in mixed micelles.⁸² This was observed for both metal complexes with DoTAC and the consequences of the difference in coordination chemistry of the metal ions are even more pronounced in the β^σ values than in the β^M (see Table 5).

Both metal ions increase the magnitude of the β^M value in mixtures with the anionic SDS since the negative net charge of 4- C_{12} -DTPA is reduced by the coordination of the positively charged metal ion, but now the interaction is strongest with the Mg^{2+} complex. Again, the difference correlates with the difference in coordination chemistry of the two metal ions. Since Mg^{2+} is coordinated preferably by the carboxylate oxygen atoms the amount of negatively charged groups is more effectively reduced by the coordination of Mg^{2+} ions compared to Ni^{2+} ions. The Mg^{2+} complex show stronger interaction than the Ni^{2+} complex also in mixed monolayer with SDS.

The coordination of Ni^{2+} ions reduces the interaction with DDAO. In mixtures of two titrating surfactants it may be more difficult to predict the effects of metal ion coordination on the interaction parameters. A possible reason for the weaker interaction may lie in the reduced electrostatics between DDAO and 4- C_{12} -DTPA as a consequence of the Ni^{2+} coordination.

8.2. Influence of the interaction parameter β^σ on ion flotation efficiency

The correlation between interactions in mixed monolayer formation, calculated by the parameter β^σ , for the Ni^{2+} -4- C_{12} -DTPA/foaming agent mixtures and the Ni^{2+} flotation efficiency was investigated at pH 5 (paper IV). 1 ppm Ni^{2+} solutions with 1.2 equivalents 4- C_{12} -DTPA and 10 equivalents of the respective foaming agent were gently floated to allow for good water drainage of the formed foam. The first 1.7 g of the foam was collected and the metal content was determined. It is clear from the results in Table 6 that the choice of foaming agent has a significant impact on the transfer of the Ni^{2+} complexes from the bulk to the foam phase during flotation. With SDS, almost no depletion of Ni^{2+} was obtained, while nearly half of

the Ni^{2+} ions were collected in the initial foam fraction, constituting less than 0.2 wt% of the bulk phase, when DoTAC was used. A contributing effect to the low Ni^{2+} depletion in the mixture with SDS may be the high foaming ability of SDS leading to relatively high liquid content in the collected foam.

Table 6. Ni^{2+} bulk depletion and phase transfer to initially formed foam during ion flotation using different 4- C_{12} -DTPA/foaming agent mixtures

foaming agent	$[\text{Ni}^{2+}]_{\text{foam}}$ (ppm)	Ni^{2+} bulk depletion (%)	β^σ Ni^{2+} -4- C_{12} -DTPA/ foaming agent
SDS	1.50	0.25	-3.6
DDAO	129	22	-6.5
DoTAC	287	47	-13.7

The interaction parameter β^σ for the different mixtures vs the Ni^{2+} bulk depletion, plotted in Figure 17, shows surprisingly good linear regression. This clearly implies that the magnitude of the interaction parameter is important for the efficiency of ion flotation in mixed surfactant systems.

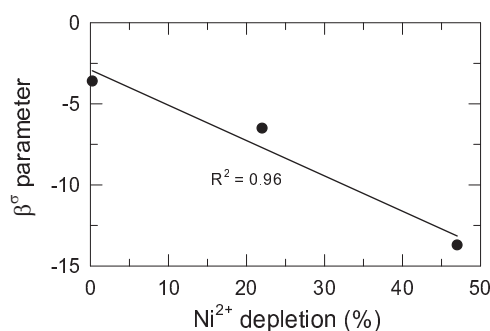


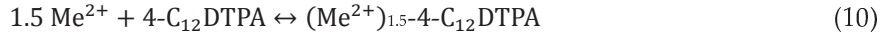
Figure 17. The interaction parameter β^σ vs Ni^{2+} bulk depletion during ion flotation of different Ni^{2+} -4- C_{12} -DTPA/foaming agent mixtures.

8.3. Ion flotation selectivity

The difference in stability constants between different ions, shown in Table 2 section 6.1, offers the possibility to selectively separate metal ions in mixtures (paper IV). The conditional stability constants with 4- C_{12} -DTPA determined at room temperature and pH 5 for Cu^{2+} and Zn^{2+} were $\log K_{\text{Cu}} = 11.9$ and $\log K_{\text{Zn}} = 9.9$, respectively. In equal molar addition of 4- C_{12} -DTPA, Cu^{2+} , and Zn^{2+} and equimolar reaction stoichiometry, this difference in $2 \log K$ units would result in ten times higher concentration of Cu^{2+} complex than Zn^{2+} complex. As shown to the left in

Figure 18, the experimental results from ion flotations of mixed metal ion solutions comprising Cu^{2+} and Zn^{2+} deviate from equimolar reaction stoichiometry; the uncomplexed metal ion concentrations that would be expected to support this are indicated by the dashed lines. This is in agreement with the results presented in section 6.2. regarding coordination of Cu^{2+} ions, where it was shown that the headgroup of 4- C_{12} -DTPA was able to bind more than one Cu^{2+} ion.

At the end of the flotation, the bulk concentration of Cu^{2+} and Zn^{2+} (to the left in Figure 18) indicates a total depletion of metal ions of approximately 1.5 ppm. This corresponds to a reaction stoichiometry of 1.5:1 between metal ions and chelating surfactant, as illustrated in eq 10;



which gives the following coupled equilibrium equation for the competitive chelation between Cu^{2+} and Zn^{2+} , and 4- C_{12} -DTPA;

$$\frac{K_{\text{Cu}}}{K_{\text{Zn}}} = \frac{[(\text{Cu}^{2+})_{1.5}\text{-4-C}_{12}\text{DTPA}][\text{Zn}^{2+}]^{1.5}}{[(\text{Zn}^{2+})_{1.5}\text{-4-C}_{12}\text{DTPA}][\text{Cu}^{2+}]^{1.5}} \quad (11)$$

where K_{Cu} and K_{Zn} are the conditional stability constants of the two metal complexes formed. To test this hypothesis against the experimental outcome, eq 11 was solved numerically and the resulting uncomplexed metal ion concentrations are indicated by the full lines in Figure 18. The latter approach clearly gives a much better compliance with the experimentally obtained data.

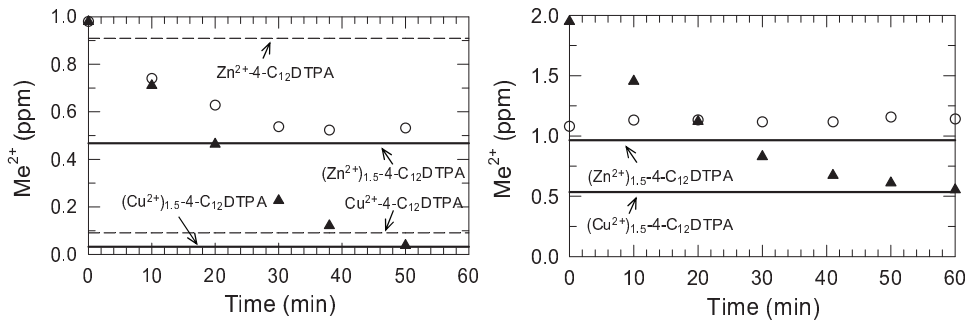


Figure 18. Ion flotation of Cu^{2+} (▲) and Zn^{2+} (○) complexes vs time for molar mixing ratio of Cu^{2+} , Zn^{2+} , 4- C_{12} -DTPA, and DDAO; 1:1:1:10 (left) and 2:1:1:10 (right). The dashed lines represent calculated concentrations of uncomplexed metal ions, assuming equimolar reaction stoichiometry with the chelating surfactant. The full lines are calculated concentrations of uncomplexed metal ions when each 4- C_{12} -DTPA is assumed able to bind 1.5 metal ions.

To further confirm this, 4-C₁₂-DTPA was added to a solution of 2 equivalents of Cu²⁺ and 1 equivalent Zn²⁺, which was floated with 10 equivalents of DDAO. The experimental results are shown to the right in Figure 18, together with calculated uncomplexed metal ion concentrations (full lines), using eq 11. A minor deviation from the targeted Zn²⁺ concentration, which obviously should have remained at 1 ppm, is noticed. Still, the calculated uncomplexed metal ion concentrations satisfy the experiments extremely well, and eq 10 is thus a very good description of the coordination reactions between 4-C₁₂-DTPA and Cu²⁺ and Zn²⁺, respectively.

9. Conclusions and further perspectives

The numerous donor atoms in the headgroups of chelating surfactants lead to rather complex solution behaviour due to a distribution of differently charged species that interact with each other, much like a mixed surfactant system where the components and mixing ratio depend on the pH. The solution behaviour of 4-C₁₂-DTPA consequently showed strong pH dependence.

The solution behaviour of 4-C₁₂-DTPA was affected by addition of metal salts due to coordination of the metal ions, which reduces the net charge, the number of dissociation states, and the steric flexibility in the headgroup.

The anomalies between surface tension and NMR diffusometry must be considered when measuring surface tension of chelating surfactants in order to correctly evaluate the results.

The simple technique of measuring the pH of the surrounding solution as a function of concentration gives valuable information regarding the interaction between adjacent aggregated surfactants in amphoteric surfactant systems, which can be used for instance to detect the cmc.

The addition of the hydrocarbon tail to the DTPA headgroup had a very limited effect on the coordination chemistry towards the studied divalent metal ions and the order of selectivity was not affected.

There was strong correlation between surfactant interaction in mixed monolayers, as calculated by the β^σ parameter, and ion flotation efficiency in mixtures of Ni²⁺ complex of the chelating surfactant 4-C₁₂-DTPA and different foaming agents.

The difference in log *K* between different metal complexes can be utilized to selectively remove the metal ion with the highest log *K* from water systems by ion flotation.

This study has provided fundamental knowledge about the solution behaviour of chelating surfactants, which is a rather unexplored research area where we can expect interesting research in the future. It was concluded from this study that the chelating surfactant showed unconventional adsorption behaviour with respect to surface saturation, increasing surface tension at concentrations above the cmc, and time dependent surface tension. To further examine these phenomena, and get more definite answers about the surface coverage, neutron reflectivity measurements would be of great interest.

The correlation to the interaction parameter in the ion flotation process could be further utilized to optimize the ion flotation efficiency. As discussed in this thesis, in a mixed system of amphoteric surfactants without added electrolyte, the interaction parameter may depend on the solution composition. This would be interesting to study in more detail, as well as the pH dependence of the interactions with differently charged ionic surfactants. Results from such a study would give additional information for strategies in ion flotation optimization.

The protonation sequence and pK_a values of EDTA and DTPA have been reported from 1H NMR studies. This technique could be used also to study the pK_a values of 4- C_{12} -DTPA, as well as its metal complexes. The latter could give information regarding the coordination of different metal ions. The pK_a values for some DTPA metal complexes can be found in the literature, but this has not been extensively studied. The UV-visible spectroscopy study regarding coordination of Cu^{2+} ions by the chelating surfactant could be extended by investigating coordination of other transition metal ions.

The influence of metal ions on the solution behaviour of 4- C_{12} -DTPA was examined in equimolar ratios in this study. Significant effects could be expected from further addition of metal ions due to the ability of the headgroup to coordinate more than one metal ion.

This study has focused on a single chelating surfactant, there are however many more possible structures for designing chelating surfactants, which may be differently suited in different applications due to their properties. Continued mapping of chelating surfactants is of great interest from this perspective.

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