

Silke Schnedl, BSc

# **Development of a Nickel-based Metallosurfactant for Biphasic Esterification of Acetic Acid**

to achieve the university degree of  
Diplom-Ingenieurin

Master's degree programme:  
Chemical and Pharmaceutical Engineering

submitted to

**Graz University of Technology**

## **Supervisor**

Ass.Prof. Dipl.-Ing. Dr.techn. Susanne Lux  
Institute of Chemical Engineering and Environmental Technology

Graz, March 2021

## **AFFIDAVIT**

I declare that I have authored this thesis independently, that I have not used other than the declared sources/resources, and that I have explicitly indicated all material which has been quoted either literally or by content from the sources used. The text document uploaded to TUGRAZonline is identical to the present master's thesis.

---

Date, Signature

## Acknowledgement

First, I would like to thank my supervisor Ass.Prof. Dipl.Ing. Dr.techn. Susanne Lux, Univ.-Prof.i.R. Dipl.Ing. Dr.techn. Matthäus Siebenhofer and Dipl.Ing. Dr.techn. Andreas Toth, without whom this work would not have been possible. I am also grateful to the entire CEET laboratory team for their kindness and help.

A big thank you goes to everyone who accompanied me during my studies and life in general.

**“Science doesn’t have all the answers, you know.” “It’s got all the best questions, though,”** – Ben Aaronovitch

## Abstract

The aim of the present work was the development of a metallosurfactant as catalyst for the reactive separation of carboxylic acids from wastewater through biphasic esterification. The catalyst was synthesised from the surfactant 4-Dodecylbenzenesulphonic acid (4-DBSA), which has already been successfully used in catalysis, and the transition metal nickel. Certain requirements must be fulfilled by the catalyst in order to be utilised effectively for biphasic esterification of carboxylic acids. These include the low solubility of the catalyst in water and the catalytic activity without formation of an emulsion in the reaction system. Due to the self-assembling properties at the interface and the associated reduction of interfacial tension, a sufficiently large mass transfer area could be provided. The synthesis of the catalyst must be simple without unnecessarily expanding the reaction system. The catalytic activity of the novel catalyst  $[\text{Ni}(\text{DBSA})_2]$  was tested for the biphasic esterification reaction of acetic acid with *n*-octanol to *n*-octyl acetate. Conversions of acetic acid of up to 37 % and separation efficiencies of up to 55 % were achieved. The interfacial tension between the aqueous and the solvent phase was reduced by up to 75 % by the metallosurfactant.

## Kurzfassung

Ziel dieser Arbeit war die Herstellung eines Metalltensides als Katalysator für die Abtrennung von Carbonsäuren aus Abwasser. Dieser Katalysator wurde aus dem Tensid 4-Dodecylbenzolsulfonsäure (4-DBSA), das bereits in der Katalyse Anwendung findet, und dem Übergangsmetall Nickel entwickelt. Um für die Veresterung von Carbonsäuren im zweiphasigen System als Katalysator eingesetzt zu werden, muss das Metalltensid gewisse Anforderungen erfüllen. Dazu zählen die geringe Wasserlöslichkeit des Katalysators, sowie die katalytische Aktivität ohne Ausbildung einer Emulsion im Reaktionssystem. Durch die Selbstorganisation an der Grenzfläche und der damit einhergehenden Verringerung der Grenzflächenspannung, kann eine ausreichend große Fläche für den Massentransfer zur Verfügung stehen. Die Herstellung des Metalltensids soll möglichst einfach sein, ohne das Reaktionssystem unnötig zu erweitern. Die katalytische Aktivität von  $[\text{Ni}(\text{DBSA})_2]$  wurde anhand der Veresterung von Essigsäure mit *n*-Octanol zu *n*-Octylacetat im zweiphasigen System überprüft. Dabei konnten Umsätze an Essigsäure von bis zu 37 % und Trenneffizienzen von bis zu 55 % erzielt werden. Die Grenzflächenspannung zwischen der wässrigen und der Lösungsmittelphase wurde durch das Metalltensid um bis zu 75 % verringert.

# Contents

1	Introduction and Motivation .....	1
2	Theoretical Background.....	3
2.1	Metallosurfactants .....	3
2.2	4-Dodecylbenzenesulphonic Acid .....	3
2.2.1	Sulphonic Acids.....	4
2.2.2	Surface-active Substances.....	4
2.2.3	Micelles .....	5
2.2.4	Emulsion .....	6
2.3	Nickel .....	7
2.3.1	Transition Metals – The d-block Elements .....	7
2.3.2	Complex Chemistry.....	7
2.3.3	Structural Elucidation .....	8
2.4	Esterification Reactions.....	9
3	Current Scientific Knowledge .....	10
3.1	4-Dodecylbenzenesulphonic Acid as Catalyst.....	10
3.2	Catalyst Modification .....	11
3.3	Solvent Selection – Green Solvents.....	13
4	Materials and Analytical Methods.....	15
4.1	Materials.....	15
4.2	Analytical Methods .....	15
4.2.1	Flame Atomic Absorption Spectroscopy (F-AAS).....	16
4.2.2	Gas Chromatography (GC) .....	17
4.2.3	Spinning Drop Tensiometer .....	17
4.2.4	Total Organic Carbon (TOC).....	19
4.2.5	Karl-Fischer Titration (KF titration) .....	19
4.2.6	Density Measurements .....	19

5	Experimental Part.....	20
5.1	Preparation of the Nickel-based Metallosurfactant Catalyst.....	20
5.1.1	Biphasic Approach .....	20
5.1.2	Direct Mixing Approach .....	21
5.1.3	Biphasic Esterification: Experimental Set-up, Parameters and Method 26	
5.2	Spinning Drop Tensiometer Measurement.....	28
6	Results and Discussion .....	30
6.1	Overall Mass Balance .....	30
6.2	Conversion and Separation Efficiency.....	31
6.3	Total Organic Carbon .....	35
6.4	Nickel in the Aqueous Phase .....	36
6.5	Density Measurements, Water Content and Rinsing.....	38
6.5.1	Density Measurements .....	38
6.5.2	Water Content.....	39
6.5.3	Rinsing.....	40
6.6	Interfacial Tension.....	41
6.7	Structural Elucidation .....	44
7	Conclusion and Outlook .....	45
	Literatur .....	47
	List of Figures .....	52
	List of Tables .....	54
	Appendix.....	56

# 1 Introduction and Motivation

Green chemistry is one of the catchphrases of our time. The United States Environmental Protection Agency (EPA) was founded in the 1970s to protect human health and the environment. It defines green chemistry as follows: "*Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal.*" [1] With the Pollution Prevention Act that was passed in the USA in 1990, the avoidance of chemical pollution and hazardous substances was brought to the fore. Before that the focus laid on reprocessing and disposal. The EPA played a central role to move green chemistry forward in its early developments. [2, 3]

At that point, there were already existing ideas and solutions to combat environmental pollution and the depletion of resources. By the mid-1990s, the different concepts developed into what we now roughly refer to as green chemistry. In 1998 Paul Anastas and John Warner published in their work "Green Chemistry: Theory and Practice" the 12 principles of green chemistry, which resulted in an established guideline for chemists. [4] The avoidance of waste is preferred to subsequent disposal or processing of waste. Other important points are the usage of safe chemicals and solvents, energy efficiency, but also the utilisation of renewable raw materials, and catalysts. [2, 5]

Chemical technology is evolving, and so is green chemistry. Anastas and Zimmerman suggested the 12 principles of green engineering in 2003. [6] In addition to the common standards for quality and safety, the focus lies on social, economic and, above all, environmental aspects. The two most important points are the life cycle assessment and the use of non-hazardous materials. The optimisation of already established, non-sustainable processes is described as a short-term goal. [6]

The pulp and paper industry produced more than 419 metric tons of paper and cardboard in 2018. [7] 42 % of the world's industrial wastewater which equal to three trillion tons come from this branch of industry alone. [8] In terms of a holistic, sustainable approach, as many by-products as possible should be recovered or



processed. Carboxylic acids are obtained as by-products during the Kraft pulping process. [9] Since the separation of the condensate from the black liquor is not economically viable, the condensate is usually burned to generate energy. [10, 11] However, carboxylic acids such as acetic acid and formic acid are important raw materials for fine chemistry, polymer production, the food industry, and also pharmaceuticals. [9, 10]

The isolation of formic acid and acetic acid from wastewater is difficult due to the formation of a ternary saddle point azeotrope. Painer et al. found the ternary saddle point azeotrope with a composition of 49.8 mole % formic acid, 39.0 mole % water and 11.2 mole % acetic acid at a pressure of 950 mbar and a boiling temperature of 105.2 °C. [12] Reactive separation methods have already proven successful separation of these two acids in dilute systems. However, reactive distillation has only been utilised for carboxylic acid concentrations above 30 w%. [13] In contrast, reactive extraction is suitable for lower concentrations of carboxylic acids. In reactive extraction mainly phosphorous and amine-based reactive extractants are employed. Talnikar et al. published a review on the recovery of carboxylic acids from wastewater including reactive distillation and reactive extraction. [14] Toth et al. used the tools of process intensification and combined liquid-liquid extraction with esterification successfully. [11] The surfactant 4-dodecylbenzenesulphonic acid (4-DBSA) served as a catalyst for the esterification of acetic acid with *n*-octanol. A separation efficiency of 57 % was achieved and a conversion of acetic acid to *n*-octyl acetate of 54 %. The drawback of the surfactant-type catalyst lies in the formation of a stable emulsion that cannot be broken down by centrifugation. As a result, the catalyst cannot be recycled, nor is it possible to separate the phases and recover the solvent. [11] The esterification reaction does occur uncatalyzed but was found to reach its equilibrium only after a few days. Sulphuric acid is a well-known catalyst for the esterification of carboxylic acids. Unfortunately, water has shown to drop the catalyst's activity up to 90 % and the catalyst is therefore not suitable for this application. [15] That leaves 4-DBSA as a promising candidate for further investigation provided that the hurdle of the formation of stable emulsions can be overcome.

In the present work, an attempt was made to modify 4-DBSA and develop a metallosurfactant catalyst that combines the advantages of a surfactant and a

transition metal. In order to be utilised as a catalyst, a few requirements must be fulfilled by the metallosurfactant. These are low water solubility, self-assembling at the interface, catalytic activity without emulsification, and simple synthesis.

## 2 Theoretical Background

### 2.1 Metallosurfactants

One of the first mentions of metallosurfactants was in the early '90s. Metallosurfactants were described as amphiphilic compounds that behave like surfactants, yet also contain a metal ion in their structure. The metal ion is either located in the head group or tail of the surfactant with the first one being the more common. It may also act as a counter ion. Combining the properties of a surfactant and a (transition) metal, these compounds form a new class of advanced materials. Metallosurfactants enable the utilisation of transition metal properties such as magnetic properties or catalytic activity at an interface. Therefore, metallosurfactants have been examined for a wide range of applications such as catalysis, anticancer agents, interfacial photophysics, magnetic resonance imaging. [16–18]

### 2.2 4-Dodecylbenzenesulphonic Acid

4-DBSA belongs to the group of sulphonic acids and is, therefore, a strong acid. As shown in Figure 2-1 4-DBSA consists of a long hydrocarbon chain and the functional group sulphonyl hydroxide. Due to its structure, the acid behaves like an anionic surfactant. Thus, the acid is used as a Bronsted acid-surfactant-combined (BASC) catalyst in various reactions to accelerate the reaction rate. Arising thereby is an emulsified system that is not desirable for liquid-liquid extractions.

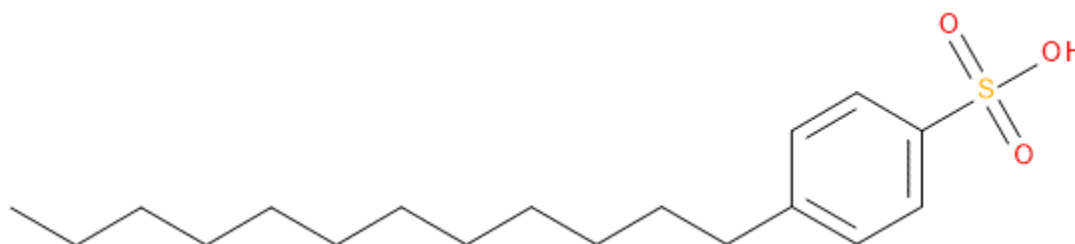


Figure 2-1 Structural formula of 4-dodecylbenzenesulphonic acid

### **2.2.1 Sulphonic Acids**

The functional  $\text{SO}_3\text{H}$ -group is characteristic for sulphonic acids. In this functional group, the sulphur atom is directly bonded to the carbon atom, and not only to the oxygen as in the case of sulphonic acid esters. Sulphonic acids are regarded as strong acids, comparable to sulphuric acid in this respect. Aromatic sulphonic acids are often not the final product but are rather used to produce colourants, drugs, or detergents. Such acids are synthesized via the sulphonation of benzene with electrophilic sulphur trioxide. Usually, oleum (sulphur trioxide dissolved in concentrated sulfuric acid) is used for this procedure. This reaction is called an electrophilic aromatic substitution. Due to their strong electrophilicity, sulphonic acid groups are frequently used as leaving groups. The reversibility of this sulphonation enables the introduction of other groups and therefore makes the acids relevant for a wide variety of syntheses. The salts of sulphonic acids are soluble in water, which is why long-chain alkyl benzene sulphonic acids react further with sodium hydroxide to form sulphonates and are used as surfactants, for example in detergents. Branched alkyl chains may no longer be used for over-the-counter products due to their long biodegradation time. Today, sodium dodecylbenzene sulphate is one of the most used anionic surfactants. [19, 20]

### **2.2.2 Surface-active Substances**

Surface-active substances (surfactants) are amphiphilic compounds. The compounds consist of a hydrophobic part in the form of hydrocarbon chains and a hydrophilic part, a polar group. These molecules reach their energetically most favourable state when they are positioned on surfaces or interfaces so that the polar and non-polar part is in the respective preferred environment. These monolayers that are formed at interfaces can change the properties of interfaces and form micelles. The interfacial tension is thereby reduced. Because of these properties, such compounds are used e.g. to modify the wettability, like detergents, or to stabilize or destabilize dispersions. The adjustment of the interface state presupposes the equilibrium between adsorption and desorption, which is why the surface activity is a dynamic phenomenon. [21]

The range of surfactants is large with molecular weights from a few hundred to several thousand grams per mole. The surfactant classes are divided by the hydrophilic, polar group. A distinction is made between anionic, cationic, non-ionic, and amphoteric

(zwitterionic) surfactants. The different classes, their polar group and examples are shown in Table 2-1. [21]

*Table 2-1 List of surfactant classes with the charge of their polar group and examples*

<b>Surfactant Class</b>	<b>Charge of the Polar Group</b>	<b>Example</b>
anionic	negative	sulphates, sulphonates, carboxylates
cationic	positive	quaternary ammonium salts
non-ionic	uncharged	glycol ether
amphoteric	positive and negative	carboxybetaine, sulphobetaine

### **2.2.3 Micelles**

Diluted surfactants in low concentrations behave in aqueous solutions like electrolytes – small, charged, dissolved ions. In contrast, higher concentrations with fully occupied interfaces cause the formation of organized aggregates, so-called micelles. If the formation occurs in non-polar media, one speaks of inverse micelles. Figure 2-2 displays a drawing of a micelle and an inverse micelle. Micelle formation is referred to as a compromise behaviour to avoid the energetically unfavourable water contact of the hydrophobic groups but to leave the polar groups in the aqueous environment. The hydrophobic effect is responsible for the association of the non-polar groups. 50-1000 surfactant molecules can be arranged in micelles. Different classes of surfactants form different micelles in terms of size and shape. Ionic surfactants build spherical micelles due to the electrostatic repulsion of the polar group with one another, whereas non-ionic surfactants preferably form cylindrical micelles. Micelle formation starts when the concentration of surfactant is above the CMC (critical micelle concentration). This specific concentration characterises the activity of the surfactant and is, therefore, relatively high for ionic surfactants compared to non-ionic surfactants, due to the repulsion of the same charges. The CMC depends on parameters such as pressure, temperature, and additives. For most industrial applications, the CMC must be exceeded to achieve the maximum surfactant effect, be it for lowering the interfacial tension, emulsification, or suspension stabilisation. A further increase in surfactant concentration leads to orderly packing of the micelles with packs called liquid crystals. Such micelle arrangements increase the viscosity. [21, 22]

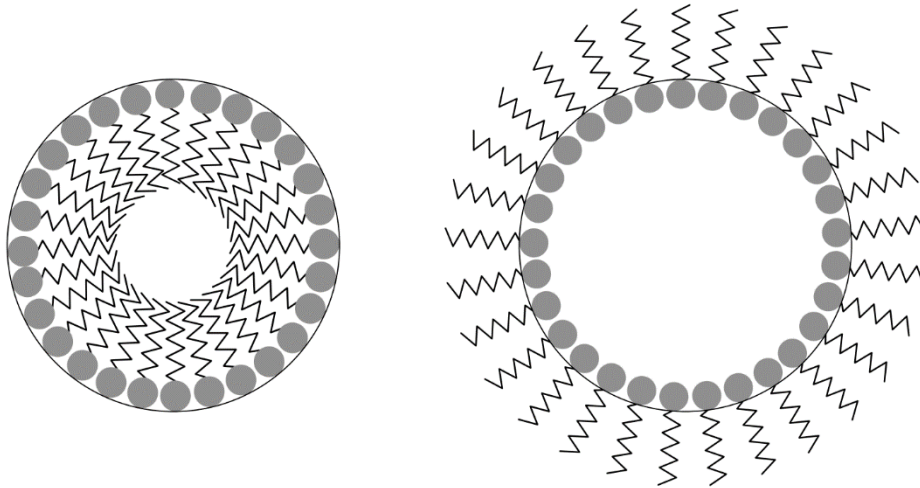


Figure 2-2 Drawing of a micelle (left) and an inverse micelle (right)

## 2.2.4 Emulsion

An emulsion is a colloidal dispersion of two immiscible liquids. One of the liquids/fluids is finely distributed in the continuous phase. The finely divided droplets are called the disperse phase, while the continuous one is also called the outer phase. In principle, a distinction is made between organic droplets dispersed in water (O / W) and aqueous droplets dispersed in the organic phase (W / O). [21, 22]

Most emulsions are thermodynamically unstable, except for microemulsions. The addition of emulsifiers, usually surfactants, facilitates the formation and makes it difficult to split the emulsion. Since emulsions are not desirable everywhere, they must be split to achieve phase separation. In order to separate the phases, the droplets must first agglomerate or coagulate and these droplet agglomerates then coalesce. These steps can be initiated using various splitting methods. Chemical splitting processes are carried out either with the help of acids or salts. In thermal processes, energy is supplied to the system in form of heat. A widespread physical splitting process is centrifugation. [21, 22]

## 2.3 Nickel

Nickel with the atomic number 28 is a ferromagnetic element. The silvery-white metal is counted as heavy metal due to its density of 8.908 g/cm<sup>3</sup> [23]. As a transition metal nickel has valence electrons in two shells (s and d). The electron configuration of nickel is [Ar] 3d<sup>8</sup> 4s. Its most common oxidation state is +2. In Pearson's Hard Soft Acid-Base (HSAB) principle Ni 2+ is seen as a borderline case.

### 2.3.1 Transition Metals – The d-block Elements

All transition elements are metals. Therefore, these elements are also called transition metals. The International Union of Pure and Applied Chemistry (IUPAC) regards transition elements as elements with an incompletely filled d-shell or elements that form ions with an incompletely filled d-shell. [24] There are four typical characteristics for transition metals: formation of colourful compounds, good catalytic activity, the ability to have many different oxidation states and the ability to form coordination complexes.

Transition metals are classified as Lewis acids which like to form coordination complexes with Lewis bases. According to the acid-base concept by Lewis, a Lewis acid is defined as an electrophilic electron pair acceptor and a Lewis base as an electron-pair donor.

### 2.3.2 Complex Chemistry

In general, a coordination complex consists of a central atom M and ligands X<sub>a</sub>, L<sub>b</sub> (a and b represent the number of the ligand). Central atoms are Lewis acids, i.e. transition metals, other metals and, more rarely, non-metals with an electron deficit. Ligands are Lewis bases, basically molecules with a free electron pair. Unlike in a normal atomic bond, the bonding electron pair comes from the ligand only. The valence of the central atom influences the thermodynamic stability of such a complex. With the same ligand, the central atom M<sup>2+</sup> is more stable than M<sup>3+</sup>. The Irving-Williams series (Mn<sup>2+</sup> < Fe<sup>2+</sup> < Co<sup>2+</sup> < Ni<sup>2+</sup> < Cu<sup>2+</sup> > Zn<sup>2+</sup>) represents another indicator for the stability of transition metal complexes regardless the type of ligands or their molecule number. [25]

According to the HSAB (Hard Soft Acid-Base) principle, the following applies to the stability of complexes and the prediction of reactions: hard acids preferably react with

hard bases and soft acids with soft bases. The bond formed between hard species has an ionic character and the bond formed between soft species has a more covalent character. Yet predictions are hard to make in inorganic chemistry. Predictions based on HSAB should not be considered carved in stone, but rather as guidelines. Hard acids are hard to polarise, are small and more highly charged. If a cation has more than one oxidation state, its higher one is considered as the harder acid ( $\text{Fe}^{3+}$  harder than  $\text{Fe}^{2+}$ ). Soft acids are easily polarisable, large and have low oxidation states such as  $\text{Pd}^{2+}$  and  $\text{Pt}^{2+}$ . There are also borderline cases like  $\text{Ni}^{2+}$  that lie in-between. [26]

The coordination number (CN) and the coordination polyhedron are decisive for the structure of the complex. The CN is the number of ligands bound to the central atom, two being the lowest and nine the highest. The most common CNs are six and four. The geometric figure of the ligands around the central atom is called a coordination polyhedron.

Possible coordination polyhedrons for CNs from two to six are:

- CN=2: linear
- CN=3: trigonal planar
- CN=4: tetrahedral or square planar
- CN=5: trigonal bipyramidal or square pyramidal
- CN=6: octahedral or trigonal prismatic

The following represent coordination complex possibilities for nickel:

- CN=6: octahedral, paramagnetic
- CN=4: square planar, diamagnetic; tetrahedral, paramagnetic
- CN=5: trigonal bipyramidal; square pyramidal

### 2.3.3 Structural Elucidation

With the help of spectroscopic methods, it is possible to determine the structure of a molecule. This usually requires a combination of several spectroscopic methods to make a reliable statement. Problems with this type of structure elucidation arise for molecules with many similarly bonded carbon atoms or few hydrogen atoms, but also with metal complexes. In the case of paramagnetic metals, nuclear magnetic

resonance (NMR) spectroscopy can only provide partial structures or no information at all. In this case, an X-ray structure analysis can be carried out on a single crystal.

## 2.4 Esterification Reactions

In general, a reaction is called esterification when an organic acid reversibly reacts with an alcohol to form an ester while eliminating water. This reaction belongs to nucleophilic substitutions. Carboxylic acids are only suitable for esterification if an acidic catalyst is used since carboxyl groups can only be protonated by strong acids. Even small proportions of protonated carbonyl groups are enough to accelerate the substitution reaction considerably since the protonated group is a very strong electrophile. The protonation by the acid is reversible. Protonated carboxylic acids can even be successfully attacked by a weak nucleophile such as alcohols. [19, 27]

Hydroxide ions are considered as poor leaving groups. To be more suitable as a leaving group the hydroxide ions are protonated with the aid of acidic catalysts – so not hydroxide but water is split off. The reverse reaction of esters with water to form carboxylic acids and alcohols is known as the hydrolysis reaction. [27]

Since these are equilibrium reactions, it is necessary to shift the reaction equilibrium to the side of the ester. Either an excess of alcohol (carboxylic acid would also be possible) can be used, or one of the products can be separated off. Figure 2-3 shows the reaction equation of the esterification reaction used in this work with acetic acid as carboxylic acid and *n*-octanol as alcohol. The newly developed catalyst (4-DBSA modified with nickel) was tested for this esterification reaction. [27]

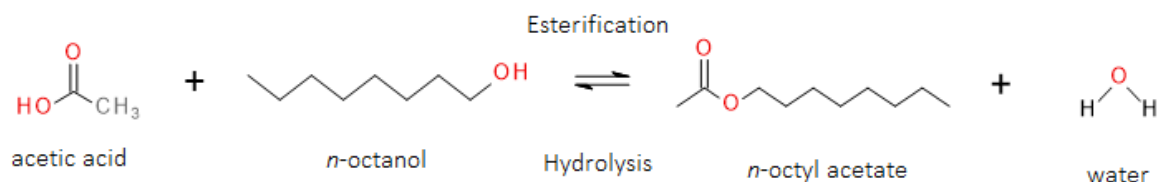


Figure 2-3 Reaction equation of the esterification of acetic acid and *n*-octanol to *n*-octyl acetate and water, and its backward equilibrium reaction



## 3 Current Scientific Knowledge

### 3.1 4-Dodecylbenzenesulphonic Acid as Catalyst

4-Dodecylbenzenesulphonic acid (4-DBSA) is a strong sulphonic acid that, due to its structure, has the properties of an anionic surfactant. Its applicability as a catalyst has been shown for Mannich-type reactions [28], etherification reactions [29, 30], esterification reactions [30–32] and the Biginelli reaction [33] amongst others. For this work, 4-DBSA is used to catalyse carboxylic acid esterification reactions. Various publications show that 4-DBSA accelerates the reaction rate and thus the equilibrium conversion can be achieved more quickly even at low temperatures than with non-catalysed reactions. This is made possible by the formation of a microemulsion. Accordingly, 4-DBSA is counted as a Bronsted acid-surfactant-combined (BASC) catalyst. [30, 34]

Saam et al. described the direct polyesterification of diols in aqueous emulsion utilising sulphuric acid, 4-DBSA, and the sodium salt of 4-DBSA as catalyst. The use of a surfactant was decisive for cation exchange across the oil-water interface. According to the authors, the degree of polymerisation surpassed expectations compared to experiments in a similar environment. [35][30]

In 2002, Manabe et al. carried out the esterification of lauric acid with 3-phenyl-1-propanol using various surfactants at 40° C for 24 h in water. Among the catalysts used, 4-DBSA performed best with a 60 % yield, which is attributed to the combined effect of the BASC catalyst. In contrast, the esterification reactions using simple Bronsted acids such as sulphuric acid or *p*-toluene sulphonic acid (TsOH) proceeded very slowly with 1 and 4 % yields. The course of the reaction of the 4-DBSA sodium salt was just as ineffective. 4-octyl benzene sulphonic acid (OBSA), whose only difference to 4-DBSA is a shorter alkyl chain of 8 and not 12 carbon atoms, resulted in a significantly slower reaction rate with 39 % conversion. This suggests that the chain length of the alkyl chain plays an important role in the catalytic effect. 4-DBSA catalysed biphasic reaction systems form emulsions which are not desirable for every application. The formation of the emulsion has already been observed for different reactions such as the Mannich reaction. This is caused by the surfactant properties of

the 4-DBSA and thus also contributes to the acceleration of the biphasic reaction since the acid is present in the aqueous phase and the alcohol in the organic phase. [30, 36]

In 2017, Zheng et al. described BASC as a new catalytic system in his publication. He referred to 4-DBSA and its usefulness as a catalyst for esterification. The formation of sufficient hydrophobic emulsion droplets on the inside enables the water to be excluded during the reaction. The acid catalyst sites at the micelle boundaries promote catalysis. Yet Zheng et al. interjected that although 4-DBSA brings advantages, it is not a catalyst that is easy to recycle due to the complicated separation process. Therefore, greener catalysts should be sought. [37]

### **3.2 Catalyst Modification**

There is hardly any literature on the modification of the catalyst 4-DBSA with a metal to form a so-called metallosurfactant. To modify the catalyst, two different approaches were followed. One is a simple approach where 4-DBSA and the nickel salt are mixed in a mortar to react. The other is inspired by the separation of heavy metals from wastewater. For the second approach, different methods were tested. When performing these individually, parameters such as temperature, concentration, and pH-value were varied, as well as the applicability of the method and the use of different metal ions. These parameters were influenced by the literature of the following paragraphs.

In 2009, Landaburu-Aguirre et al. investigated the separation of zinc from wastewater through micellar-enhanced ultrafiltration (MEUF) using sodium dodecyl sulphate (SDS) as a surfactant. The anionic surfactant was used above its critical micelle concentration (CMC). The process was carried out at room temperature. When using SDS as a surfactant, the authors recommended a surfactant to metal ratio of over 5 to be able to separate zinc effectively. This recommendation, which Huang et al. experimentally confirmed, was advocated by the results of Landaburu-Aguirre. [38]

With the help of MEUF, Samper et al. separated the metal ions  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  from synthetic wastewater. SDS and linear alkylbenzene sulfonates (LAS) were used as anionic surfactants. The selected ratio of surfactant to metal was above

5 in all experiments. When LAS were used, complete separation was possible for all metal ions except nickel, even below the critical micelle concentration. In addition to the metal and surfactant concentration, the membrane parameters were mentioned as crucial parameters for metal separation in this process since this is a membrane process. According to the authors, the pH-value of the solution should not play a role with these two surfactants. [39]

Ferella et al. utilised an anionic surfactant, 4-DBSA, and a cationic surfactant, dodecyl amine, to separate lead and arsenic ions from wastewater using MEUF. Both surfactants were added under their CMC. (CMC at 25 °C: 4-DBSA  $1.3 \cdot 10^{-3}$  M and dodecyl amine  $1.5 \cdot 10^{-2}$  M; concentration used: 4-DBSA  $10^{-5}$  M und dodecyl amine  $10^{-6}$  M). The amount of 4-DBSA used dissolved completely in water, but dodecyl amine formed lumps. A separation of over 90 % was achieved for lead in contrast to only 19 % for arsenic. The authors noted that the amount of surfactant had to be minimised to save costs but did not make any specific recommendation. [40]

Another possibility besides MEUF are ion-exchange resins. Many of the strongly acidic resins in use have sulphonic acid groups as the exchange sites, whereas weakly acidic ones have carboxylic acid groups. Strongly acidic resins can be operated over the entire pH range down to pH 1. Weakly acidic resins cannot be used at pH values below 5, as the carboxylic acid group is no longer present in its charged form then and therefore no longer has any ion exchange capacity. The protons of the acid groups are used for the ion exchange with the metals. In 2006 Gode et al. published that the ion exchange depends on the pH value, the temperature, the initial metal concentration, and the contact time. For the cations examined by Gode et al. the following series was found:  $Ce^{4+} > Fe^{3+} > Pb^{2+}$ , which suggests that metal ions with a higher oxidation number are preferred for ion exchange. [41, 42]

In 2006 Gode et al. used the ion-exchange resin Lewatit S100, which has sulphonic acid in its sodium salt form as a functional group, to remove metal from wastewater. It was shown that the separation of chromium (III) depends on the contact time, the pH value and the concentrations at the beginning. For Lewatit S100 the maximum sorption was reached at a pH of 3.5 to 4, above pH 6 precipitation occurred. The reaction time until equilibrium was approximately 150 minutes. [42]

Polyethene-graft-polystyrene sulphonic acids (PE-g-PSSA) were examined for the adsorption of Co (II), Ni (II), Cu (II), Pb (II) and Ag (I). It was found that the adsorption proceeded quickly in the first 15 minutes and that equilibrium was reached for all metal ions after 30 minutes. The authors ascribed the rapid kinetics to the negatively charged sulphonic acid groups, which are also responsible for the fact that divalent metal ions are preferred over monovalent metal ions. Experiments were carried out in a pH range from 3.1 to 6.6, with any pH adjustments being made with 1 M NaOH or 1 M HNO<sub>3</sub>. The optimum pH was found to be 6.6. [43]

Popuri et al. utilised chitosan-coated PVC beads to remove Ni (II) and Cu (II) by adsorption. The effect of the pH value on the sorption behaviour was examined. The maximum sorption of Cu (II) was reached at pH 4 and of Ni (II) at an initial pH of 5. [44] When using acidic extractants such as di-(2-ethylhexyl) phosphoric acid (DEHPA) for wastewater treatment, the following problem arises: With each extracted metal ion of charge  $z +$ , exactly  $z$  protons of the extractant are released, which leads to a drop in the pH value. As the pH falls, the extraction decreases, which means that as the extraction progresses, the pH falls, and the metal transfer decreases. This can be counteracted by adding alkalis. Experiments showed that the extraction of divalent nickel bound with DEHPA fell below 10 % when the pH value reached below 3. [45]

### **3.3 Solvent Selection – Green Solvents**

The problem of the chemical industry not being sustainable is not solely a problem at an industrial scale. To ensure a future with less organic solvent waste and unnecessary waste in general, more environmentally friendly choices must already be made at university level in research and teaching. Besides the fact that organic solvents make up the majority of synthetic chemical waste, there is also the question of how to dispose the mostly non-recyclable material. On top of that, the demand for energy to produce and/or clean the solvent is high. Often reaction conditions in a higher temperature range are required. [46]

In terms of environmental reasons, safety, and cost-efficiency, water identifies as the most desirable solvent. After more than a century of synthetic chemistry focusing on reactions in organic solvents, research in this area is still limited. Yet nature clearly

shows that chemical reactions in water are possible for water-soluble, as well as water-insoluble materials. [46, 47]

Various guidelines are available to make an environmentally more conscious decision when choosing a solvent. In addition to water, liquid polymers, supercritical liquids, ionic liquids, or supercritical carbon dioxide are generally seen as a greener alternative. Their sometimes very complex synthesis and the lack of toxicity parameters are major disadvantages. With the Chem 21 Solvent Selection guide, an attempt was made to compare already existing guidelines. The guide was created through a collaboration between various pharmaceutical groups, universities, and companies. Solvents were evaluated according to the five categories: safety, health, and environment (air, water, and waste). For each category, specific criteria were established. The colour coding system gives a quick overview. Each colour code has assigned scores. Solvents with a score from one to three are assigned the colour green, scores from four to seven are shown yellow, and scores from eight to ten are shown red. Green represents the recommended solvents, whereas red is used for overly hazardous ones. Unfortunately, neither *n*-undecane nor *n*-octanol is included in the guide. [46, 48, 49]

Tobiszewski et al. assessed 151 solvents under the aid of "Technique for Order of Preference by Similarity to Ideal Solution" (TOPSIS) analysis to sort them into three different clusters. Alternatives such as ionic liquids or eutectic solvents were not listed due to a lack of data. The division was made into three clusters and rankings within the clusters. For the division into clusters, variables such as melting point, boiling point, water-solubility, Henry's constant, surface tension, and others were used. The ranking within the cluster was in turn determined by variables such as the LD<sub>50</sub>, flammability, flash point, half-life biodegradation. *n*-Undecane stands at the top of cluster two which consists of water-insoluble compounds with high boiling points. According to this guide, when a water-insoluble solvent is required *n*-undecane represents the first choice. [50]

## 4 Materials and Analytical Methods

### 4.1 Materials

Table 4-1 shows the materials used for the preparation of the catalyst and the subsequent esterification experiments. All chemicals were utilised as supplied without further purification.

*Table 4-1 List of chemicals used for the catalyst preparation and the esterification experiments. The list includes the names of the chemical compounds, their molecular formula, CAS-number, purity, and the manufacturer*

Name of Compound	Molecular Formula	CAS-number	Purity	Manufacturer
Nickel(II) hydroxide	Ni(OH) <sub>2</sub>	12054-48-7	-	Sigma-Aldrich
4-dodecylbenzenesulphonic acid	C <sub>18</sub> H <sub>30</sub> O <sub>3</sub> S	121-65-3	>95%	Sigma-Aldrich
<i>n</i> -octanol	C <sub>8</sub> H <sub>17</sub> OH	111-87-5	>98%	Sigma-Aldrich
<i>n</i> -undecane	C <sub>11</sub> H <sub>24</sub>	1120-21-4	>99%	Sigma-Aldrich
Acetic acid	CH <sub>3</sub> COOH	64-19-7	>99%	ChemLab

### 4.2 Analytical Methods

In Table 4-2 an overview of the analytical equipment utilised in this work is shown. The individual methods were applied for the following: The amount of nickel in the aqueous phase after the reaction was determined through flame atomic absorption spectrometry (AAS). Gas chromatography (GC) was used to monitor the reaction progress and calculate the yield of carboxylic acid ester. The interfacial tensions of different liquid-liquid systems were measured with a spinning drop tensiometer. A total organic carbon (TOC) analyser was utilised to determine the residual organic carbon in the aqueous phase after the reactive separation step. A Karl-Fischer titrator was used to measure the water content in the organic phase.

Table 4-2 List of analytical equipment with model and manufacturer

<b>Equipment</b>	<b>Model</b>	<b>Manufacturer</b>
Flame atomic absorption spectrometer	AAAnalyst 400	Perkin Elmer
Gas chromatographer	GC 2010 Plus	Shimadzu
Spinning drop tensiometer	Dataphysics SVT 20N	Dataphysics
Total organic carbon analyser	TOC- L	Shimadzu
Karl- Fischer titrator	TitroLine 7500 KF	SI Analytics
Densimeter	SVM 3000	Anton Paar

#### **4.2.1 Flame Atomic Absorption Spectroscopy (F-AAS)**

An atomic absorption spectrometer (AAS) is made up of the following four units: radiation source, atomisation unit, monochromator, and detector. Hollow cathode lamps containing the element to be analysed are used as the radiation source. These emit the line spectrum of the respective element.

In F-AAS a flame is used as the atomisation unit. The liquid sample is sprayed into the combustion chamber using a nebuliser, where it is mixed with a fuel gas (acetylene) and oxidant (synthetic air). Only the finest particles of the aerosol get into the flame, where the sample is atomised. The individual atoms absorb radiation emanating from the corresponding hollow cathode lamp. Behind it, the monochromator with the exit slit ensures that the spectral line of the element is selected and can be measured in the detector placed downstream.

Before the measurements could be started, the samples had to be diluted to the correct concentration range with dilute nitric acid (if necessary). Also, for each element separate calibration solutions were prepared which were measured before the actual samples. The sample concentration should be within the measured calibration range. For the measurement of the calibration and sample solutions, prefabricated methods for determining nickel were used. Before starting the measurement, the flame was burned out for about 15 minutes to remove any impurities.

#### **4.2.2 Gas Chromatography (GC)**

Gas chromatography is based on the principle of the interaction between the analyte and the stationary phase, the GC column. A precisely defined sample volume is injected using a heated injector. The sample is completely evaporated and then transported through the column by a carrier gas (mobile phase). The individual analytes interact differently with the active layer of the separation column, which means that the retention times of the substances are different. One (or more) detectors are attached to the end of the column. In this case, a thermal conductivity detector (TCD) and a flame ionisation detector (FID) were used in parallel. The peaks caused by the retention time are characteristic sizes of the individual substances and thus enable quantification.

A GC 2010 Plus from Shimadzu was used for the analysis. A ZB WAXplus<sup>TM</sup> column with a length of 60 m, an internal diameter of 0,32 mm and a layer thickness of 50  $\mu\text{m}$  was selected as the separation column. The method ZB-WAXplus-OcOH was used to track the reaction progress.

#### **4.2.3 Spinning Drop Tensiometer**

Spinning drop tensiometry enables the measurement of interfacial tensions between immiscible fluids. The measurement is carried out in a horizontally rotating capillary. As a rule, the denser fluid represents the continuous phase in which there is a drop in the discontinuous phase. The centrifugal force acts through the rotation of the capillary and causes a cylindrical deformation of the drop. This occurs since the centrifugal force pushes the denser liquid towards the capillary walls while the less dense drop is pushed towards the axis of rotation. The drop deformation leads to an increase in the drop's interface. Since the interfacial tension counteracts the centrifugal force, the drop reaches a stable shape when the forces are in equilibrium. The interfacial tension can be determined from the drop shape in its equilibrium state. [51, 52]

Bernard Vonnegut developed the classical approach for the determination of the interfacial tension with the spinning drop method. In this approach, gravitation is neglected, and the length of the drop is assumed to be significantly larger than its radius (length to radius ratio of over four). Therefore, the drop's shape in the



calculations is presented as a cylinder with hemispherical ends. The empirical formula (Equation 1) for the interfacial tension is derived from the drop's minimum energy in an equilibrium state. [53]

$$\sigma = \frac{\Delta\rho R^3 \omega^2}{4} \quad \text{Equation 1}$$

- $\sigma$  interfacial tension
- $\Delta\rho$  density difference between phases
- $R$  drop radius
- $\omega$  angular frequency

The advantage of the Young-Laplace method is that it takes the curvature of the drop into account. According to the Young-Laplace equation (Equation 2) the interfacial tension, the curvature of the drop and the Laplace pressure are related. This approach can be used for spherical and non-spherical drop shapes. [52]

$$\Delta P = \sigma * \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad \text{Equation 2}$$

- $\Delta P$  pressure difference between phases
- $\sigma$  interfacial tension
- $R_i$  maximum curvature radii (i=1,2)

While the Young-Laplace method takes the curvature into account, the method by Cayias, Schechter and Wade is based on the width and the diameter of the drop. Therefore, this approach is less accurate than the one of Young-Laplace. [54]

To measure the different interfacial tensions a Dataphysics SVT 20N spinning drop tensiometer was used. The equipment included an adjustable platform (angle) to position the drop, a moving camera, and a thermostat. For higher temperatures starting from 50 °C an additional cooling device (a cryostat) was necessary. Detailed

information on the preparation process, the measuring and cleaning of the capillary can be found in chapter 5.2.

#### **4.2.4 Total Organic Carbon (TOC)**

A TOC measurement determines the total content of organic carbon in a sample. It is a widely used method in environmental analysis. In water and air, the TOC gives information about the contamination state with foreign substances. For this research, the TOC is relevant for the catalyst production to determine how much organic carbon is still in the aqueous phase after the formation of the metallosurfactant. The concentration of all species occurring in the aqueous phase, except for 4-DBSA and  $[\text{Ni}(\text{DBSA})_2]$ , is determined via GC measurements. With the help of the GC measurements, the so-called  $\text{TOC}_{\text{max}}$  can be calculated. Since inorganically bound carbon is not specified and all other compounds are included in the  $\text{TOC}_{\text{max}}$ , the measured TOC value gives information about the consumption of 4-DBSA.

The sample preparation included, if necessary, the dilution of the sample with ultrapure water. The sample tube was placed in an autosampler and then measured using TOC-L from Shimadzu. The provided method "niki.met" was used for the measurement.

#### **4.2.5 Karl-Fischer Titration (KF titration)**

The Karl-Fischer titration is a volumetric titration method to determine the water content in a sample. The water content in the catalyst solution was measured at different stages of the preparation process (before/after rinsing, after the esterification). The analysis of the samples was performed with a SI Analytics TitroLine 7500 KF under the use of a KF1100 electrode. For the titration, the two-component reagents Titrant 5 and Aquastar from Merck were used.

#### **4.2.6 Density Measurements**

All density measurements were carried out using Anton Paar's SVM 3000 viscometer. The densities were measured at 25 °C, and for a few selected samples at 60 °C to provide the necessary data for the spinning drop tensiometer.

## 5 Experimental Part

### 5.1 Preparation of the Nickel-based Metallosurfactant Catalyst

Two different approaches for the preparation of the catalyst were followed:

- biphasic approach with the nickel salt dispersed in water and the surfactant dissolved in the solvent phase
- direct mixing of 4-DBSA and a nickel salt in a ceramic mortar

#### 5.1.1 Biphasic Approach

Before this thesis, different methods have been tested for the biphasic approach. Information on this can be found in the Supporting Information of Toth's publication. [55] The main findings include: The surfactant 4-DBSA was successfully modified to lose its emulsifying property. During the experiments, a few problems arose i.e. instability of the complex, poor catalytic activity, solubility problems, and phase separation problems. For the modification of the 4-DBSA different metal cations (Fe(III), Fe(II), Ni(II)) were experimented with. In some cases, iron cations were successfully used to prepare a catalyst solution. However, the catalytic activity of these catalyst solutions was negligible which was tested in esterification experiments. Catalyst solutions made with nickel cations showed to have a higher catalytic activity and to suppress the emulsifying behaviour almost completely. The best results were achieved with the method presented in the next subchapter. Therefore, the catalysts of this approach were all made by this method. The drawback of this method is that solubility in the solvent phase (*n*-undecane) without *n*-octanol present is low.

### **5.1.1.1 Developed Method for Catalyst Preparation as a Solution**

This method is applicable for surfactant concentrations from millimoles up to 10 w% of the solvent phase. Above all, sufficient stirring time and sufficient thermal activation are decisive. The method includes the following steps:

- 4-DBSA completely dissolved in the solvent phase in a beaker
- Ni(OH)<sub>2</sub> is dispersed in deionised water in a separate beaker
- The solvent phase is transferred to the aqueous phase (the reaction mass becomes viscid).
- The reaction mass is stirred for 10 minutes before it is heated up to ~80 °C and stirred for another 90 minutes.
- The catalyst solution (solvent phase) is separated from the aqueous phase.

### **5.1.2 Direct Mixing Approach**

This preparation procedure was started by adding nickel(II) hydroxide in powder form to liquid 4-DBSA in a porcelain mortar. A pestle was used to mix the chemicals thoroughly. No change in the temperature of the reaction mixture was perceived during this step, but bubble formation (presumably due to the inclusion of oxygen) was observed. Various stoichiometric ratios of nickel to 4-DBSA (1:1, 1:2, 1:4) were tested. These were chosen under consideration of the possible oxidation states of nickel (+2, +4). The combination of the educts resulted in a paste. After the mixing process, the paste was dried at ambient conditions. Varied parameters in this step of the preparation were the mixing time of the chemicals in the porcelain mortar and the drying time of the paste. Figure 5-1 shows the paste during different steps of the preparation process: right after mixing, after 40 minutes of drying and after 210 minutes of drying. At the surface, a clear change in appearance can be observed. Then the dried paste was attempted to be dissolved in a solvent.



Figure 5-1 Metallosurfactant catalyst with the stoichiometric ratio of 1:2 (nickel to 4-DBSA) right after mixing (left), 40 minutes of drying (middle), and 210 minutes of drying (right)

### 5.1.2.1 Developed method for the catalyst preparation as paste

For the preparation of the catalyst, a stoichiometric ratio of 1:2 of nickel to surfactant is used. The procedure includes the following steps:

- 4-DBSA is weighed into the mortar
- Ni(OH)<sub>2</sub> is weighed in the correct ratio in a weighing boat
- To avoid inhaling of the finely powdered nickel hydroxide, the powder is transferred into the mortar under the laboratory hood from the weighing boat
- When the hood is almost closed, a pestle is used for at least 20 minutes to mix the reactants.\* At the beginning, the nickel hydroxide powder must be mixed carefully with 4-DBSA to minimise the loss of the powder.
- The paste must now be left to dry for at least 48 hours before it can be dissolved.

\*A 20-minute mixing is sufficient for pastes up to 18 g of 4-DBSA<sub>95%</sub>.

### 5.1.2.2 Solubility

Initially, an attempt was made to dissolve varying amounts of the dried paste in different solvents and solvent mixtures at ambient temperature. Catalyst pastes with stoichiometric ratios of 1:2 and 1:4 for nickel to surfactant were tested. No significant differences were observed between the two ratios. The amount of dried paste is given in weight per cent. These experiments were carried out with the thought in mind to use *n*-undecane as the solvent phase in the subsequent esterification experiments. "*Similia similibus solventur*" is a rule of thumb that is regularly used in chemistry to predict solubility. According to this rule, the compound to be dissolved is soluble in a solvent with a similar structure to its own. So, to enhance the dissolving behaviour modifying agents (polarity) and heat were used.

The catalyst paste is neither soluble in pure *n*-undecane nor water. As modifying agents Cyanex 923, di-(2-ethylhexyl) phosphoric acid (DEHPA) and *n*-octanol were utilised. Cyanex 923 is a phosphine oxide consisting mainly of a mixture of four trialkylphosphine oxides. [56] DEHPA is an organophosphoric acid. Both compounds are used in solvent extraction. [57–61] Cyanex 923 and DEHPA did not qualify as suitable modifying agents. However, *n*-octanol was identified as a suitable modifier and solvent. In solubility experiments with a solvent mixture of 70 w% *n*-undecane and 30 w% *n*-octanol, up to 5 w% catalyst was dissolved in the mixture at a temperature of 90 C. In Figure 5-2 the result of the solubility experiment is shown without (left flask) and with additional heating (right flask). In the round-bottomed flask on the left-hand side, the catalyst paste is not fully dissolved, whereas in the round-bottomed flask on the right-hand side the catalyst paste is completely dissolved. Various combinations of these two solvents were tested, with the mixture 70 w% *n*-undecane and 30 w% *n*-octanol identifying as the most appropriate. Mixtures with lower *n*-octanol content did not perform as well in terms of catalyst solubility even when substituted with other modifying agents. Furthermore, tests showed, that the catalyst dissolves in pure *n*-octanol when heated. The maximum catalyst load dissolved in pure *n*-octanol is 28 w% (Figure 5-3).



*Figure 5-2 Catalyst paste dissolved in the solvent mixture 70w % *n*-undecane/30 w% *n*-octanol; left: no additional heating was used - the paste is not fully dissolved; right: additional heating at 70 °C for 1h - the paste is fully dissolved*

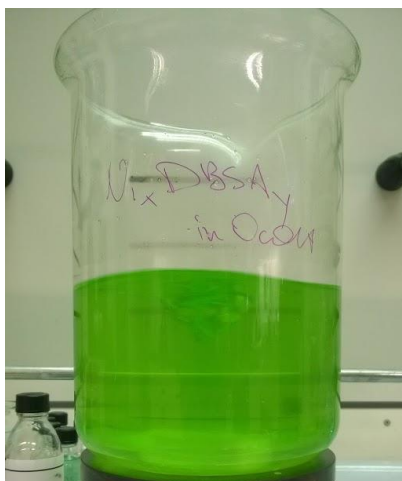


Figure 5-3 Catalyst solution with a catalyst load of 28 w% in pure *n*-octanol

Since the alcohol *n*-octanol qualified as a suitable solvent, other alcohols were also tested. Methanol and ethanol were found to be suitable solvents even without heating. Other solvents that were tested were chloroform (soluble), hexane (non-soluble), dimethyl sulfoxide (colour change, suggests ligand displacement) and isopropanol (whitish precipitate).

### 5.1.2.3 Rinsing and Water Saturation

Since the esterification reaction of acetic acid with *n*-octanol is biphasic the catalyst solution must not form an emulsion on contact with water. Therefore, deionised water was carefully pipetted under the solvent phase containing the catalyst to test its behaviour when in contact with water. As displayed in Figure 5-4, emulsification occurred at the interfacial surface area (and in some cases over the entire solvent phase), but the primary phase separation had occurred immediately. Since 4-DBSA was the only surfactant present in the system, this implied that unbound 4-DBSA was still present. To wash out the residual unbounded surfactant, the catalyst solution was rinsed with deionised water in a separating funnel. Besides, the solution was saturated with water to counteract the co-extraction of water during the esterification reaction. Consequently, the volume of both phases should stay approximately constant throughout the reaction. KF-titration, interfacial tension and density measurements were carried out for two different catalyst solutions before they were rinsed, after they were rinsed, and after the esterification. These measurements were performed to document the effect of water saturation on the catalyst solution.

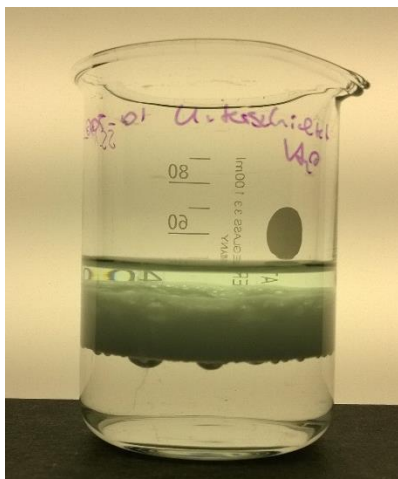


Figure 5-4 Catalyst solution SS\_AT\_005\_01 (2,5w % catalyst in 70 w% *n*-undecane/30 w% *n*-octanol) underlaid with deionised water. The system is emulsified at the interface and parts of the solvent phase

The executed experiments resulted in the following procedure to dissolve the catalyst paste:

- The dried catalyst is weighed into a beaker
- The desired amount of *n*-octanol is added to the beaker
- For catalyst loads up to 5 w% 1 hour of stirring at 70 °C is sufficient. Catalyst loads above 5 w% require stirring for 1.5 hours at a temperature of 90 °C
- Allow cooling to room temperature in air
- Rinse the dissolved catalyst once with deionised water in a separation funnel, await phase separation.
- Separate the solvent phase from the aqueous phase to use in the esterification reaction

#### 5.1.2.4 Crystallisation

Crystallisation techniques used in classical preparative chemistry were tested. The catalyst paste was dissolved in suitable solvents and solvent mixtures. Then all possible combinations of the following methods were appraised: The catalyst in solution was stored open or with a cling film on the beaker and at room temperature or in the fridge. To initiate the crystallisation process non-soluble solvents were dropwise added, the beaker glass was scratched, and/or a broken glass tip was added to the catalyst solution. Various rounds of rinsing the catalyst and drying, filtration through a filter syringe, or fluted filters didn't show any results. As solvents, all the solvents mentioned in chapter 5.1.2.2 were used. (Combinations: different solvents and storing at room temperature; different solvents and storing in the fridge; different solvents,



addition of a non-soluble solvent and storing at room temperature; different solvents, addition of a non-soluble solvent and storing in the fridge; different solvents, scratching glass, adding a glass tip and storing at room temperature; different solvents, scratching glass, adding a glass tip and storing in the fridge; different solvents, filtration and storing at room temperature; different solvents, filtration and storing in the fridge; different solvents, filtration, dissolving again and storing at room temperature; different solvents, filtration, dissolving again and storing in the fridge; different solvents, filtration, dissolving again, addition of a non-soluble solvent and storing at room temperature; different solvents, filtration, dissolving again, addition of a non-soluble solvent and storing in the fridge; different solvents, filtration, dissolving again, scratching glass, adding a glass tip and storing at room temperature; different solvents, filtration, dissolving again, scratching glass, adding a glass tip and storing in the fridge)

#### **5.1.2.5 Stability**

To get a sense of the stability of the dissolved catalyst, an acid or base was added to the catalyst solution. For this purpose, catalyst solutions with 5 w% of catalyst dissolved in *n*-octanol were used. The addition of sulphuric acid (concentrated and diluted) immediately built white flakes, which slowly vanished with time. After standing for a while, a turquoise, crystalline precipitate formed (same day). The appearance of the precipitate indicates nickel sulphate hexahydrate. When concentrated acetic acid was added, a fine, white precipitate formed. Consequently, the catalyst may not be used for reactions that contain strong acids or weak concentrated acids. The catalyst solution's viscosity increased under the dropwise addition of sodium hydroxide and white, gelatinous precipitate occurred. Thus, the usage of the catalyst is not advised in the presence of a base.

#### **5.1.3 Biphasic Esterification: Experimental Set-up, Parameters and Method**

The biphasic esterification experiments were carried out at 60 °C for three hours. The ratio of the aqueous phase (water, acetic acid) to the solvent phase ([Ni(DBSA)<sub>2</sub>] in *n*-octanol or *n*-octanol and *n*-undecane) was 1:1 with a total reaction volume of 300 ml. As initial concentration of acetic acid 1 mol/l was chosen. The stoichiometric ratio between the reactants acetic acid and *n*-octanol was 1:1. 1 mol/l was chosen as the

initial concentration for acetic acid in the aqueous phase. The stirring speed was varied between 380 rpm and 800 rpm depending on the stirring bar and catalyst used.

All reactions were carried out in a 500 ml three-necked flask with a reflux condenser in the middle to minimise evaporation losses. The two outer openings were utilised to monitor the temperature of the reaction mass with a temperature sensor and for the addition of the acid through a cannula. As heat source a magnetic stirrer hotplate was used, and a cryostat connected to the reflux condenser was used for cooling. To make handling easier and ensure an easy installation and removal of the three-necked flask, a laboratory scissor jack was placed under the heating plate and a suitable heating attachment was placed on the heating plate.

Deionised water was placed in the three-necked flask. Prior to installing the three-necked flask into the apparatus the solvent phase including the catalyst was filled into it. The reaction mixture should be heated to 60 °C and stirred. The stirrer speed was chosen so that the reaction mixture was mixed thoroughly. During the heating process, the required amount of concentrated acetic acid was weighed into a disposable syringe. When the reaction temperature was reached, the acetic acid was injected via the cannula and the reaction started. A sample was taken from the aqueous and solvent phase every 30 minutes. For this purpose, the stirrer was stopped, phase separation was awaited, and 0.2 ml samples were taken in each case. After three hours, the reaction was terminated by turning off the heat source. The entire product mixture was then weighed and transferred to a separating funnel to gravitationally settle. Both phases were weighed separately to be able to establish a mass balance.

The metallosurfactants shown in Table 5-1 served as catalysts for the esterification reaction. This table shows the metal to surfactant ratio of the catalyst, the amount of catalyst based on the solvent phase, how the solvent phase is composed and whether the dissolved catalyst was rinsed with deionised water.

Table 5-1 List of metallosurfactant catalysts used for the esterification reaction. The list includes the metal to surfactant ratio of the catalyst, the catalyst loading, the composition of the solvent phase and whether the dissolved catalyst was rinsed or not. Unless stated otherwise catalyst solutions were prepared via the direct mixing approach. The mixture solvent phase is composed of 70 w% undecane and 30 w% n-octanol

Experiment	Ni:4-DBSA	w% catalyst	Solvent	Rinsed
SS_AT_015	1:2	5	OcOH	yes
SS_AT_016	1:2	5	OcOH	yes
SS_AT_068	1:2	10	OcOH	yes
SS_AT_069	1:2	10	OcOH	yes
SS_AT_062	1:2	28	OcOH	yes
SS_AT_071	1:2	28	OcOH	yes
SS_AT_063	1:2	28	OcOH	yes
SS_AT_010	1:4	5	OcOH	no
SS_AT_070	1:4	5	OcOH	yes
SS_AT_009	1:2	5	mixture	no
SS_AT_076	1:2	5	mixture	yes
SS_AT_012 <sup>1</sup>	1:4	5	mixture	-
SS_AT_075 <sup>1</sup>	1:4	5	mixture	-
SS_AT_074	1:4	5	mixture	yes
SS_AT_073	1:4	5	mixture	yes

<sup>1</sup>catalyst solutions were prepared via the biphasic approach

## 5.2 Spinning Drop Tensiometer Measurement

For the determination of interfacial tension via spinning drop tensiometry water was used as continuous phase and the catalyst solution (or solvent) served as discontinuous phase. The manufacturer describes three ways of filling the capillary, two of them were tested. One drop of discontinuous phase was placed on the wall of the capillary with a syringe. Then the continuous phase was tried to be transferred bubble-free into the capillary, if possible, from the bottom of the capillary to the top. Thereby the drop must not detach from the wall. It was not possible to fill the capillary with water without destroying the drop. The second method tested proved to be successful. Deionised water is placed in the capillary. Bubbles adhering to the bottom are tapped out. The capillary is placed horizontally, and one drop of the discontinuous phase is positioned on the wall of the capillary with a GC-syringe.

Before starting the measurements, calibration is necessary. For this purpose, two methods are available, automatic calibration and manual calibration. For all

measurements, automatic calibration was used according to the manual of the manufacturer.

Measurements are taken over a range of rotational speed rates. The rotational speed must not be too low, otherwise, buoyancy occurs. Therefore, measured values must be roughly constant. To measure the drop, the drop must be approximately stable. Three analysing modes are available. Whenever possible Laplace-Young (LY) is preferred. Cayias-Schechter-Wade (CSW) and Vonnegut (VG) are only used if the drop shape does not allow a full profile, since LY is the most accurate. While LY does take the drop's curvature into account, CSW is based on the width and diameter of the drop and VG only on the width. CSW is chosen when only one side of the drop is measurable, and VG is used for drops with a length to radius ratio of over four.

Since the cleanliness of the capillary has a big impact on the results, two procedures were created for cleaning the capillary. One for cleaning after a successful measurement of the catalyst solution in water and one for the case of an emulsion formation in the capillary. For the former, the capillary is flushed two to three times with isopropanol, two times with tetrahydrofuran (THF), and then placed in the vacuum drying cabinet to dry for at least one hour. For the latter, a bottle brush and isopropanol are used to clean the capillary from all visible residuals. Then the capillary is washed two times with isopropanol and two times with THF. Afterwards, the capillary is dried in a vacuum drying cabinet for at least one hour.

## 6 Results and Discussion

The preparation of a catalyst solution can be seen as successful if the catalytic activity is sufficient enough, emulsification is prevented, and the experiment is reproducible. Figure 6-1 displays two different outcomes. In the picture on the left, the whole solvent phase is emulsified, whereas, in the picture on the right, a clear solvent phase can be seen. Some experiments proved to be more promising than others.



Figure 6-1 Phase separation after *the esterification reaction with two different catalyst solutions*. Left: SS\_AT\_070; right: SS\_AT\_015

### 6.1 Overall Mass Balance

After the esterification, the reaction mixture was weighed to establish a mass balance. Additionally, the separated phases were also weighed. Table 6-1 shows the initial weight of the educt, the weight of the product as well as the experimental error for each esterification reaction. The error is given in percentage and represents the change in mass. All error values lie below 2 % which is an acceptable deviation. The experimental run SS\_AT\_063 (direct mixing approach, 28 w%, Ni:4-DBSA 1:2, *n*-octanol) stands out with an error of only 0.2 %. However, this experiment aberrates in terms of reaction performance from the other two esterification reactions carried out with the same parameters. Among the preparations for this experiment, an error must have occurred since the repetition of this experiment (SS\_AT\_071) matched the expectations and the results of experiment SS\_AT\_062. For the rest of the results and discussion part experiment SS\_AT\_063 will be excluded.

Table 6-1 List of esterification reactions with educt weight, product weight, and the error of the mass balance. Unless stated otherwise catalyst solutions were prepared via the direct mixing approach. The mixture solvent phase is composed of 70 w% n-undecane and 30 w% n-octanol.

Experiment	Ni:4-DBSA	w% cat	Solvent	Educt [g]	Product [g]	Error
SS_AT_009	1:2	5	mixture	259.29	254.4	1.9%
SS_AT_010	1:4	5	OcOH	273.6	268.5	1.9%
SS_AT_012 <sup>1</sup>	1:4	5	mixture	266.38	261.56	1.8%
SS_AT_015	1:2	5	OcOH	274.58	269.31	1.9%
SS_AT_016	1:2	5	OcOH	276.07	272.19	1.4%
SS_AT_062	1:2	28	OcOH	266.38	262.2	1.6%
SS_AT_063	1:2	28	OcOH	266.38	266.1	0.2%
SS_AT_068	1:2	10	OcOH	266.38	261.9	1.7%
SS_AT_069	1:2	10	OcOH	266.38	261.6	1.8%
SS_AT_070	1:4	5	OcOH	266.38	261.7	1.8%
SS_AT_071	1:2	28	OcOH	266.35	261.3	1.9%
SS_AT_073	1:4	5	mixture	259.99	255.5	1.7%
SS_AT_074	1:4	5	mixture	266.39	261.9	1.7%
SS_AT_075 <sup>1</sup>	1:4	5	mixture	267.81	262.8	1.9%
SS_AT_076	1:2	5	mixture	266.3	261.4	1.8%

<sup>1</sup>catalyst solutions were prepared via the biphasic approach

## 6.2 Conversion and Separation Efficiency

As a measure for the catalytic activity, the conversion of acetic acid ( $X_{HAc}$ ) was determined. For this calculation Equation 3 was used, in which  $C_{HAc,0}$  represents the initial concentration of acetic acid in the aqueous phase and  $C_{HAc,t}$  the total concentration at the end of the esterification determined in both phases.

$$X_{HAc} = \frac{C_{HAc,0} - C_{HAc,t}}{C_{HAc,0}} \quad \text{Equation 3}$$

The separation efficiency ( $SE_{HAc}$ ) gives information on the removal of acetic acid from the aqueous phase. The calculations of  $X_{HAc}$  and  $SE_{HAc}$  are very similar. Instead of the total acetic acid concentration at the end, only the concentration of acetic acid in the aqueous phase at the end was used (Equation 4).

$$SE_{HAc} = \frac{C_{HAc,0} - C_{HAc,aqu,t}}{C_{HAc,0}} \quad \text{Equation 4}$$

In Table 6-2 the determined conversion and separation efficiency values are listed.

It can be seen that the separation efficiency is higher than the conversion for all experiments. In experiments with a mixed solvent phase, the  $SE_{HAC}$  is around 10 % higher than  $X_{HAC}$ . If only *n*-octanol was used, the  $SE_{HAC}$  is up to 30 % higher than  $X_{HAC}$ . Although the highest conversions were achieved in the experiments SS\_AT\_070 (direct mixing approach, 5 w%, Ni:4-DBSA 1:4, *n*-octanol), SS\_AT\_076 (direct mixing approach, 5 w%, Ni:4-DBSA 1:2, solvent mixture), and SS\_AT\_074 (direct mixing approach, 5 w%, Ni:4-DBSA 1:4, solvent mixture), the catalysts used are not the most promising. The phase separation of the three experiments was poor due to the occurrence of emulsification – the modification of 4-DBSA was not successful in these cases. From Table 6-2 it can be also seen that increasing the catalyst load from 5 w% to 28 w% does not change the separation efficiency perceivably, whereas the conversion increases. Moreover, catalyst solutions by the biphasic approach were identified as non-further pursuable due to the failed suppression of emulsion formation and low separation efficiency.

Table 6-2 Conversion of acetic acid ( $X_{HAC}$ ) and separation efficiency of acetic acid ( $SE_{HAC}$ ) from the aqueous phase. Unless stated otherwise catalyst solutions were prepared via the direct mixing approach. The mixture solvent phase is composed of 70 w% undecane and 30 w% *n*-octanol

Experiment	Ni:4-DBSA	w% catalyst	Solvent	$X_{HAC}$	$SE_{HAC}$
SS_AT_015	1:2	5	OcOH	27%	53%
SS_AT_016	1:2	5	OcOH	27%	54%
SS_AT_068	1:2	10	OcOH	23%	48%
SS_AT_069	1:2	10	OcOH	26%	49%
SS_AT_062	1:2	28	OcOH	35%	55%
SS_AT_071	1:2	28	OcOH	37%	54%
SS_AT_010	1:4	5	OcOH	25%	55%
SS_AT_070	1:4	5	OcOH	54%	67%
SS_AT_009	1:2	5	mixture	33%	40%
SS_AT_076	1:2	5	mixture	58%	66%
SS_AT_012 <sup>1</sup>	1:4	5	mixture	26%	36%
SS_AT_075 <sup>1</sup>	1:4	5	mixture	21%	32%
SS_AT_074	1:4	5	mixture	45%	52%
SS_AT_073	1:4	5	mixture	18%	27%

<sup>1</sup>catalyst solutions were prepared via the biphasic approach

Figure 6-2 depicts the conversion of acetic acid with *n*-octanol as solvent phase. *n*-Octanol acts as reactant and solvent. The Figure clearly shows that catalysts dissolved in *n*-octanol with a nickel to surfactant ratio of 1:2 show more consistent results than catalysts with a ratio of 1:4. Increasing the catalyst load to 28 w% lead to

a higher conversion of acetic acid. Besides, the utilisation of *n*-octanol as solvent phase prevented emulsification completely when using catalysts prepared with a ratio of 1:2. Consequently, catalysts dissolved in pure *n*-octanol with a nickel-surfactant ratio of 1:2 identify themselves as most promising.

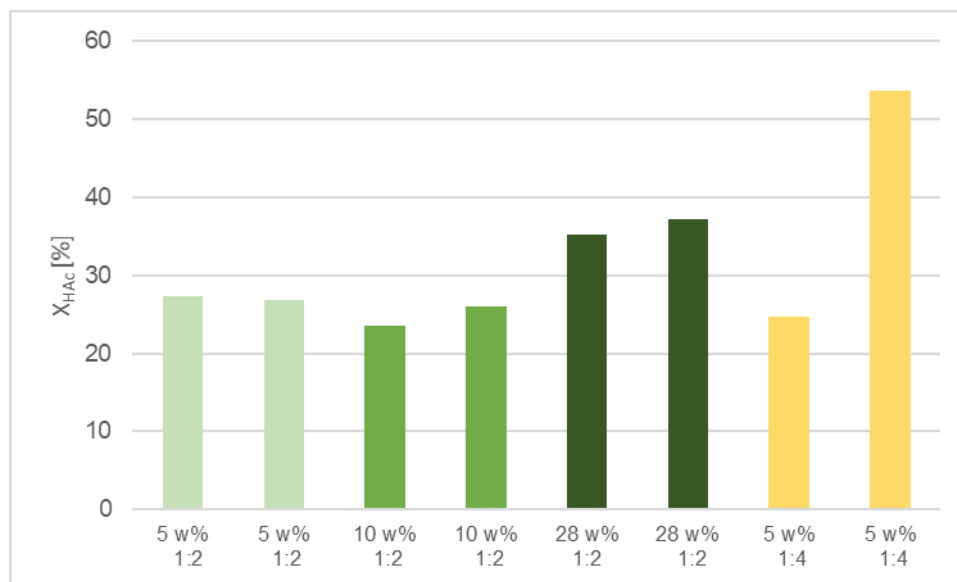


Figure 6-2 Effect of *n*-octanol as solvent phase on acetic acid conversion with different catalysts. All catalysts were synthesised via the direct mixing approach. For the catalyst preparation nickel to surfactant ratios of 1:2 (green bars) and 1:4 (yellow bars) were used. The esterification was carried out with an initial concentration of 1 mol/l acetic acid, and a phase ratio of 1, at 60 °C for three hours.

In esterification reactions using the solvent mixture 70 w% *n*-undecane and 30 w% *n*-octanol the formation of an emulsion could not be prevented. Furthermore, conversion differs greatly for experiments with catalysts prepared via the direct mixing approach (both nickel to surfactant ratios). This can be seen in Figure 6-3. Catalyst solutions by the biphasic approach were identified as non-further pursuable. The level of conversion was comparable to experiments carried out with the same catalyst load in *n*-octanol, yet emulsification occurred, and the separation efficiency was lower.



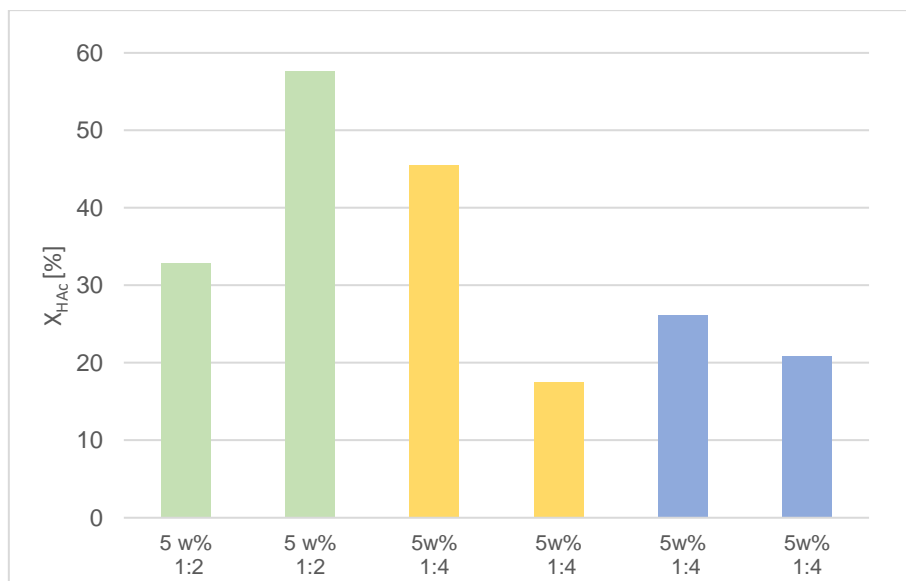


Figure 6-3 Effect of the solvent mixture 70 w% *n*-undecane and 30 w% *n*-octanol as solvent phase on acetic acid conversion with different catalysts. Catalysts were synthesized either via the direct mixing approach (green bars, yellow bars) or the biphasic approach (blue bars). For the catalyst preparation nickel to surfactant ratios of 1:2 (green bars) and 1:4 (yellow bars, blue bars) were used. The esterification was carried out with an initial concentration of 1 mol/l acetic acid, and a phase ratio of 1, at 60 °C for three hours.

To describe the course of the acetic acid concentration during the reaction in more detail, samples were taken every 30 minutes and measured using GC. Sampling was started with a staggering time ( $t_{start} = 15\text{min}$ ,  $t_{start} = 30\text{min}$ ) so that the sample quantity taken from each experiment was within a tolerable range. The concentration profile for the esterification reactions carried out with a 5 w% catalyst loading in *n*-octanol can be seen in Figure 6-4.

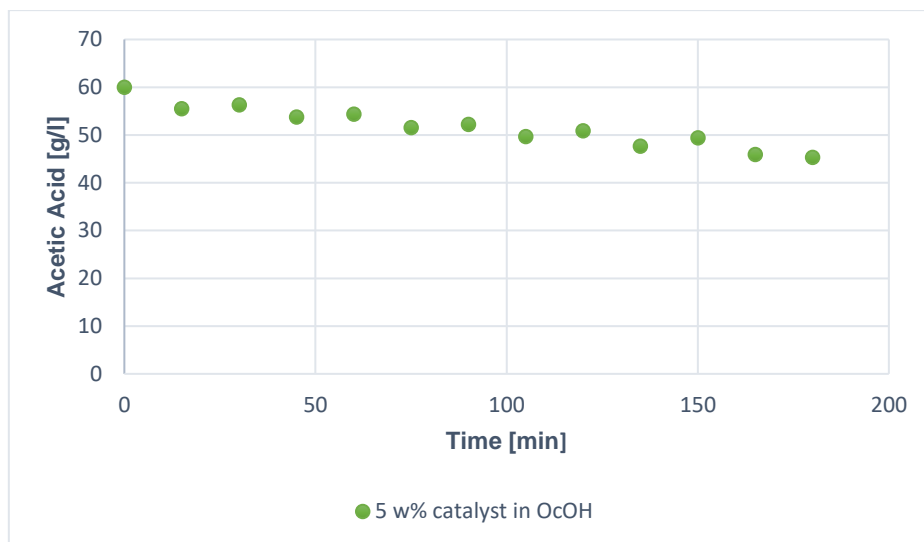


Figure 6-4 Concentration course of acetic acid throughout the esterification reaction. GC measurements from experiments SS\_AT\_015 and SS\_AT\_016 were combined to obtain the profile. Catalyst solutions with a catalyst load of 5 w% in *n*-octanol and a nickel to surfactant ratio of 1:2 were used. The esterification was carried out with an initial concentration of 1 mol/l acetic acid, *n*-octanol as solvent phase and a phase ratio of 1 at 60 °C

### 6.3 Total Organic Carbon

In order to calculate the maximum TOC value, the carbon content of each compound was determined first. For this calculation Equation 5 was used. The  $TOC_{max}$  was then calculated from the sum of the carbon content of the individual compounds  $C_{content}$  multiplied by the concentration of this compound  $c_{compound}$  in grams per litre (Equation 6). The concentration of the compounds (*n*-octanol, *n*-octyl acetate, acetic acid) was taken from GC measurements of the aqueous phase.

$$C_{content} = \frac{MW_C * Number_{C-Atoms}}{MW_{Compound}} \quad \text{Equation 5}$$

$$TOC_{max} = \sum C_{content} * c_{compound} \quad \text{Equation 6}$$

If the sample was diluted before the TOC measurement, it had to be calculated back to the undiluted concentration. Table 6-3 shows the carbon content in the aqueous phase after the esterification. The determined carbon content is (apart from one value)

greater than the previously calculated  $TOC_{max}$ . This indicates that there may be a residue of 4-DBSA in the aqueous phase after the reaction, as this is the only organic component in the reaction mixture that was not detected by GC analysis.

Table 6-3 List of the calculated  $TOC_{max}$  and the measured TOC in the aqueous phase after the esterification and their difference. Unless stated otherwise catalyst solutions used in the esterification were prepared via the direct mixing approach.

<b>Experiment</b>	<b><math>TOC_{max}</math></b>	<b><math>TOC_{measured}</math></b>	<b>Difference</b>
	<b>[g/l]</b>	<b>[g/l]</b>	<b>[g/l]</b>
SS_AT_009	17.09	19.08	1.99
SS_AT_010	13.70	15.38	1.68
SS_AT_012 <sup>1</sup>	18.09	19.24	1.15
SS_AT_015	12.58	15.01	2.43
SS_AT_016	12.80	15.94	3.14
SS_AT_062	11.93	14.21	2.28
SS_AT_068	12.05	15.12	3.07
SS_AT_069	12.20	15.46	3.26
SS_AT_070	8.39	8.29	-0.10
SS_AT_071	11.57	13.88	2.31
SS_AT_073	16.14	20.66	4.52
SS_AT_075 <sup>1</sup>	15.93	21.11	5.18
SS_AT_076	8.95	11.50	2.55

<sup>1</sup>catalyst solutions were prepared via the biphasic approach

## 6.4 Nickel in the Aqueous Phase

The nickel content in the aqueous phase was measured via F-AAS. Nickel standard solutions of 4, 3, 2, 1, and 0,5 mg/l were used for the calibration. Dilute nitric acid was utilised as a solvent. In Table 6-4 the concentrations of nickel in the aqueous phase after the reaction are shown. Instantly noticeable is the nickel concentration of experiment SS\_AT\_010 (direct mixing approach, 5 w%, Ni:4-DBSA 1:4, *n*-octanol) with a value of 178.3 mg/l. This high concentration is partly due to the excess nickel in the catalyst preparation. To wash out the residual nickel in further experiments the catalyst solutions were rinsed with deionized water. The experiments SS\_AT\_009 and SS\_AT\_076 were carried out with the same catalyst solutions (direct mixing approach, 5 w%, Ni:4-DBSA 1:2, solvent mixture) except for one difference. The catalyst solution for the experiment SS\_AT\_076 was rinsed with deionised water and SS\_AT\_009 was

not. The rinsing led to a significant decrease of nickel from 33.9 mg/l to 4.3 mg/l in the aqueous phase. According to the general wastewater ordinance, the limiting value for nickel concentrations is 0.5 mg/l. [62] All determined concentrations are distinctly above this limiting value. The lowest measured concentrations are a power of ten above the limit. Experiments that performed well in terms of conversion and phase separation exceeded the limiting value at around two powers of ten. Yet, since rinsing the catalyst solution with deionised water reduced the nickel concentration in water to almost a tenth of the initial concentration, it should be investigated whether the rinsing process can be further optimised (e.g. rinsing several times). Another possibility to reduce the nickel contamination might lie in using the reactant 4-DBSA slightly in excess in the catalyst production. Thereby more nickel might be bound to 4-DBSA. Excessive unbound 4-DBSA is easier removed from the catalyst solution given that 4-DBSA has proven to be easily removed by rinsing.

*Table 6-4 Nickel concentrations in [mg/l] in the aqueous phase after the esterification reactions. Unless stated otherwise catalyst solutions used in the esterification were prepared via the direct mixing approach.*

<b>Experiment</b>	<b>Ni:4-DBSA</b>	<b>w% catalyst</b>	<b>Solvent</b>	<b>Rinsed</b>	<b>Ni [mg/l]</b>
SS_AT_015	1:2	5	OcOH	yes	58.5
SS_AT_016	1:2	5	OcOH	yes	57.2
SS_AT_068	1:2	10	OcOH	yes	74.8
SS_AT_069	1:2	10	OcOH	yes	76.9
SS_AT_062	1:2	28	OcOH	yes	40.2
SS_AT_071	1:2	28	OcOH	yes	59.3
SS_AT_010	1:4	5	OcOH	no	178.3
SS_AT_070	1:4	5	OcOH	yes	5.6
SS_AT_009	1:2	5	mixture	no	33.9
SS_AT_076	1:2	5	mixture	yes	4.3
SS_AT_012 <sup>1</sup>	1:4	5	mixture	-	69.7
SS_AT_075 <sup>1</sup>	1:4	5	mixture	-	76.7
SS_AT_073	1:4	5	mixture	yes	56.3

<sup>1</sup>catalyst solutions were prepared via the biphasic approach

## 6.5 Density Measurements, Water Content and Rinsing

### 6.5.1 Density Measurements

All density measurements were carried out using Anton Paar's SVM 3000 viscometer. Unless otherwise stated, density measurements were performed at 25 °C. In Table 6-5 the density of the used catalyst solutions can be seen. In comparison the densities of *n*-octanol and *n*-undecane are:  $\rho_{n\text{-OcOH}}=0.86 \text{ g/cm}^3$  and  $\rho_{n\text{-undecane}}=0.74 \text{ g/cm}^3$ . Due to the lower density of the *n*-undecane, the catalyst solutions with a mixed solvent phase have a lower density. Furthermore, catalyst solutions with a higher catalyst load also possess a significantly higher density than catalyst solutions with a lower catalyst load. This follows from the fact, that 4-DBSA and nickel are inherently heavier compounds.

Table 6-5 List of the measured densities of the catalyst solutions in [g/cm<sup>3</sup>]. Unless stated otherwise catalyst solutions were prepared via the direct mixing approach.

Experiment	Ni:4-DBSA	w% cat	Solvent	Density[g/cm <sup>3</sup> ]
SS_AT_015	1:2	5	OcOH	0.847
SS_AT_016	1:2	5	OcOH	0.846
SS_AT_068	1:2	10	OcOH	0.861
SS_AT_069	1:2	10	OcOH	0.861
SS_AT_062	1:2	28	OcOH	0.912
SS_AT_071	1:2	28	OcOH	0.917
SS_AT_010	1:4	5	OcOH	0.846
SS_AT_070	1:4	5	OcOH	0.846
SS_AT_009	1:2	5	mixture	0.779
SS_AT_076	1:2	5	mixture	0.808
SS_AT_012 <sup>1</sup>	1:4	5	mixture	0.783
SS_AT_075 <sup>1</sup>	1:4	5	mixture	0.785
SS_AT_073	1:4	5	mixture	0.781

<sup>1</sup>catalyst solutions were prepared via the biphasic approach

Interfacial tension measurements using spinning drop tensiometry were performed at 25 °C and 60 °C since the esterification experiments were carried out at 60 °C. For the spinning drop tensiometer, the densities of the catalyst solutions at the measuring temperatures are necessary. These measurements are listed in Table 6-6. Both catalysts were dissolved in *n*-octanol, have a nickel to surfactant ratio of 1:2 and were rinsed with deionised water before the measurements.

Table 6-6 Densities of catalyst solutions at various temperatures (25 °C, 60 °C)

Sample	w% cat	Temperature [°C]	Density [g/cm <sup>3</sup> ]
SS_AT_046	5	25	0.843
SS_AT_046	5	60	0.819
SS_AT_022	28	25	0.939
SS_AT_022	28	60	0.913

## 6.5.2 Water Content

The water content in the solvent phase was determined via KF-titration. In Table 6-7 the water content of three different catalyst solutions before and after the esterification reaction can be seen. The difference before and after the esterification reaction is only for the samples of experiment SS\_AT\_012 (biphasic approach, 5 w%, Ni:4-DBSA 1:4, solvent mixture) higher before than after the reaction. Since in this experiment emulsification was not completely suppressed the slightly higher water content before the reaction may be accounted to sample taking from a partly emulsified system. In the case of the other two catalyst solutions, water was co-extracted during the esterification. For SS\_AT\_010 (direct mixing approach, 5 w%, Ni:4-DBSA 1:4, *n*-octanol) the water content increased sevenfold.

Table 6-7 Water content in the solvent phase by Karl Fischer before and after the reaction. Samples ending with K were taken before the esterification reaction, samples ending with 180 were taken after the reaction.

Sample	H <sub>2</sub> O [%]
SS_AT_009_K	1.20
SS_AT_009_180	2.13
SS_AT_012_K	3.06
SS_AT_012_180	2.88
SS_AT_010_K	0.97
SS_AT_010_180	6.66

Due to this finding, all following titrations were undertaken with water-saturated catalyst solutions. Additionally, the triple determination was performed after the esterification only. In Table 6-8 all catalyst solutions used in esterification experiments are listed. From this table it can be seen that the water saturation increases with increased catalyst load. The difference between values obtained for double determined esterification reactions is insignificant for water-saturated catalyst solutions which can be seen in Figure 6-5.

Table 6-8 Water content by Karl Fischer of previously water-saturated catalyst solutions after the esterification

Sample	Ni:4-DBSA	w% cat	Solvent	Rinsed	H <sub>2</sub> O [%]
SS_AT_015	1:2	5	OcOH	yes	6,18
SS_AT_016	1:2	5	OcOH	yes	6,44
SS_AT_068	1:2	10	OcOH	yes	8,37
SS_AT_069	1:2	10	OcOH	yes	8,42
SS_AT_062	1:2	28	OcOH	yes	14,77
SS_AT_071	1:2	28	OcOH	yes	16,66

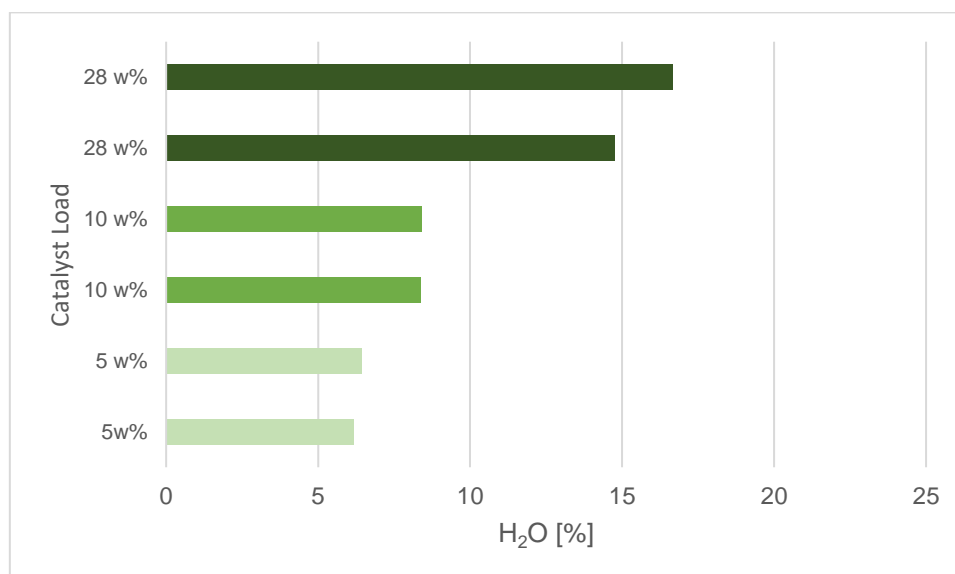


Figure 6-5 Water content in water-saturated catalyst solutions after esterification reactions. Each esterification was carried out with an initial acetic acid concentration of 1 mol/l, a phase ratio of 1 for three hours at 60 °C. The catalyst solutions were prepared via the direct mixing approach with a nickel to surfactant ratio of 1:2 and dissolved in *n*-octanol.

### 6.5.3 Rinsing

To rinse the catalyst solution with water as part of the preparation process proved to be a massive factor in improving the catalyst solution's properties. As stated in the previous subchapter 5.1.2.3, water is co-extracted during the esterification reaction. Therefore, two catalyst solutions with 5 w% catalyst loads in *n*-octanol were prepared and their water content and densities were measured before rinsing, after rinsing and after the esterification. Table 6-9 clearly states that the change in water content after rinsing is negligibly small compared to the change when in contact with water for the first time.

Additionally, rinsing also removed nickel and surfactant residues. On the one hand, this led to a lower nickel load in the aqueous phase and, on the other hand, had a strong influence on phase separation. Furthermore, water saturation made it possible to carry out interfacial tension measurements.

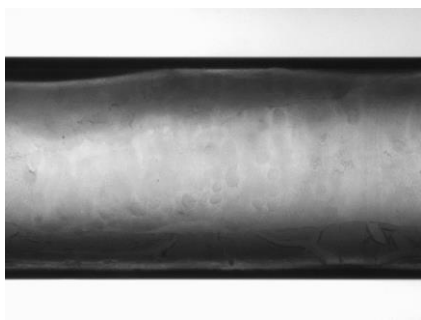
*Table 6-9 Water content and density of two catalyst solutions before rinsing (K1), after rinsing (K2) and after the esterification (180). Both catalyst solutions had a catalyst load of 5 w% in n-octanol and a nickel to surfactant ratio of 1:2.*

<b>Sample</b>	<b>H<sub>2</sub>O [%]</b>	<b>Density [g/cm<sup>3</sup>]</b>
SS_AT_015_K1	0.83	0.8336
SS_AT_015_K2	6.81	0.8424
SS_AT_015_180	6.18	0.8468
SS_AT_016_K1	0.80	0.8336
SS_AT_016_K2	7.25	0.8422
SS_AT_016_180	6.44	0.8455

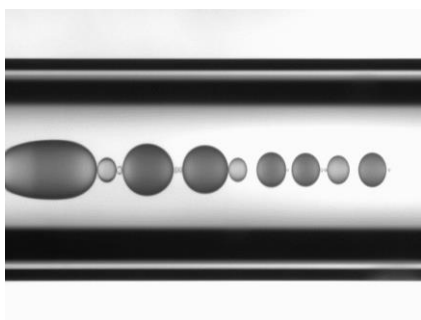
## 6.6 Interfacial Tension

Initially, a few problems arose when trying to measure the interfacial tension of catalyst solutions in water with the SVT 20N spinning drop tensiometer. After figuring out how to fill the capillary with both phases, the next challenge emerged. The measurement itself turned out to be difficult because either the entire system began to emulsify (Figure 6-6 a) or the interior of the drops (Figure 6-6 b.). In the second case, it was possible to obtain measured values, but they were not constant and therefore could not be further used. The picture in Figure 6-6 c depicts a well-shaped drop without any signs of emulsification. A rinsed catalyst solution was used for this measurement. Rinsing removed residual 4-DBSA, hence no emulsification occurred. The CMC of 4-DBSA lies at  $5.5 \cdot 10^{-4}$  mol/l [63] and is, therefore, quickly exceeded.

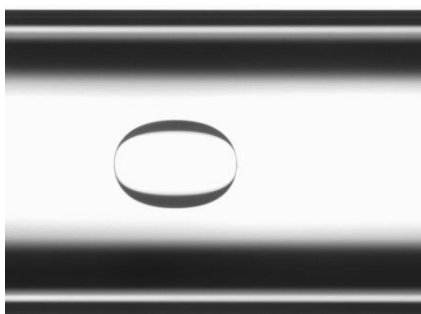




a) Complete emulsification of 4-DBSA in the solvent mixture in the measurement capillary



b) Drops of unrinsed catalyst solution with a catalyst load of 5 w% in n-octanol. The internal emulsification of the drops is due to residual surfactant.



c) A stable drop of rinsed catalyst solution with a catalyst load of 5 w% in n-octanol.

Figure 6-6 Pictures of the capillary during spinning drop measurements with deionised water as continuous phase at 25 °C. a) Complete emulsification of the capillary with 4-DBSA dissolved in the solvent mixture as discontinuous phase. b) Internal emulsification of unrinsed catalyst solution drops (5 w% in n-octanol) used as discontinuous phase. c) Stable drop of rinsed catalyst solution with a catalyst load of 5 w% in n-octanol as discontinuous phase.

When using the solvent mixture as the discontinuous phase in the spinning drop experiments, a change of up to roughly 65 % in interfacial tension was found. All three catalyst solutions lowered the interfacial tension significantly compared to the system using solely the solvent mixture. The interfacial tension values according to the methods of LY, CSW and VG can be taken from Table 6-10.

Table 6-10 Interfacial tensions determined via spinning drop tensiometry. Interfacial tensions are given according to the methods of LY, CSW and VG. Deionised water was used as a continuous phase for all measurements. The solvent mixture consists of 70 w% *n*-undecane/30 w% *n*-octanol. Measurements were performed at 25 °C.

Sample	LY [mN/m]	CSW [mN/m]	VG [mN/m]
solvent mixture	10.9	10.87	10.68
SS_AT_008	3.4	3.48	3.42
SS_AT_009	7.77	7.77	7.6
SS_AT_012	3.89	3.92	3.86

As catalyst solutions prepared by the direct approach with a nickel to surfactant ratio of 1:2 in pure *n*-octanol showed the overall best performance in terms of phase separation behaviour and conversion, interfacial tension measurements were carried out at 25 °C and 60 °C. 60 °C being the temperature where the esterification is executed. Measurements were taken for catalyst loads of 5 w% and 28 w% at both temperatures. For the catalyst solutions, no significant temperature dependencies were found, as can be seen in Figure 6-7. Reduction of interfacial tension was found up to 33 % for the lower catalyst load and up to 75 % for the higher catalyst load. This reduction in interfacial tension leads to a high mass transfer area at the interface, which is vital for the catalytic activity in a biphasic system.

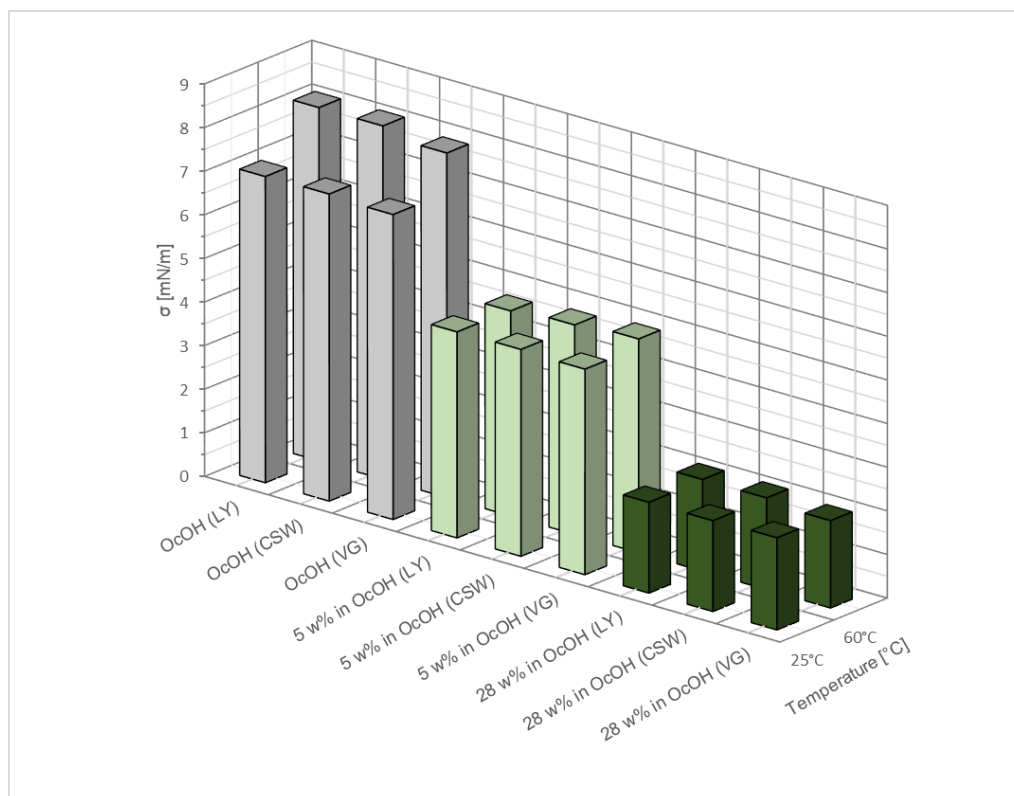


Figure 6-7 Interfacial tensions of the system water/ *n*-octanol, water/ *n*-octanol with 5 w% catalysts and water/ *n*-octanol with 28 w% catalysts at 25 °C and 60 °C. Interfacial tensions are given based on the models of LY, CSW and VG

## 6.7 Structural Elucidation

To determine the structure of the catalyst, an attempt was made to obtain information through NMR measurements. Assoc. Prof. Dipl. Ing. Dr. tech. Fischer kindly performed a  $^1\text{H}$  NMR measurement of the 4-DBSA and the catalyst and a  $^{13}\text{C}$  NMR measurement of 4-DBSA. Unfortunately, it was not possible to obtain a  $^{13}\text{C}$  spectrum of the catalyst. Additionally, no clear proposition for a structure of the metallosurfactant could be given. Yet the spectra indicated that some kind of reaction had happened and the  $^1\text{H}$  spectrum of the catalyst also showed its paramagnetic property given by the nickel.

Toth et al. were able to propose a structure for the nickel-based metallosurfactant. The catalyst was analysed via inductively coupled plasma optical emission spectroscopy (ICP-OES) and infrared (IR) spectroscopy. ICP-OES was utilised to measure the sulphur and nickel content in the catalyst samples. The content of these two elements made it possible to infer a stoichiometric ratio which is 1: 2 of nickel to sulphur. The IR spectra imply a bonding between the nickel and the  $\text{SO}_3^-$  group. Therefore the proposed structure is built by a nickel ion and two molecules of 4-DBSA as illustrated in Figure 6-8. [55]

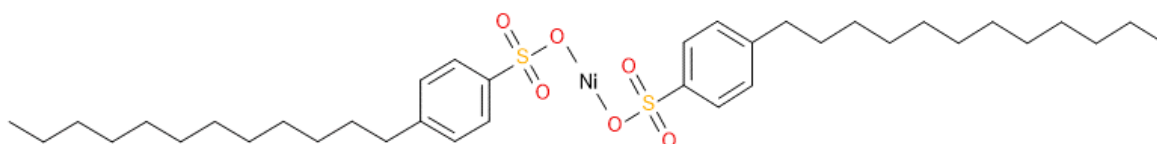


Figure 6-8 Proposed structure of the metallosurfactant  $[\text{Ni}(\text{DBSA})_2]$  built by a nickel cation and two molecules of 4-DBSA

## 7 Conclusion and Outlook

A novel metallosurfactant catalyst for the reactive separation of acetic acid from water through biphasic esterification was developed. For this purpose, 4-DBSA was modified with the transition metal nickel to suppress the emulsifying property of 4-DBSA. The metallosurfactant catalyst  $[\text{Ni}(\text{DBSA})_2]$  was obtained by combining nickel hydroxide and 4-DBSA. It was possible to prevent the emulsification of the biphasic reaction system of aqueous acetic acid and *n*-octanol for esterification while achieving conversions of acetic acid up to 37 %. For the synthesis and further processing of the catalyst, the aim was to keep both steps simple and the additional energy consumption low.

During the experiments, it became clear that the simple approach of direct mixing is superior to the biphasic preparation procedure. The esterification experiments with catalysts of the second approach were not reproducible. Besides, the first variant impresses with its simplicity. A procedure was developed to dissolve the catalyst. As a solvent phase, pure *n*-octanol is preferable to a mixture of *n*-undecane and *n*-octanol. On one hand, pure *n*-octanol shows better results in terms of phase separation, and on the other hand, since *n*-octanol is used as alcohol in the esterification, no additional component is added to the system. Subsequent recovery of the solvent is thus facilitated.

Rinsing the dissolved catalyst with deionised water in a separating funnel was identified as a key step in the preparation of the catalyst solution. Rinsing removes residues of 4-DBSA and nickel. Thereby the emulsification of the system was prevented and, supplementary the content of nickel in the aqueous phase was significantly reduced. Since the nickel content was still above the legal limit of 0.5 mg/l, there is an urge for optimisation regarding this matter. [62] Besides, the catalyst solution was saturated by being washed out with water, which counteracted the co-extraction of water during the esterification.

With the aid of spinning drop tensiometry, the interfacial tension between the aqueous and various solvent phases were determined. Using the metallosurfactant, it was possible to measure reductions in interfacial tension both for mixed solvent phases (up

to 65 %) and *n*-octanol (up to 75 %). No temperature dependency was found for the catalyst solutions. These results clearly show that the surfactant property of 4-DBSA is still present in the metallosurfactant. Thus, by reducing the interfacial tension, a large area is available for mass transfer. This is important because the reactants are present in different phases and the esterification reaction takes place at the aqueous-solvent interface. Acetic acid is present in the aqueous phase while *n*-octanol acts as a reactant and forms the solvent phase. The converted compound *n*-octyl acetate is dissolved in the solvent phase.

Keeping sustainability issues in mind, the next step must be the recovery of the solvent *n*-octanol. For this purpose, the transesterification of *n*-octyl acetate into a lower-boiling acetate as part of reactive distillation might be a possibility. In the course of this, the suitability of the catalyst [Ni(DBSA)<sub>2</sub>] for transesterification might be tested as well. The aim is a high solvent recovery rate.

With the potential shown, [Ni(DBSA)<sub>2</sub>] might be investigated to be utilised as a catalyst for further reactions. Therefore, reactions in which 4-DBSA has already been tested or those that take place in a biphasic reaction system are particularly suitable. Also, experiments of [Ni(DBSA)<sub>2</sub>] in other solvents would be of interest. As part of the sustainability aspect, the behaviour of the catalyst should also be examined for greener alternatives.

## Literatur

- [1] United States Environmental Protection Agency, *Definition of Green Chemistry*, <https://www.epa.gov/greenchemistry/basics-green-chemistry>.
- [2] P. T. Anastas, M. M. Kirchhoff, *Accounts of chemical research* **2002**, 35 (9), 686 – 694. DOI: 10.1021/ar010065m.
- [3] ACS Chemistry for Life, *Green Chemistry History*, <https://www.acs.org/content/acs/en/greenchemistry/what-is-green-chemistry/history-of-green-chemistry.html>.
- [4] P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press **1998**.
- [5] P. T. Anastas, T. C. Williamson, in *Green Chemistry*, Vol. 626, ACS Symposium Series (Eds: P. T. Anastas, T. C. Williamson), American Chemical Society, Washington, DC **1996**.
- [6] P. T. Anastas, J. B. Zimmerman, *Environmental science & technology* **2003**, 37 (5), 94A-101A. DOI: 10.1021/es032373g.
- [7] Verband Deutscher Papierfabriken e.V., *Papier Kompass: 2020*, [https://www.vdp-online.de/fileadmin/0002-VDP/07\\_Dateien/7\\_Publikationen/Kompass\\_de.pdf](https://www.vdp-online.de/fileadmin/0002-VDP/07_Dateien/7_Publikationen/Kompass_de.pdf) **2020**.
- [8] R. Toczyłowska-Mamińska, *Renewable and Sustainable Energy Reviews* **2017**, 78 (4), 764 – 772. DOI: 10.1016/j.rser.2017.05.021.
- [9] L. Reyes, C. Nikitine, L. Vilcocq, P. Fongarland, *Green Chem.* **2020**, 22 (23), 8097 – 8115. DOI: 10.1039/D0GC02627A.
- [10] D. Painer, S. Lux, A. Graftschatter, A. Toth, M. Siebenhofer, *Chemie Ingenieur Technik* **2017**, 89 (1-2), 161 – 171. DOI: 10.1002/cite.201600090.
- [11] A. Toth, S. Lux, D. Painer, M. Siebenhofer, *React. Chem. Eng.* **2018**, 3 (6), 905 – 911. DOI: 10.1039/c8re00194d.
- [12] D. Painer, S. Lux, M. Siebenhofer, *Chemie Ingenieur Technik* **2015**, 87 (6), 843 – 847. DOI: 10.1002/cite.201400130.
- [13] B. Saha, *Catalysis Today* **2000**, 60 (1-2), 147 – 157. DOI: 10.1016/S0920-5861(00)00326-6.
- [14] V. D. Talnikar, Y. S. Mahajan, *Korean J. Chem. Eng.* **2014**, 31 (10), 1720 – 1731. DOI: 10.1007/s11814-014-0202-4.
- [15] Y. Liu, E. Lotero, J. G. Goodwin, *Journal of Molecular Catalysis A: Chemical* **2006**, 245 (1-2), 132 – 140. DOI: 10.1016/j.molcata.2005.09.049.

- [16] M. Marín-García, N. Benseny-Cases, M. Camacho, Y. Perrie, J. Suades, R. Barnadas-Rodríguez, *Dalton transactions (Cambridge, England 2003)* **2018**, 47 (40), 14293 – 14303. DOI: 10.1039/c8dt01584h.
- [17] Pradeep, G. Kaur, G. R. Chaudhary, U. Batra, *Journal of Colloid and Interface Science* **2020**, 562, 598 – 607. DOI: 10.1016/j.jcis.2019.11.073.
- [18] P. C. Griffiths, I. A. Fallis, T. Chuenpratoom, R. Watanesk, *Advances in colloid and interface science* **2006**, 122 (1-3), 107 – 117. DOI: 10.1016/j.jcis.2006.06.010.
- [19] A. Wollrab, *Organische Chemie: Eine Einführung für Lehramts- und Nebenfachstudenten*, 4th ed., Springer Berlin Heidelberg, Berlin, Heidelberg **2014**.
- [20] H. P. Latscha, U. Kazmaier, H. Klein, *Organische Chemie: Chemie-Basiswissen II*, 7th ed., Springer Berlin Heidelberg, Berlin, Heidelberg **2016**.
- [21] L. L. Schramm, *Emulsions, foams, and suspensions: Fundamentals and applications*, Wiley-VCH, Weinheim, Great Britain **2010**.
- [22] G. Wagner, (None), *Waschmittel: Chemie, Umwelt, Nachhaltigkeit*, 4th ed., Wiley-VCH, Weinheim **2010**.
- [23] A. Holleman, E. Wiberg, N. Wiberg, *Lehrbuch der anorganischen Chemie*, 102nd ed., De Gruyter, Berlin **2007**.
- [24] M. Nič, J. Jirát, B. Košata, A. Jenkins, A. McNaught, *IUPAC Compendium of Chemical Terminology*, IUPAC, Research Triangle Park, NC **2009**.
- [25] H. Irving, R. J. P. Williams, *J. Chem. Soc.* **1953**, 3192. DOI: 10.1039/JR9530003192.
- [26] R. G. Pearson, *J. Am. Chem. Soc.* **1963**, 85 (22), 3533 – 3539.
- [27] J. Clayden, N. Greeves, S. Warren, *Organic Chemistry*, 2nd ed., Oxford University Press, Oxford, New York **2012**.
- [28] K. Manabe, Y. Mori, S. Kobayashi, *Tetrahedron* **2001**, 57 (13), 2537 – 2544. DOI: 10.1016/S0040-4020(01)00081-3.
- [29] K. Song, Y. Chu, L. Dong, J. Song, D. Wang, *Journal of Molecular Catalysis A: Chemical* **2008**, 282 (1-2), 144 – 148. DOI: 10.1016/j.molcata.2007.12.003.
- [30] K. Manabe, S. Iimura, X.-M. Sun, S. Kobayashi, *J. Am. Chem. Soc.* **2002**, 124 (40), 11971 – 11978. DOI: 10.1021/ja026241j.
- [31] Y. Han, Y. Chu, *Journal of Molecular Catalysis A: Chemical* **2005**, 237 (1-2), 232 – 237. DOI: 10.1016/j.molcata.2005.04.058.

- [32] A. Alegría, J. Cuellar, *Applied Catalysis B: Environmental* **2015**, 179 (6), 530 – 541. DOI: 10.1016/j.apcatb.2015.05.057.
- [33] M. A. Bigdeli, G. Gholami, E. Sheikhhosseini, *Chinese Chemical Letters* **2011**, 22 (8), 903 – 906. DOI: 10.1016/j.cclet.2010.12.030.
- [34] M. Shiri, M. A. Zolfigol, *Tetrahedron* **2009**, 65 (3), 587 – 598. DOI: 10.1016/j.tet.2008.09.085.
- [35] M. Baile, Y. J. Chou, J. C. Saam, *Polymer Bulletin* **1990**, 23 (3), 251 – 257. DOI: 10.1007/BF01032438.
- [36] J. Zhao, H. Guan, W. Shi, M. Cheng, X. Wang, S. Li, *Catalysis Communications* **2012**, 20, 103 – 106. DOI: 10.1016/j.catcom.2012.01.014.
- [37] Y. Zheng, Y. Zheng, S. Yang, Z. Guo, T. Zhang, H. Song, Q. Shao, *Green Chemistry Letters and Reviews* **2017**, 10 (4), 202 – 209. DOI: 10.1080/17518253.2017.1342001.
- [38] J. Landaburu-Aguirre, V. García, E. Pongrácz, R. L. Keiski, *Desalination* **2009**, 240 (1-3), 262 – 269. DOI: 10.1016/j.desal.2007.11.077.
- [39] E. Samper, M. Rodríguez, M. A. de La Rubia, D. Prats, *Separation and Purification Technology* **2009**, 65 (3), 337 – 342. DOI: 10.1016/j.seppur.2008.11.013.
- [40] F. Ferella, M. Prisciandaro, I. de Michelis, F. Veglio', *Desalination* **2007**, 207 (1-3), 125 – 133. DOI: 10.1016/j.desal.2006.07.007.
- [41] F. Fu, Q. Wang, *Journal of Environmental Management* **2011**, 92 (3), 407 – 418. DOI: 10.1016/j.jenvman.2010.11.011.
- [42] F. Gode, E. Pehlivan, *Journal of hazardous materials* **2006**, 136 (2), 330 – 337. DOI: 10.1016/j.jhazmat.2005.12.021.
- [43] M. M. Nasef, H. Saidi, Z. Ujang, K. Z. M. Dahlan, *J. Chil. Chem. Soc.* **2010**, 55, 421 – 427. DOI: 10.4067/S0717-97072010000400002.
- [44] S. R. Popuri, Y. Vijaya, V. M. Boddu, K. Abburi, *Bioresource technology* **2009**, 100 (1), 194 – 199. DOI: 10.1016/j.biortech.2008.05.041.
- [45] V. S. Kislik, *Solvent extraction: Classical and novel approaches*, Elsevier, Oxford **2012**.
- [46] B. H. Lipshutz, F. Gallou, S. Handa, *ACS Sustainable Chem. Eng.* **2016**, 4 (11), 5838 – 5849. DOI: 10.1021/acssuschemeng.6b01810.



- [47] S. Narayan, J. Muldoon, M. G. Finn, V. V. Fokin, H. C. Kolb, K. B. Sharpless, *Angewandte Chemie (International ed. in English)* **2005**, *44* (21), 3275 – 3279. DOI: 10.1002/anie.200462883.
- [48] D. Prat, A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehada, P. J. Dunn, *Green Chem.* **2016**, *18* (1), 288 – 296. DOI: 10.1039/C5GC01008J.
- [49] ACS GCI Pharmaceutical Roundtable, *ACS GCI Pharmaceutical Roundtable Solvent Selection Guide: Version 2.0* **2011**.
- [50] M. Tobiszewski, S. Tsakovski, V. Simeonov, J. Namieśnik, F. Pena-Pereira, *Green Chem.* **2015**, *17* (10), 4773 – 4785. DOI: 10.1039/C5GC01615K.
- [51] DataPhysics Instruments GmbH, *SVT 25: Spinning Drop Video Tensiometer für die Messung niedriger bis ultraniedriger Grenzflächenspannungen*, [https://www.dataphysics-instruments.com/Downloads/SVT25\\_DE.pdf?v=1.1](https://www.dataphysics-instruments.com/Downloads/SVT25_DE.pdf?v=1.1) **2003**.
- [52] J. Viades-Trejo, J. Gracia-Fadrique, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2007**, *302* (1-3), 549 – 552. DOI: 10.1016/j.colsurfa.2007.03.033.
- [53] B. Vonnegut, *Review of Scientific Instruments* **1942**, *13* (1), 6 – 9. DOI: 10.1063/1.1769937.
- [54] A. Couper, R. Newton, C. Nunn, *Colloid & Polymer Sci* **1983**, *261* (4), 371 – 372. DOI: 10.1007/BF01413946.
- [55] A. Toth, S. Schnedl, D. Painer, M. Siebenhofer, S. Lux, *ACS Sustainable Chem. Eng.* **2019**, *7* (22), 18547 – 18553. DOI: 10.1021/acssuschemeng.9b04667.
- [56] E. Dziwinski, J. Szymanowski, *Solvent Extraction and Ion Exchange* **1998**, *16* (6), 1515 – 1525. DOI: 10.1080/07366299808934592.
- [57] R. D. Abreu, C. A. Morais, *Minerals Engineering* **2014**, *61* (5), 82 – 87. DOI: 10.1016/j.mineng.2014.03.015.
- [58] D. Li, C. Wang, *Hydrometallurgy* **1998**, *48* (3), 301 – 312. DOI: 10.1016/S0304-386X(97)00080-7.
- [59] M. Mohammadi, K. Forsberg, L. Kloo, J. La Martinez De Cruz, Å. Rasmuson, *Hydrometallurgy* **2015**, *156* (6), 215 – 224. DOI: 10.1016/j.hydromet.2015.05.004.
- [60] B. R. Reddy, D. N. Priya, *Journal of Power Sources* **2006**, *161* (2), 1428 – 1434. DOI: 10.1016/j.jpowsour.2006.05.044.
- [61] W. Wang, Y. Pranolo, C. Y. Cheng, *Separation and Purification Technology* **2013**, *108*, 96 – 102. DOI: 10.1016/j.seppur.2013.02.001.

- [62] 1996\_186\_0: *Bundesgesetzblatt für die Republik Österreich*.
- [63] V. I. Petrenko, M. V. Avdeev, V. M. Garamus, L. A. Bulavin, V. L. Aksenov, L. Rosta, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2010**, 369 (1-3), 160 – 164. DOI: 10.1016/j.colsurfa.2010.08.023.

## List of Figures

FIGURE 2-1 STRUCTURAL FORMULA OF 4-DODECYLBENZENESULPHONIC ACID.....	3
FIGURE 2-2 DRAWING OF A MICELLE (LEFT) AND AN INVERSE MICELLE (RIGHT).....	6
FIGURE 2-3 REACTION EQUATION OF THE ESTERIFICATION OF ACETIC ACID AND N-OCTANOL TO N-OCTYL ACETATE AND WATER, AND ITS BACKWARD EQUILIBRIUM REACTION .....	9
FIGURE 5-1 METALLOSURFACTANT CATALYST WITH THE STOICHIOMETRIC RATIO OF 1:2 (NICKEL TO 4-DBSA) RIGHT AFTER MIXING (LEFT), 40 MINUTES OF DRYING (MIDDLE), AND 210 MINUTES OF DRYING (RIGHT) .....	22
FIGURE 5-2 CATALYST PASTE DISSOLVED IN THE SOLVENT MIXTURE 70W % N-UNDECANE/30 W% N-OCTANOL; LEFT: NO ADDITIONAL HEATING WAS USED - THE PASTE IS NOT FULLY DISSOLVED; RIGHT: ADDITIONAL HEATING AT 70 °C FOR 1H - THE PASTE IS FULLY DISSOLVED .....	23
FIGURE 5-3 CATALYST SOLUTION WITH A CATALYST LOAD OF 28 W% IN PURE N-OCTANOL.....	24
FIGURE 5-4 CATALYST SOLUTION SS_AT_005_01 (2,5W % CATALYST IN 70 W% N-UNDECANE/30 W% N- OCTANOL) UNDERLAID WITH DEIONISED WATER. THE SYSTEM IS EMULSIFIED AT THE INTERFACE AND PARTS OF THE SOLVENT PHASE .....	25
FIGURE 6-1 PHASE SEPARATION AFTER <i>THE ESTERIFICATION REACTION WITH TWO DIFFERENT CATALYST SOLUTIONS. LEFT: SS_AT_070; RIGHT: SS_AT_015</i> .....	30
FIGURE 6-2 EFFECT OF N-OCTANOL AS SOLVENT PHASE ON ACETIC ACID CONVERSION WITH DIFFERENT CATALYSTS. ALL CATALYSTS WERE SYNTHESISED VIA THE DIRECT MIXING APPROACH. FOR THE CATALYST PREPARATION NICKEL TO SURFACTANT RATIOS OF 1:2 (GREEN BARS) AND 1:4 (YELLOW BARS) WERE USED. THE ESTERIFICATION WAS CARRIED OUT WITH AN INITIAL CONCENTRATION OF 1 MOL/L ACETIC ACID, AND A PHASE RATIO OF 1, AT 60 °C FOR THREE HOURS. ....	33
FIGURE 6-3 EFFECT OF THE SOLVENT MIXTURE 70 W% N-UNDECANE AND 30 W% N-OCTANOL AS SOLVENT PHASE ON ACETIC ACID CONVERSION WITH DIFFERENT CATALYSTS. CATALYSTS WERE SYNTHESIZED EITHER VIA THE DIRECT MIXING APPROACH (GREEN BARS, YELLOW BARS) OR THE BIPHASIC APPROACH (BLUE BARS). FOR THE CATALYST PREPARATION NICKEL TO SURFACTANT RATIOS OF 1:2 (GREEN BARS) AND 1:4 (YELLOW BARS, BLUE BARS) WERE USED. THE ESTERIFICATION WAS CARRIED OUT WITH AN INITIAL CONCENTRATION OF 1 MOL/L ACETIC ACID, AND A PHASE RATIO OF 1, AT 60 °C FOR THREE HOURS. ....	34
FIGURE 6-4 CONCENTRATION COURSE OF ACETIC ACID THROUGHOUT THE ESTERIFICATION REACTION. GC MEASUREMENTS FROM EXPERIMENTS SS_AT_015 AND SS_AT_016 WERE COMBINED TO OBTAIN THE PROFILE. CATALYST SOLUTIONS WITH A CATALYST LOAD OF 5 W% IN N-OCTANOL AND A NICKEL TO SURFACTANT RATIO OF 1:2 WERE USED. THE ESTERIFICATION WAS CARRIED OUT WITH AN INITIAL CONCENTRATION OF 1 MOL/L ACETIC ACID, N-OCTANOL AS SOLVENT PHASE AND A PHASE RATIO OF 1 AT 60 °C .....	35
FIGURE 6-5 WATER CONTENT IN WATER-SATURATED CATALYST SOLUTIONS AFTER ESTERIFICATION REACTIONS. EACH ESTERIFICATION WAS CARRIED OUT WITH AN INITIAL ACETIC ACID CONCENTRATION	

OF 1 MOL/L, A PHASE RATIO OF 1 FOR THREE HOURS AT 60 °C. THE CATALYST SOLUTIONS WERE PREPARED VIA THE DIRECT MIXING APPROACH WITH A NICKEL TO SURFACTANT RATIO OF 1:2 AND DISSOLVED IN N-OCTANOL.....	40
FIGURE 6-6 PICTURES OF THE CAPILLARY DURING SPINNING DROP MEASUREMENTS WITH DEIONISED WATER AS CONTINUOUS PHASE AT 25 °C. A) COMPLETE EMULSIFICATION OF THE CAPILLARY WITH 4-DBSA DISSOLVED IN THE SOLVENT MIXTURE AS DISCONTINUOUS PHASE. B) INTERNAL EMULSIFICATION OF UNRINSED CATALYST SOLUTION DROPS (5 W% IN N-OCTANOL) USED AS DISCONTINUOUS PHASE. C) STABLE DROP OF RINSED CATALYST SOLUTION WITH A CATALYST LOAD OF 5 W% IN N-OCTANOL AS DISCONTINUOUS PHASE.....	42
FIGURE 6-7 INTERFACIAL TENSIONS OF THE SYSTEM WATER/ N-OCTANOL, WATER/ N-OCTANOL WITH 5 W% CATALYSTS AND WATER/ N-OCTANOL WITH 28 W% CATALYSTS AT 25 °C AND 60 °C. INTERFACIAL TENSIONS ARE GIVEN BASED ON THE MODELS OF LY, CSW AND VG .....	43
FIGURE 6-8 PROPOSED STRUCTURE OF THE METALLOSURFACTANT [Ni(DBSA) <sub>2</sub> ] BUILT BY A NICKEL CATION AND TWO MOLECULES OF 4-DBSA.....	44

## List of Tables

TABLE 2-1 LIST OF SURFACTANT CLASSES WITH THE CHARGE OF THEIR POLAR GROUP AND EXAMPLES .....	5
TABLE 4-1 LIST OF CHEMICALS USED FOR THE CATALYST PREPARATION AND THE ESTERIFICATION EXPERIMENTS. THE LIST INCLUDES THE NAMES OF THE CHEMICAL COMPOUNDS, THEIR MOLECULAR FORMULA, CAS-NUMBER, PURITY, AND THE MANUFACTURER.....	15
TABLE 4-2 LIST OF ANALYTICAL EQUIPMENT WITH MODEL AND MANUFACTURER .....	16
TABLE 5-1 LIST OF METALLOSURFACTANT CATALYSTS USED FOR THE ESTERIFICATION REACTION. THE LIST INCLUDES THE METAL TO SURFACTANT RATIO OF THE CATALYST, THE CATALYST LOADING, THE COMPOSITION OF THE SOLVENT PHASE AND WHETHER THE DISSOLVED CATALYST WAS RINSED OR NOT. UNLESS STATED OTHERWISE CATALYST SOLUTIONS WERE PREPARED VIA THE DIRECT MIXING APPROACH. THE MIXTURE SOLVENT PHASE IS COMPOSED OF 70 W% UNDECANE AND 30 W% N-OCTANOL .....	28
TABLE 6-1 LIST OF ESTERIFICATION REACTIONS WITH EDUCT WEIGHT, PRODUCT WEIGHT, AND THE ERROR OF THE MASS BALANCE. UNLESS STATED OTHERWISE CATALYST SOLUTIONS WERE PREPARED VIA THE DIRECT MIXING APPROACH. THE MIXTURE SOLVENT PHASE IS COMPOSED OF 70 W% N-UNDECANE AND 30 W% N-OCTANOL. ....	31
TABLE 6-2 CONVERSION OF ACETIC ACID ( $X_{HAC}$ ) AND SEPARATION EFFICIENCY OF ACETIC ACID ( $SE_{HAC}$ ) FROM THE AQUEOUS PHASE. UNLESS STATED OTHERWISE CATALYST SOLUTIONS WERE PREPARED VIA THE DIRECT MIXING APPROACH. THE MIXTURE SOLVENT PHASE IS COMPOSED OF 70 W% UNDECANE AND 30 W% N-OCTANOL .....	32
TABLE 6-3 LIST OF THE CALCULATED $TOC_{MAX}$ AND THE MEASURED TOC IN THE AQUEOUS PHASE AFTER THE ESTERIFICATION AND THEIR DIFFERENCE. UNLESS STATED OTHERWISE CATALYST SOLUTIONS USED IN THE ESTERIFICATION WERE PREPARED VIA THE DIRECT MIXING APPROACH.....	36
TABLE 6-4 NICKEL CONCENTRATIONS IN [MG/L] IN THE AQUEOUS PHASE AFTER THE ESTERIFICATION REACTIONS. UNLESS STATED OTHERWISE CATALYST SOLUTIONS USED IN THE ESTERIFICATION WERE PREPARED VIA THE DIRECT MIXING APPROACH. ....	37
TABLE 6-5 LIST OF THE MEASURED DENSITIES OF THE CATALYST SOLUTIONS IN [G/CM <sup>3</sup> ]. UNLESS STATED OTHERWISE CATALYST SOLUTIONS WERE PREPARED VIA THE DIRECT MIXING APPROACH. ....	38
TABLE 6-6 DENSITIES OF CATALYST SOLUTIONS AT VARIOUS TEMPERATURES (25 °C, 60 °C) .....	39
TABLE 6-7 WATER CONTENT IN THE SOLVENT PHASE BY KARL FISCHER BEFORE AND AFTER THE REACTION. SAMPLES ENDING WITH K WERE TAKEN BEFORE THE ESTERIFICATION REACTION, SAMPLES ENDING WITH 180 WERE TAKEN AFTER THE REACTION. ....	39
TABLE 6-8 WATER CONTENT BY KARL FISCHER OF PREVIOUSLY WATER-SATURATED CATALYST SOLUTIONS AFTER THE ESTERIFICATION .....	40
TABLE 6-9 WATER CONTENT AND DENSITY OF TWO CATALYST SOLUTIONS BEFORE RINSING (K1), AFTER RINSING (K2) AND AFTER THE ESTERIFICATION (180). BOTH CATALYST SOLUTIONS HAD A CATALYST LOAD OF 5 W% IN N-OCTANOL AND A NICKEL TO SURFACTANT RATIO OF 1:2.....	41

TABLE 6-10 INTERFACIAL TENSIONS DETERMINED VIA SPINNING DROP TENSOMETRY. INTERFACIAL TENSIONS ARE GIVEN ACCORDING TO THE METHODS OF LY, CSW AND VG. DEIONISED WATER WAS USED AS A CONTINUOUS PHASE FOR ALL MEASUREMENTS. THE SOLVENT MIXTURE CONSISTS OF 70 W% N-UNDECANE/30 W% N-OCTANOL. MEASUREMENTS WERE PERFORMED AT 25 °C. .... 43

## **Appendix**

Article publication in ACS Sustainable Chemistry and Engineering (2019)

## Interfacial Catalysis in Biphasic Carboxylic Acid Esterification with a Nickel-Based Metallosurfactant

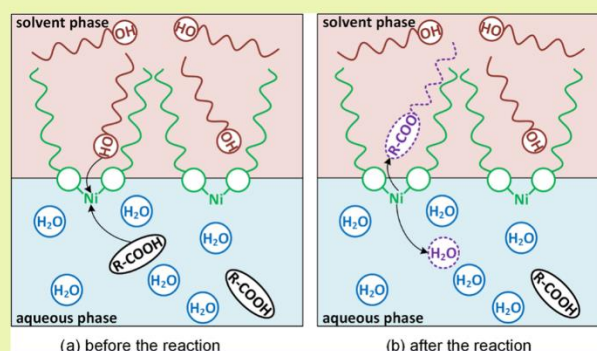
Andreas Toth,<sup>\*†</sup> Silke Schnedl, Daniela Painer,<sup>†</sup> Matthäus Siebenhofer, and Susanne Lux

Institute of Chemical Engineering and Environmental Technology, NAWI Graz Central Lab Biobased Products, Graz University of Technology, Inffeldgasse 25c/III, 8010 Graz, Austria

## Supporting Information

**ABSTRACT:** A metallosurfactant catalyst was developed to address the requirements for the utilization of low-molecular-weight carboxylic acids from dilute effluents. The catalyst Ni(DBSA)<sub>2</sub> combines transition-metal catalysis of nickel ions and surfactant catalysis of 4-dodecylbenzenesulfonic acid (4-DBSA). Requirements for the metallosurfactant catalyst are low water solubility, high catalytic activity in biphasic esterification, and self-assembling properties at the interface. Ni(DBSA)<sub>2</sub> was tested for applicability in the interfacial catalysis of esterification of dilute acetic acid with the solvent 1-octanol and resulted in an octyl acetate yield of 31.3%. Under identical reaction conditions, Ni(DBSA)<sub>2</sub> performed better than sulfuric acid with a yield of 1.7%. The limited catalytic performance of sulfuric acid is caused by the presence of sulfuric acid mainly in the aqueous phase. In contrast, Ni(DBSA)<sub>2</sub> is dissolved in the solvent and assembles at the aqueous/solvent interface where the reaction takes place. Additionally, the metallosurfactant lowers the interfacial tension between 1-octanol and deionized water by up to 75%, thus enhancing mass transfer. Compared to catalysis with 4-DBSA in emulsion, the catalytic performance of Ni(DBSA)<sub>2</sub> dropped by 62%, but this drawback is compensated by the complete suppression of emulsification. With Ni(DBSA)<sub>2</sub>, the development of a catalyst was achieved, which self-enhances its catalytic performance in the interfacial catalysis through increased mass transfer area due to its surfactant properties.

**KEYWORDS:** esterification, transition-metal, reactive extraction, metallosurfactant, interfacial catalysis



## INTRODUCTION

Low-molecular-weight carboxylic acids are formed during the processing of biomass, such as pulping of wood, and are mostly present at low concentrations in aqueous effluents. These carboxylic acids represent a potential source for renewable products and holistic use of biomass feedstock. Acetic acid as a platform chemical is one of the main low-molecular-weight byproducts formed during pulping via the cleavage of the acetyl group from hemicellulose. Common practice in industry to treat these byproducts is to thicken the effluent containing mainly lignin and carboxylic acids followed by incineration. Referring to the global annual pulp capacity, the incineration of such valuable constituents represents a huge waste of resources but is accepted state of the art due to economic reasons. Using this source requires appropriate process technologies. High excess of water, low concentration of the carboxylic acids, and formation of (quasi-)azeotropic mixtures specify the major problems to be tackled for distillative or reactive separation.<sup>1</sup>

Esterification combined with simultaneous extraction of the low-molecular-weight carboxylic acids, i.e., formic acid, acetic acid, propionic acid, and butyric acid, with 1-octanol in an emulsified regime is a promising technological approach.<sup>2</sup> The solvent is a mixture of the reactant 1-octanol, the diluent *n*-

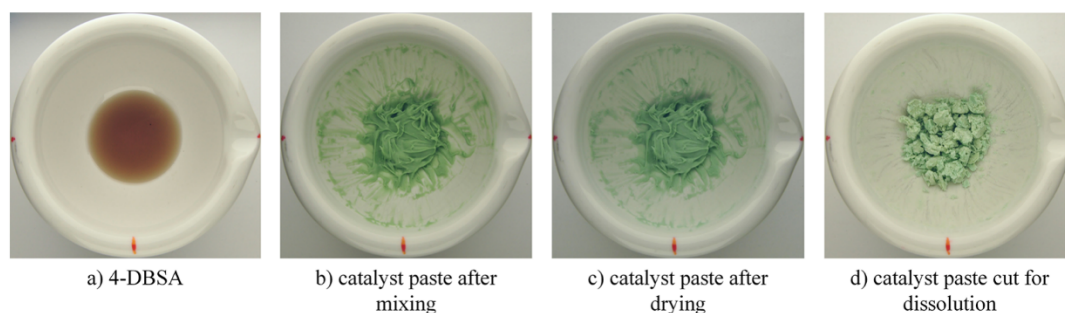
undecane, and the catalyst 4-dodecylbenzenesulfonic acid (4-DBSA). Due to esterification, acetic acid, which is almost insoluble in the solvent, is transformed to octyl acetate, which shows higher solubility in the solvent phase. The concept relies on the Brønsted-acid catalytic activity and surfactant capability of 4-DBSA.<sup>3–6</sup> Emulsification caused by this anionic surfactant generates a quasi-homogeneous reaction regime. Such a regime provides negligible mass transfer control of the reaction combined with the advantages of quasi-homogeneous catalysis of the biphasic esterification reaction.<sup>2,7,8</sup> Acetic acid esterified to octyl acetate with 1-octanol with a conversion up to 54% and an overall acid separation efficiency of 57% underlines the applicability of the proposed concept.<sup>2</sup> However, the deployment of 4-DBSA is highly limited, as increased concentrations cause the formation of stable emulsions. Splitting of stable emulsions cannot be performed by a simple centrifugation step. The ambivalence of emulsification providing the intensifying part of the process concept yet causing the huge obstacle of formation of stable emulsions inspired the search

**Received:** August 9, 2019

**Revised:** September 10, 2019

**Published:** October 12, 2019





**Figure 1.** Preparation steps of the nickel-metallosurfactant catalyst  $\text{Ni}(\text{DBSA})_2$ : (a) 4-DBSA before admixture of  $\text{Ni}(\text{OH})_2$ ; (b) catalyst paste right after mixing of 4-DBSA and  $\text{Ni}(\text{OH})_2$ ; (c) catalyst paste after 3 days storage at ambient conditions; and (d) cut catalyst paste prepared for dissolution in the solvent phase.

for a more convenient catalyst. This preferably water-insoluble catalyst is sought to show catalytic activity at the interface in biphasic esterification without the formation of stable emulsions, while maintaining a high mass transfer area through reduced interfacial tension. The concept of combined extraction/transesterification was also successfully applied by Likozar et al.<sup>7–9</sup> for utilizing high-molecular-weight fatty acids as biofuels. Likozar et al. developed a model capable of describing the superposition of extraction and reaction and implemented the process in a continuous tubular reactor.

Transition-metal ions catalyze esterification reactions as shown by Liu et al.<sup>10</sup> for noble metals like palladium and rhodium, or by Weires et al.<sup>11</sup> for nickel. With the surfactant catalyst 4-dodecylbenzenesulfonic acid as a basis, the most obvious approach was to make use of its ion-exchange capability, as already applied in transition-metal extraction and to, thus, control the surfactant properties with transition-metal ions. Exemplarily, transition-metal extraction has been published by Samper et al.<sup>12</sup> and Ferella et al.<sup>13</sup> Samper et al. used sodium dodecyl sulfate and linear alkylbenzene sulfonate to perform micellar-enhanced ultrafiltration to remove divalent heavy-metal ions like  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$  from aqueous effluent. The metal ions are fixed to the anionic surfactant in micelles and then separated from the effluent via ultrafiltration. Ferella et al. used dodecylbenzenesulfonic acid (anionic) in comparison to dodecylamine (cationic) for the separation of  $\text{Pb}^{2+}$  and  $\text{As}^-$  in a similar approach. Both used the surfactants at concentrations below their respective critical micelle concentration (CMC) and reported an effective separation for the use of anionic surfactants. The chemical interaction between metal ions and the surfactant molecules leads to an immobilization of the resulting compounds. This immobilization allows selective positioning of these compounds. In the present case, the metal ions fixed to surfactant molecules may either be soluble in the solvent phase or in the aqueous phase and therefore be immobilized in the respective phase.<sup>14</sup> The thus produced substances are called metal–surfactant complexes or metallosurfactants.

The self-assembling capability of the metallosurfactant molecules in micelles or other nanostructures allows application in various fields such as preparation of nanoparticles, in medicine, and in catalysis.<sup>15–17</sup> Most effort has been made in the development of water-soluble metallosurfactants for systems where the respective reactants are dissolved either in the aqueous or in the organic phase and reaction takes place at the interphase.<sup>17–19</sup>

In the present work, the reactants for esterification are dissolved in different phases (carboxylic acid mainly in the aqueous phase; alcohol in the solvent phase). Based on the emulsification process concept,<sup>2</sup> 1-octanol was chosen as the alcohol for esterification and acetic acid as model carboxylic acid. Acetic acid was used at  $1 \text{ mol L}^{-1}$  to mirror the harsh reaction conditions for esterification due to a high water excess. Together with the reactant 1-octanol, the ester octyl acetate forms the solvent phase, meeting the aim of removing and upgrading the low-molecular-weight carboxylic acid from the aqueous phase. It is desirable to keep the catalyst in the solvent phase to avoid contamination of the aqueous phase and to enable recycling of the catalyst with the solvent phase. Therefore, a metallosurfactant catalyst based on 4-dodecylbenzenesulfonic acid and nickel ions was developed. This catalyst is capable of catalyzing biphasic esterification at low temperatures, which are essential in aqueous effluent treatment to minimize the energy demand. The combination of two nontoxic components allows the suppression of emulsification and therefore energy-efficient phase separation after reactive extraction.

## EXPERIMENTAL METHODS

**Materials.** 4-Dodecylbenzenesulfonic acid (>95%, mixture of isomers, 4-DBSA, Sigma-Aldrich), nickel(II) hydroxide ( $\text{Ni}(\text{OH})_2$ , Sigma-Aldrich), sulfuric acid (96%,  $\text{H}_2\text{SO}_4$ , Carl Roth), *n*-undecane (>99%, Sigma-Aldrich), 1-octanol (>98%, Sigma-Aldrich), and acetic acid (>99%, ChemLab) were used as supplied without further purification.

**Preparation of Metallosurfactant Catalyst.** The metallosurfactant catalyst was synthesized by adding nickel(II) hydroxide powder to liquid 4-dodecylbenzenesulfonic acid (4-DBSA) in a ceramic mortar. Different stoichiometric ratios of nickel to 4-DBSA were used corresponding to the possible oxidation states of nickel (+2, +4). After thorough mixing, the obtained paste was dried at ambient conditions for three days. The dried paste was then admixed to a solvent and heated to  $90^\circ\text{C}$  with constant stirring until it was fully dissolved. For solvent selection, mixtures of *n*-undecane with Cyanex 923 or di-(2-ethylhexyl)phosphoric acid (DEHPA) together with 1-octanol as well as pure *n*-undecane and pure 1-octanol were tested. Figure 1 displays the catalyst preparation steps from pure 4-DBSA (a) to admixing nickel(II) hydroxide (b), drying (c), and cutting (d) for dissolution in the solvent phase. In a separating funnel, the catalyst solution was rinsed with deionized water to wash out unreacted nickel and 4-DBSA. Additionally, the solution was saturated with water to reduce loss of aqueous phase due to co-extraction of water during kinetic experiments.

Alternatively, the transition metals iron(II) chloride hexahydrate, iron(III) chloride tetrahydrate, and nickel(II) sulfate hexahydrate were tested but not further used due to undesired dissolution

behavior (e.g., iron(III) chloride), instability of the produced metallosurfactant (e.g., iron(II) chloride), and incapability to prevent the formation of emulsions. Additional information can be found in the Supporting Information (Table S1 and Figure S1).

**Biphasic Esterification in Batch Experiments.** Kinetic performance of the synthesized metallosurfactant catalysts was evaluated for the biphasic esterification of acetic acid as a model compound in the aqueous phase (deionized water) and 1-octanol as the reactant in the solvent phase. This biphasic esterification was performed in a batch setup consisting of a 500 mL three-neck flask with a condenser atop. The latter was operated at 2.5 °C to reduce losses through evaporation. A magnetic stirrer (Heidolph MR Hei-Standard) with a heating plate stirred and heated the reaction mass with a total volume of 300 mL. Temperature of the reaction mass was controlled with a temperature sensor (Heidolph EKT 3001). Sulfuric acid was chosen as a standard mineral acid catalyst for carboxylic acid catalysis.<sup>20</sup> Further, 4-DBSA served as a benchmark for surfactant catalysis. For catalyst load, a low level and a high level were chosen, equivalent to 5 and 28 wt % of Ni(DBSA)<sub>2</sub>, respectively. The high level represents the maximum catalyst load in pure 1-octanol due to its solubility characteristics. A phase ratio (solvent to aqueous feed) of 1, initial acetic acid concentration of 1 mol L<sup>-1</sup>, a reaction time of 3 h, and a reaction temperature of 60 °C were kept constant for all kinetic investigations. A stirrer speed of 500 rpm was chosen to ensure thorough mixing of the two phases.

The catalyst was dissolved in the solvent and filled into the three-neck flask together with deionized water. This biphasic mixture was then heated up to the desired reaction temperature. Acetic acid was added with a syringe to the aqueous phase, initiating the reaction after the reaction temperature was reached. For sampling, every 30 min, the stirrer was stopped and after phase separation, samples were taken from both phases (0.2 mL each). Sampling from emulsion was done from the center of the reaction broth (1 mL) immediately after stopping the stirrer. The thus obtained emulsion sample was centrifuged for 10 min to obtain clear samples of both phases for gas chromatography (GC) analysis. At the end of each experiment, phases were separated either by gravitational settling in a separating funnel or in a benchtop centrifuge (Heraeus Labofuge 400) at rcf 2383 for 30 min in case of emulsification. The overall mass balance error was below 1.8%.

## ANALYSIS TECHNIQUES

**Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).** Catalyst solutions were analyzed for nickel and sulfur content in an inductively coupled plasma optical emission spectroscope (ICP-OES) performed by BIOENERGY 2020+ GmbH. Solvent samples were prepared via acid digestion.

**Infrared (IR) Spectroscopy.** As nickel excludes NMR analysis due to its paramagnetic properties, structure characterization was performed using IR spectroscopy. A Bruker Alpha II spectrometer was used with a Platinum ATR. A spectral range of 4000–400 cm<sup>-1</sup> was analyzed with a spectral resolution of 2 cm<sup>-1</sup>.

**Spinning Drop Tensiometry.** Interfacial tension between solvent/catalyst mixtures and deionized water was measured with a Dataphysics spinning drop video tensiometer SVT20. The measuring chamber with the rotating capillary was temperature controlled to ensure accurate results. For the calculation of the interfacial tension  $\sigma$ , three different models were applied, depending on the drop shape: Vonnegut (VG), Laplace–Young (LY), and Cayias–Schechter–Wade (CSW).

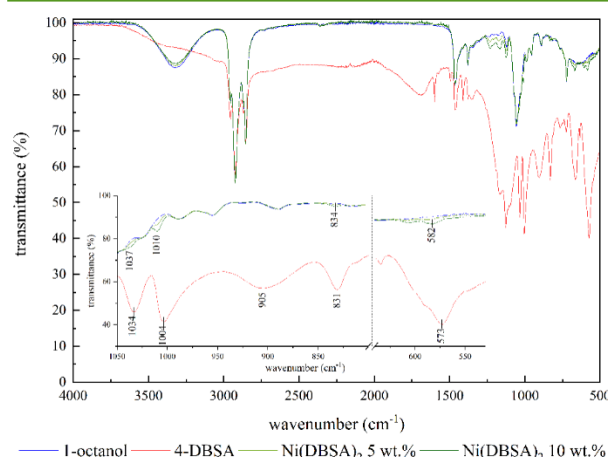
**Gas Chromatography.** Samples of liquid phases were analyzed in Shimadzu GC2010plus equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) in parallel operation. A Zebtron ZB WAXplus column with 60 m length, 0.32 mm inner diameter, and a film thickness

of 0.5  $\mu\text{m}$  was used. The gas chromatograph was operated in split mode (split ratio 120) with helium as the carrier gas. Injection via AOC 20i/s autosampler was done at 250 °C; the detectors were operated at 270 °C. The oven program started with a hold at 40 °C for 6.5 min and a temperature plateau at 60 °C for 2.5 min. This was followed by another temperature plateau at 120 °C held for 2 min and a final increase to 200 °C without a hold time. The heating rate in between the temperature plateaus was 20 °C min<sup>-1</sup>. The samples were precooled to 5 °C in the autosampler and injected undiluted. The relative standard error of the measurements was in the order of 1.3% for the analysis with FID and 2.5% for TCD.

## RESULTS AND DISCUSSION

**Catalyst Selection and Characterization.** 1-Octanol exhibited outstanding performance as a solvent with respect to extraction efficiency, catalyst load and stability, and phase separation behavior compared to the other tested solvents (*n*-undecane, Cyanex 923, DEHPA, 1-octanol, and mixtures thereof; further details in the Supporting Information). Extraction efficiency for metallosurfactant experiments with 1-octanol as solvent was above 53%. Metallosurfactant catalysts with nickel are best suited for the biphasic esterification of all investigated transition-metal ions (Fe(III), Fe(II), and Ni(II)), as the complexes offer high stability in the solvent phase coupled with almost no tendency to emulsify. Only the nickel-metallosurfactant with a stoichiometric ratio (4-DBSA to nickel) of 2 exhibits appropriate stability and catalytic performance together with the desired prevention of emulsification.

The nickel-metallosurfactant catalyst Ni(DBSA)<sub>2</sub> dissolved in 1-octanol was analyzed via ICP-OES and IR spectroscopy. The former confirmed a stoichiometric ratio of nickel to sulfur in the catalyst solution of 2 even after rinsing with deionized water. Figure 2 displays the IR spectra of 4-DBSA, 1-octanol, and two concentrations of Ni(DBSA)<sub>2</sub> dissolved in 1-octanol including the bands involved in the bonding of nickel and 4-DBSA. In the 4-DBSA spectrum, these bands show up at 573, 831, 905, 1004, and 1034 cm<sup>-1</sup>. The band at 573 cm<sup>-1</sup> is assigned to the bending and the bands at 1004 and 1034 cm<sup>-1</sup>



**Figure 2.** IR spectra of 4-dodecylbenzenesulfonic acid (red), 1-octanol (blue), 5 wt % Ni(DBSA)<sub>2</sub> in 1-octanol (light green), and 10 wt % Ni(DBSA)<sub>2</sub> in 1-octanol (dark green). Inset: focused areas of wavenumbers 1050–800 and 650–500 cm<sup>-1</sup>.

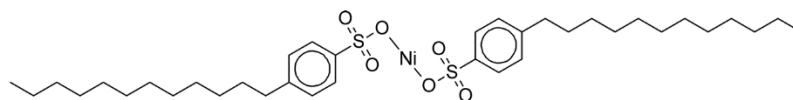


Figure 3. Proposed structure of the nickel-metallosurfactant  $\text{Ni}(\text{DBSA})_2$  with a divalent nickel ion and two 4-DBSA molecules.

to the symmetric stretching of the sulfonic acid group. The out-of-phase bending of the OH group in the sulfonic acid group is represented by bands at 831 and 905  $\text{cm}^{-1}$ .<sup>21</sup> Resulting from the ion-exchange bonding of two sulfonic acid groups to a single nickel ion, the sulfonic acid group bands are slightly shifted to 582, 834, 1010, and 1037  $\text{cm}^{-1}$ . The band at 905  $\text{cm}^{-1}$  disappears completely, indicating a bonding between  $\text{SO}_3^-$  and the nickel ion, suggesting a structure as displayed in Figure 3.

**Kinetic Performance of  $\text{Ni}(\text{DBSA})_2$  in Biphasic Esterification.** The kinetic performance of  $\text{Ni}(\text{DBSA})_2$  was evaluated based on the octyl acetate yield and compared to that of sulfuric acid and 4-dodecylbenzenesulfonic acid as catalysts. Octyl acetate was only detected in the solvent phase by GC analysis as described in the analysis techniques section. Table 1 summarizes the excess of water in the reaction system,

Table 1. Summary of Initial Molar Excess of Water and 1-octanol and Total Amount of Catalyst with Low Level and High Level Equivalent to 5 and 28 wt % of  $\text{Ni}(\text{DBSA})_2$ , Respectively

		molar excess of water to acetic acid	molar excess of 1-octanol to acetic acid	total amount of catalyst $[\text{cat}]_T$
$\text{Ni}(\text{DBSA})_2$	low	51.7	6.1	0.0070 mol <sub>Ni</sub> <sup>a</sup>
	high	51.8	4.3	0.0323 mol <sub>Ni</sub> <sup>a</sup>
sulfuric acid	low	52.0	6.4	0.0084 mol <sub>H</sub> <sup>b</sup>
	high	52.1	6.4	0.0397 mol <sub>H</sub> <sup>b</sup>
4-DBSA	low	52.5	6.4	0.0089 mol <sub>H</sub> <sup>b</sup>
	high	51.7	6.4	0.0395 mol <sub>H</sub> <sup>b</sup>
uncatalyzed	-	52.2	6.4	-

<sup>a</sup>Basis for the calculation is the amount of nickel from ICP-OES analysis with 3260 kg<sub>Ni</sub> kg<sub>5wt% solution</sub><sup>-1</sup> for low level and 16 300 kg<sub>Ni</sub> kg<sub>28wt% solution</sub><sup>-1</sup> for high level. <sup>b</sup>Basis for the calculation is the number of H<sup>+</sup>-ion equivalents: for sulfuric acid 0.019588 equiv g<sub>H<sub>2</sub>SO<sub>4</sub>96%</sub><sup>-1</sup> and for 4-DBSA 0.003154 equiv g<sub>4-DBSA,95%</sub><sup>-1</sup>.

the excess of 1-octanol to acetic acid, and the total amount of catalyst used in equivalent to 5 wt % (low level) and 28 wt % (high level) of  $\text{Ni}(\text{DBSA})_2$ . The basis for the calculation of catalyst load of sulfuric acid and 4-DBSA is their H<sup>+</sup>-ion equivalent and for  $\text{Ni}(\text{DBSA})_2$  the amount of nickel determined by ICP-OES. Selection of the amount of nickel as the basis for the metallosurfactant calculation was performed with the assumption that the catalytic activity of the metallosurfactant is based on the Brønsted acid/base interaction.

Figure 4 compares the octyl acetate yield achieved by the different catalysts with the uncatalyzed reaction. Sulfuric acid is widely used in the esterification of carboxylic acids, as it is highly efficient for concentrated reaction systems. In contrast, sulfuric acid is nearly inactive in the present system with a molar excess of water beyond 52 (see Table 1). Addition of sulfuric acid to the aqueous phase improves the extraction efficiency of acetic acid, as more undissociated and therefore extractable acetic acid is available. However, the achievable

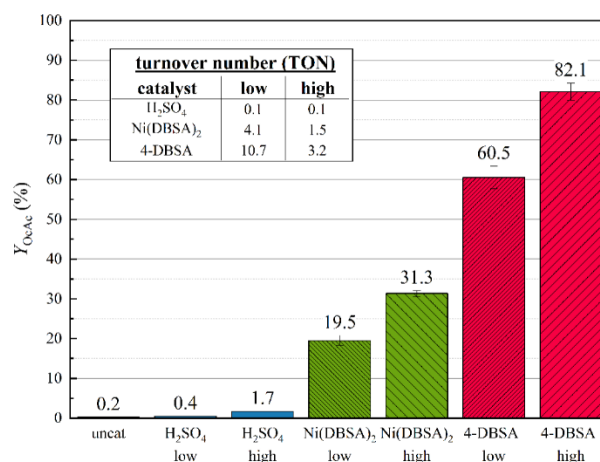


Figure 4. Octyl acetate yield  $Y_{\text{OAc}}$  and turnover number (TON) for low and high levels of different catalysts. Catalysts used:  $\text{H}_2\text{SO}_4$  (blue bars),  $\text{Ni}(\text{DBSA})_2$  (green bars), and 4-dodecylbenzenesulfonic acid (red bars) at 60 °C, 1-octanol as solvent phase, acetic acid concentration of 1 mol  $\text{L}^{-1}$ , phase ratio 1, stirrer speed 500 rpm, and error bars determined from three parallel experiments.

yield of octyl acetate for sulfuric acid catalysis is in the same order of magnitude as the uncatalyzed reference with 0.4% for the low level and 1.7% for the high level catalyst load. Location of the catalyst within the biphasic reaction system explains this effect. In contrast to the self-assembling (metallo)surfactant molecules, sulfuric acid is preferably present in the aqueous bulk phase and not at the interface, where the reaction takes place. Performance of 4-DBSA on the other hand is the upper benchmark in this case. The strong acidic properties and the emulsification induced by its surfactant ability allow yields between 60.5% (low level) and 82.1% (high level). The latter seems to be the maximum achievable yield from the interpretation of the octyl acetate concentration curve. The difference in the catalytic performance is also displayed by the difference in the turnover number (TON). The TON was calculated as the ratio of the amount of octyl acetate produced ( $n_{\text{OAc}}$ ) to the amount of catalyst used ( $n_{\text{CAT}}$ ) according to eq 1.

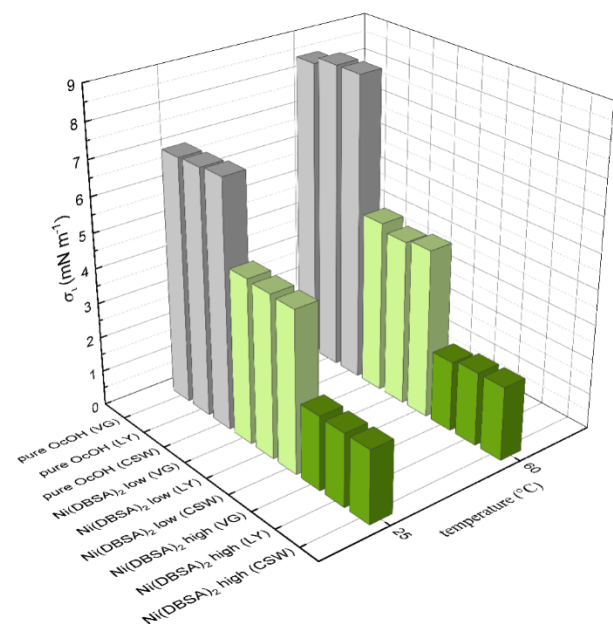
$$\text{TON} = \frac{n_{\text{OAc}}}{n_{\text{CAT}}} \quad (1)$$

For the given reaction conditions, the TON for low level of 4-DBSA with 10.7 is 2 orders of magnitude higher than the TON of sulfuric acid with 0.1. Regardless of its catalytic activity, 4-DBSA faces the problem of the formation of stable emulsions in the used load range. Emulsions formed by both levels of catalyst load cannot be split solely by gravitational force. Centrifugation or other means of emulsion splitting needs to be applied, increasing the complexity of the process and preventing the use of standard equipment (e.g., stirred extraction columns).

The nickel-metallosurfactant  $\text{Ni}(\text{DBSA})_2$  clearly exhibits catalytic activity, as confirmed by 19.5% octyl acetate yield for

the low level and 31.3% for the high level catalyst load. Yields are below that of low level 4-DBSA catalysis (60.5%), but clearly above the uncatalyzed reaction (0.2%) and the high level of sulfuric acid catalysis (1.7%). TON for Ni(DBSA)<sub>2</sub> of 4.1 and 1.5 for low and high level catalyst load, respectively, lies between sulfuric acid and 4-DBSA. It should be noted that the ratio between TON of Ni(DBSA)<sub>2</sub> and 4-DBSA is better for the high catalyst load, as TON highly decreases from low to high level of 4-DBSA.

The advantage of Ni(DBSA)<sub>2</sub> compared to the other catalysts lies in the complete prevention of emulsification, at the same time allowing intensive phase contact as a consequence of low interfacial tension. Adjustment of interfacial tension through the nickel-metallosurfactant enables a quasi-homogeneous state during reaction, with phase separation behavior comparable with the surfactant-free system. Interfacial tension of pure 1-octanol as well as of low and high metallosurfactant load in 1-octanol in water was measured with spinning drop video tensiometry. The measured interfacial tension  $\sigma_i$  for 25 and 60 °C is shown in Figure 5. A

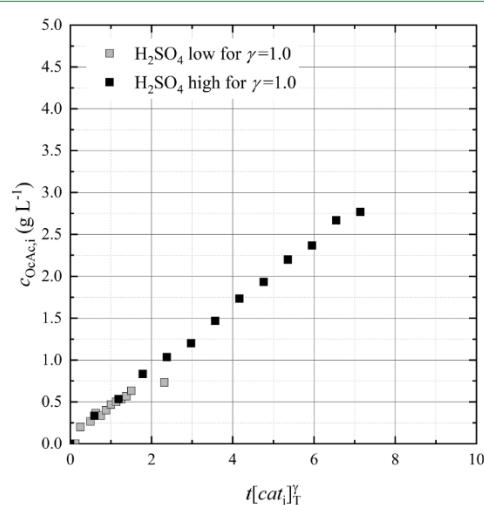


**Figure 5.** Interfacial tension  $\sigma_i$  between solvent/metallosurfactant mixtures and deionized water at 25 and 60 °C evaluated with models of Vonnegut (VG), Laplace–Young (LY), and Cayias–Schechter–Wade (CSW). Pure 1-octanol (OcOH) in gray, low level load of Ni(DBSA)<sub>2</sub> in 1-octanol in light green, and high level load of Ni(DBSA)<sub>2</sub> in 1-octanol in dark green.

reduction of the interfacial tension between solvent phase and deionized water between 34 and 44% for low metallosurfactant load and between 70 and 75% for high metallosurfactant load was observed. While measurement with 4-DBSA containing solvent was not possible due to immediate emulsification in the measurement capillary, the high metallosurfactant load with a  $\sigma_i$  of 2.1 mN m<sup>-1</sup> showed a phase separation behavior similar to that of the surfactant-free reference system. Additional information regarding spinning drop measurements can be found in the Supporting Information. The immediate emulsification can be explained by the catalyst load of 4-DBSA, which is orders of magnitude higher than the critical micelle concentration of 4-DBSA (CMC = 5.51 × 10<sup>-4</sup> mol

L<sup>-1</sup>)<sup>22</sup> for both levels of catalyst load. Within the investigated temperature range, no significant temperature dependency of the metallosurfactant containing solvent phases was observed.

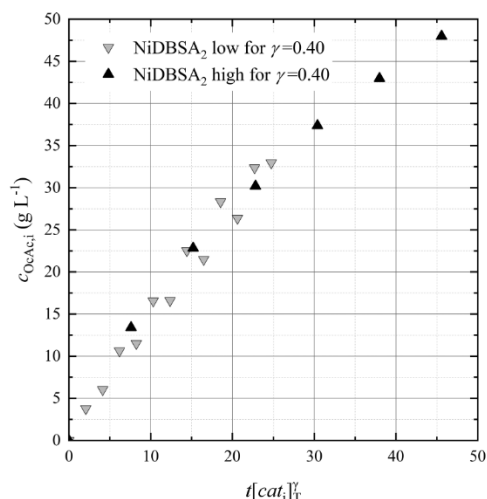
**Order in Catalyst.** The order in catalyst was determined by applying the graphical method proposed by Burés.<sup>23,24</sup> Main advantage of this straightforward method is that it uses the experimentally derived reactant concentration to determine the order in catalyst without further calculations. In addition, this method equally works for experiments with a low number of data points or data with a high experimental error. Reaction profiles of the investigated catalysts at both load levels are combined with a normalized time scale. For that purpose, the product concentration (concentration of octyl acetate in the solvent phase  $c_{\text{OcAc},i}$ ) is plotted over a time normalized by the total amount of catalyst raised to the power of  $\gamma$ , which represents the order in catalyst. This normalized time  $t[\text{cat}_i]_T^\gamma$  is adjusted until the reaction profiles are overlapping. Figure 6



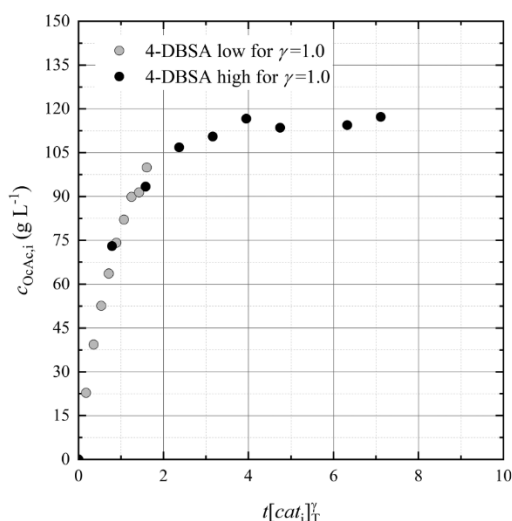
**Figure 6.** Octyl acetate reaction profiles from biphasic esterification with normalized time scale according to Burés<sup>23,24</sup> for catalysis with low and high level sulfuric acid load; order in catalyst  $\gamma = 1.0$ ; reaction temperature 60 °C.

shows the results of this method for sulfuric acid, Figure 7 for Ni(DBSA)<sub>2</sub>, and Figure 8 for 4-DBSA as catalysts. Table 1 depicts the total amount of catalyst used for this analysis method.

Both, sulfuric acid and 4-DBSA have an order in catalyst of  $\gamma = 1.0$ . This suggests that all active sites of these two catalysts are involved in catalysis. Nevertheless, the maximum concentration of octyl acetate for the sulfuric acid catalyzed experiments was at about 2.9 g L<sup>-1</sup>, while in 4-DBSA catalyzed experiments, the maximum concentration was around 129 g L<sup>-1</sup>. This remarkable difference is a consequence of the catalyst location in the system. While 4-DBSA molecules are located at the interface and therefore available for catalysis, sulfuric acid (and its H<sup>+</sup> ions) are distributed mainly in the aqueous phase. An estimated partition coefficient<sup>25</sup>  $\log K_{\text{OW}}$  of -2.2 supports this assumption. It follows, that the active sites of sulfuric acid are not available at the place of reaction (at the interface) in a sufficient quantity. In contrast to sulfuric acid, the nickel-metallosurfactant is located at the interphase as 4-DBSA. Despite a reduced catalytic activity indicated by an order in catalyst of  $\gamma = 0.4$ , the maximum concentration of octyl acetate was at 59 g L<sup>-1</sup>.



**Figure 7.** Octyl acetate reaction profiles from biphasic esterification with normalized time scale according to Burés<sup>23,24</sup> for catalysis with low and high level Ni(DBSA)<sub>2</sub> load; order in catalyst  $\gamma = 0.4$ ; reaction temperature 60 °C.



**Figure 8.** Octyl acetate reaction profiles from biphasic esterification with normalized time scale according to Burés<sup>23,24</sup> for catalysis with low and high level 4-DBSA load; order in catalyst  $\gamma = 1.0$ ; reaction temperature 60 °C.

## CONCLUSIONS

A metallosurfactant based on the anionic surfactant 4-dodecylbenzenesulfonic acid and divalent nickel (Ni(DBSA)<sub>2</sub>) is suitable for the interfacial catalysis of biphasic esterification of low-molecular-weight carboxylic acids with 1-octanol. Although the catalytic performance is below that of 4-dodecylbenzenesulfonic acid, the metallosurfactant shows excellent characteristics, as it does not induce emulsification. With this catalyst, an octyl acetate yield of up to 31.3% was obtained, compared to 0.2% yield in the uncatalyzed reference experiment. Even a reduction of the interfacial tension of around 75% to 2.1 mN m<sup>-1</sup> due to the metallosurfactant load did not result in emulsification nor hindered the phase separation. 1-Octanol as a solvent for Ni(DBSA)<sub>2</sub> prevents the metallosurfactant from precipitating during reaction and shows satisfying extraction performance for carboxylic acids extrac-

tion. Utilizing 1-octanol as a reactive solvent provides sufficient excess for the esterification of the carboxylic acid and driving force for the extraction of carboxylic acid. Biphasic esterification enhanced by interfacial catalysis with Ni(DBSA)<sub>2</sub> allows the utilization of dilute low-molecular-weight carboxylic acids for holistic use of biomass feedstock.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b04667.

Table with investigated solvent mixtures, metal ions, and reason for exclusion; pictures of metallosurfactant mixtures displaying undesired solution behavior or instability; and pictures of spinning drop video tensiometry (PDF)

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: andreas.toth@tugraz.at. Tel: +43 316 873 7460.

### ORCID

Andreas Toth: 0000-0001-9162-5863

Daniela Painer: 0000-0002-9210-0820

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge the contribution of Tanja Weiß in the experimental work and the advice of Ao.Univ.-Prof. Mag. Dr.rer.nat. Robert Schennach from the Institute of Solid State Physics at Graz University of Technology in IR spectra interpretation.

## ABBREVIATIONS

4-DBSA, 4-dodecylbenzenesulfonic acid; CMC, critical micelle concentration; DEHPA, di-(2-ethylhexyl)phosphoric acid; FID, flame ionization detector; GC, gas chromatography; ICP-OES, inductively coupled plasma optical emission spectroscopy; TCD, thermal conductivity detector; TON, turnover number;  $c_i$ , concentration; cat, amount of catalyst;  $i$ , component/phase/catalyst  $i$ ; OcAc, octyl acetate;  $t$ , time;  $T$ , total;  $Y$ , yield;  $\gamma$ , order in catalyst;  $\sigma$ , interfacial tension

## REFERENCES

- (1) Painer, D.; Lux, S.; Graftschatter, A.; Toth, A.; Siebenhofer, M. Isolation of Carboxylic Acids from Biobased Feedstock. *Chem. Eng. Technol.* **2017**, *89*, 161–171.
- (2) Toth, A.; Lux, S.; Painer, D.; Siebenhofer, M. Intensification of esterification through emulsification: isolation of dilute low molecular weight carboxylic acids. *React. Chem. Eng.* **2018**, *3*, 905–911.
- (3) Manabe, K.; Iimura, S.; Sun, X.-M.; Kobayashi, S. Dehydration Reactions in Water. Brønsted Acid–Surfactant–Combined Catalyst for Ester, Ether, Thioether, and Dithioacetal Formation in Water. *J. Am. Chem. Soc.* **2002**, *124*, 11971–11978.
- (4) Shiri, M.; Zolfigol, M. A. Surfactant-type catalysts in organic reactions. *Tetrahedron* **2009**, *65*, 587–598.

(5) Zhao, J.; Guan, H.; Shi, W.; Cheng, M.; Wang, X.; Li, S. A Brønsted–Lewis-surfactant-combined heteropolyacid as an environmental benign catalyst for esterification reaction. *Catal. Commun.* **2012**, *20*, 103–106.

(6) Zheng, Y.; Zheng, Y.; Yang, S.; Guo, Z.; Zhang, T.; Song, H.; Shao, Q. Esterification synthesis of ethyl oleate catalyzed by Brønsted acid–surfactant-combined ionic liquid. *Green Chem. Lett. Rev.* **2017**, *10*, 202–209.

(7) Likozar, B.; Levec, J. Effect of process conditions on equilibrium, reaction kinetics and mass transfer for triglyceride transesterification to biodiesel: Experimental and modeling based on fatty acid composition. *Fuel Process. Technol.* **2014**, *122*, 30–41.

(8) Likozar, B.; Levec, J. Transesterification of canola, palm, peanut, soybean and sunflower oil with methanol, ethanol, isopropanol, butanol and tert-butanol to biodiesel: Modelling of chemical equilibrium, reaction kinetics and mass transfer based on fatty acid composition. *Appl. Energy* **2014**, *123*, 108–120.

(9) Likozar, B.; Pohar, A.; Levec, J. Transesterification of oil to biodiesel in a continuous tubular reactor with static mixers: Modelling reaction kinetics, mass transfer, scale-up and optimization considering fatty acid composition. *Fuel Process. Technol.* **2016**, *142*, 326–336.

(10) Liu, B.; Hu, F.; Shi, B.-F. Recent Advances on Ester Synthesis via Transition-Metal Catalyzed C–H Functionalization. *ACS Catal.* **2015**, *5*, 1863–1881.

(11) Weires, N. A.; Caspi, D. D.; Garg, N. K. Kinetic Modeling of the Nickel-Catalyzed Esterification of Amides. *ACS Catal.* **2017**, *7*, 4381–4385.

(12) Samper, E.; Rodríguez, M.; de La Rubia, M. A.; Prats, D. Removal of metal ions at low concentration by micellar-enhanced ultrafiltration (MEUF) using sodium dodecyl sulfate (SDS) and linear alkylbenzene sulfonate (LAS). *Sep. Purif. Technol.* **2009**, *65*, 337–342.

(13) Ferella, F.; Prisciandaro, M.; De Michelis, I.; Veglio, F. Removal of heavy metals by surfactant-enhanced ultrafiltration from wastewaters. *Desalination* **2007**, *207*, 125–133.

(14) Hanson, B. E. New directions in water soluble homogeneous catalysis. *Coord. Chem. Rev.* **1999**, *185-186*, 795–807.

(15) de la Iglesia, P.; Jaeger, V. W.; Xi, Y.; Pfaendtner, J.; Pozzo, L. D. Structure Characterization and Properties of Metal-Surfactant Complexes Dispersed in Organic Solvents. *Langmuir* **2015**, *31*, 9006–9016.

(16) Parera, E.; Comelles, F.; Barnadas, R.; Suades, J. New surfactant phosphine ligands and platinum(II) metallocenes. Influence of metal coordination on the critical micelle concentration and aggregation properties. *Langmuir* **2010**, *26*, 743–751.

(17) Sinou, D. Asymmetric Organometallic-Catalyzed Reactions in Aqueous Media. *Adv. Synth. Catal.* **2002**, *344*, 221–237.

(18) Dwars, T.; Paetzold, E.; Oehme, G. Reactions in micellar systems. *Angew. Chem., Int. Ed.* **2005**, *44*, 7174–7199.

(19) Lipshutz, B. H.; Gallou, F.; Handa, S. Evolution of Solvents in Organic Chemistry. *ACS Sustainable Chem. Eng.* **2016**, *4*, 5838–5849.

(20) Riemenschneider, W.; Bolt, H. M. Esters, Organic. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley: 2010; Vol. 74, pp 245–266.

(21) Hajduchova, Z.; Pach, L.; Lokaj, J. Adsorption of dodecylbenzenesulfonic acid on the alumina particles in the preparation of alumina foam. *Ceram.-Silik.* **2018**, *62*, 138–145.

(22) Petrenko, V. I.; Avdeev, M. V.; Garamus, V. M.; Bulavin, L. A.; Aksenov, V. L.; Rosta, L. Micelle formation in aqueous solutions of dodecylbenzene sulfonic acid studied by small-angle neutron scattering. *Colloids Surf., A* **2010**, *369*, 160–164.

(23) Burés, J. A Simple Graphical Method to Determine the Order in Catalyst. *Angew. Chem., Int. Ed.* **2016**, *55*, 2028–2031.

(24) Burés, J. Variable Time Normalization Analysis: General Graphical Elucidation of Reaction Orders from Concentration Profiles. *Angew. Chem., Int. Ed.* **2016**, *55*, 16084–16087.

(25) *Estimation Programs Interface Suite*, version 4.11 (Update 2017); United States Environmental Protection Agency: Washington, DC, 2012.