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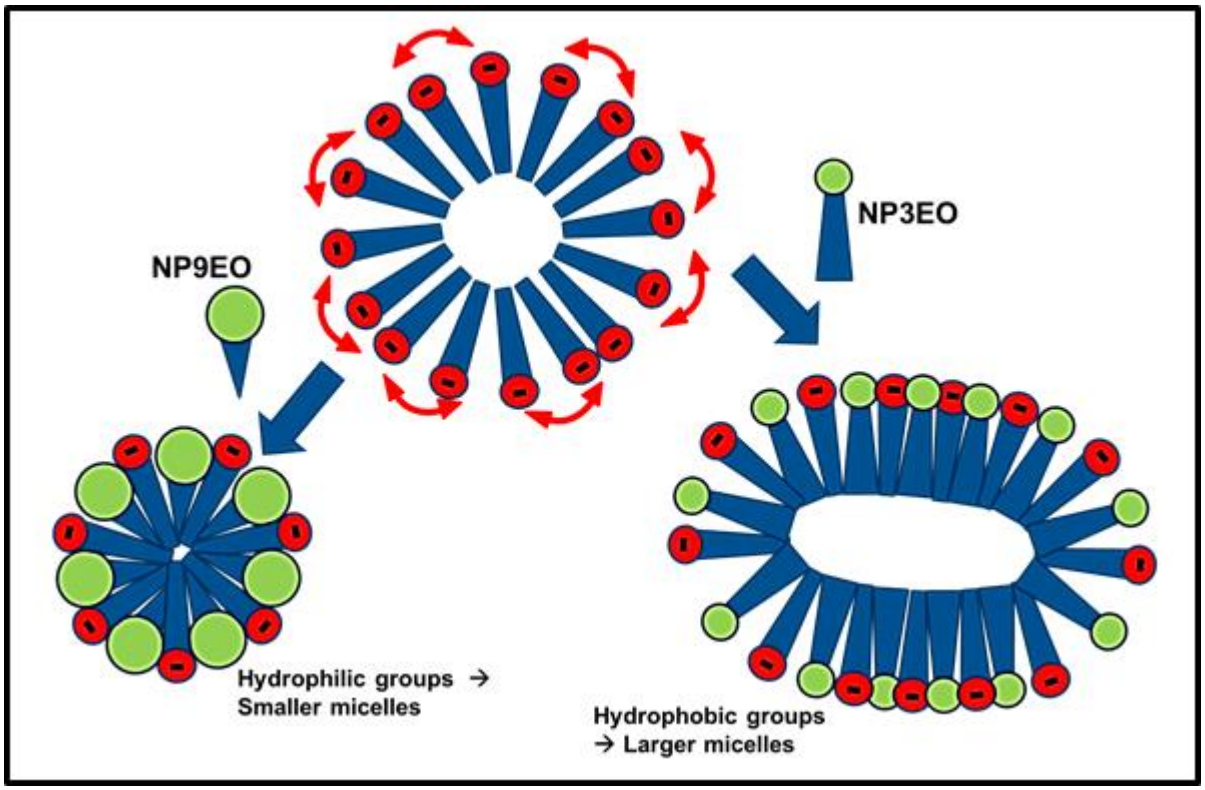

Distribution of Surfactants in Mixed Micelles

Thesis for the Bachelor of Science in Chemical Engineering

LOVISA PETTERSSON AND SOFIA HOLMBERG

Department of Chemical and Biological Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
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ABSTRACT

Surface active agents are used in many different applications as cleaning and wetting agents, dispersants, corrosion inhibitors, softeners, collectors etc. It is well known that surfactant mixtures usually provide much better properties than the surfactants alone. Surfactant mixtures in water form mixed micelles. In this study physico-chemical properties of the mixed micelles, formed from zwitterionic (alkyl sodium ether sarcosinate (DS100)) and nonionic (nonylphenol ethoxylates (NPEO)) surfactants, were investigated.

Results obtained by the use of dynamic surface tension measurements indicate that nonionic surfactants increase the efficiency of the zwitterionic. The surface tension decreases more rapidly when mixed micelles are formed. There is an optimum for the degree of ethoxylation (DE=>1 - <9) for nonylphenol in case of, investigated in this study, alkyl sodium ether sarcosinate. NPEOs with DE=2-4 reduced the surface tension fastest and most. Results of diffusion NMR studies indicate that the size of the micelles follows bellow order: DS100+NP3EO>DS100>DS100+NP9EO.

SAMMANFATTNING

Ytaktiva ämnen (tensider) används i stor utsträckning inom flera olika applikationer såsom vätande medel, dispergeringsmedel, korrosionsinhibitorer, mjukgörare, uppsamlare etc. Det är väl känt att tensidblandningar oftast genererar bättre egenskaper än enskilda tensider. Tensidblandningar formulerade i vatten bildar mixade miceller. I den här studien undersöks de fysikal-kemiska egenskaperna hos de mixade micellerna, som bildats från zwitterjoniska (alkyl natrium sarcosinate (DS100)) och nonjoniska (nonylfenol etoxilat (NFEO)) tensider.

De erhållna resultaten från de dynamiska ytspänningsmätningarna indikerar att de nonjoniska tensiderna ökar effektiviteten hos den zwitterjoniska. Ytspänningen minskar snabbare då de mixade micellerna bildas. Det finns en optimal etoxileringsgrad ((DE=>1 - <9) för nonylphenol tillsammans med alkyl natrium sarcosinate, vilket undersökts i denna studie. Nonylfenol etoxilat med DE=2-4 reducerar ytspänningen snabbast och mest. Resultaten från diffusions NMR- mätningarna indikerar att storleken på micellerna följer följande ordning. DS100+NP3EO>DS100>DS100+NP9EO.

ACRONYMS

NMR	Nuclear Magnetic Resonance
CD_3OD	Deuterated methanol
D_2O	Deuterated water
Pyridine reagents solution	phtalic anhydride /pyridine /4-methyl-aminopyridine
DDMICI	1,3-Didecyl-2-methyl imidazolin chloride
Surfactant	Surface active agent
CMC	Critical micelle concentration
CPP	Critical packing parameter
GC	Gas chromatography
NPEO	Nonylphenol ethoxylate
DS100	Alkyl sodium ether sarcosinate
DE	Degree of ethoxylation
D	Diffusion coefficient

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1. INTRODUCTION

1.1 Background

Surfactants (surface active compounds) are very widely used in a number of different application fields as cleaning and wetting agents, dispersants, adhesion promoters, ignition improvers, etc. Hence it is well known that surfactant mixtures provide much better properties than surfactants alone. This phenomenon is known as a synergetic effect. However it is not always clear how the surfactants interact with each other in order to provide the improved performance.

In the field of mining, surfactants or surfactant mixtures are used for the separation of minerals from mixtures of minerals in a process so called beneficiation. For the selective beneficiation of phosphorus containing minerals a mixture of zwitterionic surfactant with nonionic is usually used. For that particular purpose alkyl sodium ether sarcosinate is used as an amphoteric surfactant and ethoxylated nonylphenol represents a nonionic surfactant. However not all nonylphenol ethoxylates work in the same way. There is an interval of an optimal degree of polymerization of nonylphenol that provide the best beneficiation selectivity results.

The work is focused on an investigation of five different nonylphenol ethoxylate with a different degree of ethoxylation in mixtures with sodium sarcosinate. Evaluation of a critical micelle concentration (CMC) and nuclear magnetic resonance (NMR) spectroscopy are important tools for the investigation of mixed micelles.

The bachelor thesis, in chemical engineering at Chalmers University of Technology, is performed at AkzoNobel Surface Chemistry in Stenungsund, Sweden. The work is carried out for ten weeks and started in October 2013.

1.2 Aim

The aim of this bachelor thesis work was to investigate:

a) Synergetic effect of different mixtures of nonylphenol ethoxylate and alkyl sodium ether sarcosinate with a help of surface chemistry measurements.

b) Distribution of these surfactants in mixed micelles by the use of diffusion NMR technique.

2. THEORY

2.1 Surfactants

Surface active agents or surfactants are substances that are recognized by its ability to adsorb at a surface or between two unmixable phases. Surfactants can adsorb between different phases for instance liquid-liquid, liquid-vapour and solid-liquid. The adsorption of a surfactant between phases results in a decrease of the free energy between these phases. [1].

The ability to adsorb at an interphase refers to the structure of surfactants. A surfactant generally consists of a lyophobic and a lyophilic part. When water is used as a liquid phase terms as a hydrophobic (often a hydrocarbon chain) and a hydrophilic part (a particular polar group) are used. [1][2]

The surfactants can be produced from different raw materials and therefore, they may be divided into oleo-chemically based and petro-chemically based surfactants. Surfactants based on oleo-chemicals are made from renewable raw materials.
Surfactants can also be found in the nature, often referred to as polar lipids and are very common in all living organisms. The surfactants in living organisms have the same function as in technical systems. [1]

Due to the polar group surfactants are categorized into nonionic and ionic surfactants.

2.1.1. Nonionic surfactants

Surfactants that have an uncharged polar group are referred to as nonionic surfactant. The most common uncharged polar group is a polyoxyethylene group, synthesized from ethylene oxides (EO) via polymerization. Other important nonionics are propoxylated alcohols, ethoxylated/propoxylated alcohols and alkylpolyglucosides. [2]
The hydrophobic chain can be straight or branched. Depending on the hydrophilic chain length the surfactants have different properties and therefore are used in different technical applications. Industrial uses include detergents and wetting agents among others.
One of the widely used nonionic surfactant is nonylphenol ethoxylate (NPEO); see figure 1. Commercially available NPEO has a polar group containing 1-50 EO groups. [3]

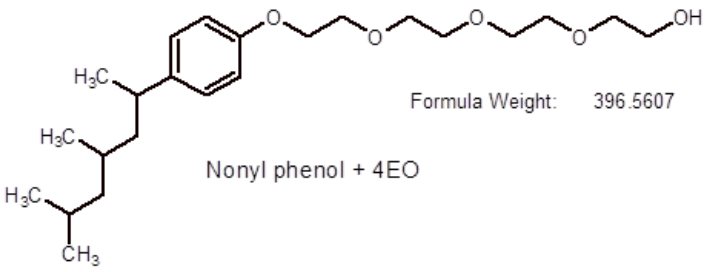


Figure 1. Structure of ethoxylated nonylphenol.

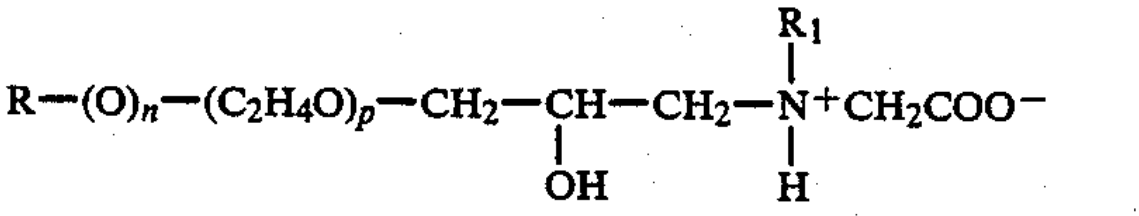
2.1.2. Ionic surfactants.

There are three types of ionic surfactants: anionic, cationic and zwitterionic (amphoteric).

Anionic surfactants are the most common group of surfactants. The largest group of anionics is carboxylates that are widely used in cleaning products as soaps. Alkylbenzene sulfonate is another representative of anionics that are commonly used in household detergents and different industrial applications. Hence other chemical groups can also represent the polar group, for instance sulphate or carbonate. The counterions that are mostly used are sodium, potassium, ammonium, calcium and protonated alkyl amines. [1][2]

Surfactants, containing positively charged polar group are referred as cationic surfactants, which are subdivided into primary, secondary, tertiary amines and quaternary ammonium salts. Cationic surfactants can be used as antistatic, herbicides, fabric softeners and corrosion inhibitors due to their ability to interact with negatively charged surfaces. [1] [2]

Zwitterionic (amphoteric) surfactants are surfactants containing both negative and positive charge and have pH-dependent properties. [2] Alkylbethaines and alkylaminopropionates are the largest families in the group of the amphoteric surfactants. Zwitterionics are commonly used in shampoos and cosmetic products due to their excellent dermatological properties. [1]



Where n=0 or 1; R is alkyl=C4-C18; p=0-5; R1=CH_3

Figure 2. Molecular structure of alkyl ether sarcosinate.

One special type of zwitterionic is alkyl sodium ether sarcosinate, which is an N-alkyl derivate synthesized from alkene oxide and amino acid, see figure 2. Such surfactants are used in a highly selective beneficiation of complex phosphorus containing ores and in pharmaceutical applications. [4]

2.2 Micelles, critical micelle concentration and surface tension

An important property of surfactants is the ability to form aggregates, so called micelles. The formation is an alternative for adsorption between two unmixable phases. Micelles are surface not active and represent just a reservoir for surfactant unimers. In a polar medium, for instance water, the free energy is reduced, since the hydrophobic groups are not in contact with water, see figure 3. [1]

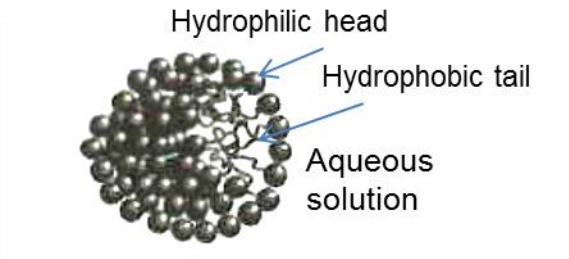


Figure 3. Spherical micelle in aqueous solution. [1]

The formation of the micelles starts at the critical micelle concentration (CMC), which means that the surface tension is kept more or less constant after this point. Surface tension is related to the attractive forces (which originate from dispersion, dipole-dipole forces and hydrogen bonding) between molecules in a solution. The attractive forces for a molecule in a bulk solution are the same in all directions but for a surfactant at the surface there is a lack of attraction in one direction. This asymmetry is the origin for the surface energy [1] In addition; CMC depends on chemical structure, temperature and co-solute. [1] [5]

Surface tension can be measured as static or dynamic surface tension [1]. Dynamic surface tension is used to measure the reduction rate of the surface tension for different surfactants. The static surface tension is instead used to determine the surface tension between the phases at equilibrium. [6]. In order to determine CMC only the static surface tension method is used. However sometimes CMC for ionic surfactant can be determined by the use of conductivity measurements. [7]

The results of CMC measurements can be used to determine the hydrophilic group area (a), which is used when the Critical packing parameter (CPP), or the surfactant number is determined. This parameter is also related to the length of the hydrophobic part in the core (l_{max}) and the volume of the hydrophobic part in the micellar core (v), according to equation 1. [1]

$$\mathrm{CPP} = \frac{v}{(a * l_{max})} \qquad (1)$$

Depending on the CPP value, the micelle can be spherical, cylindrical etc., see figure 4. When the CPP value reaches approximately ≥ 1, the surfactants can pack into either lamellar micelles in aqueous media or reversed micelles in nonpolar media. [5] The size, shape and surfactant number may change depending on changes in temperature, surfactant concentration, additive in the liquid phase and chemical structure of the surfactants [5]

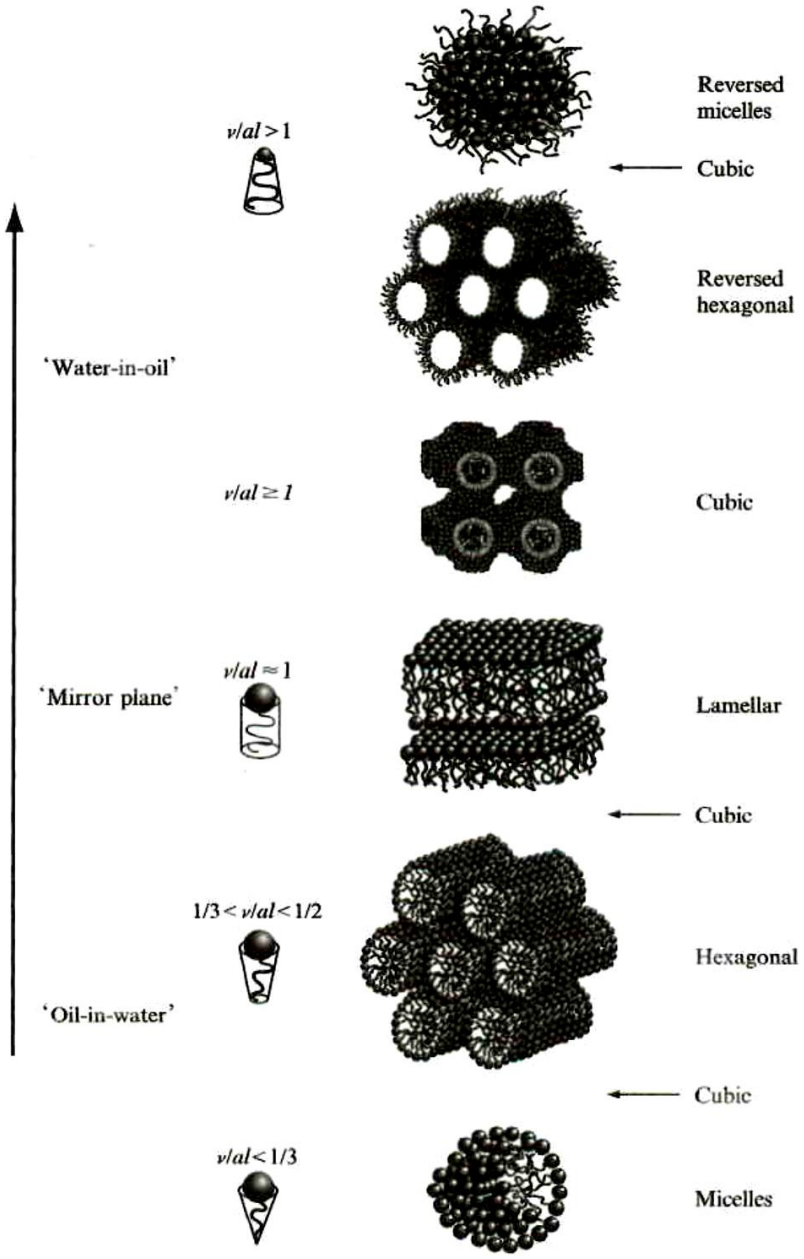


Figure 4 Depending on the CPP value different micelle structures are formed. [1]

2.3 Mixed micelles

If two surfactants are mixed in a solution, mixed micelles are formed. The purpose of mixing surfactants is to achieve a synergetic effect, which means that the produced effect is greater than the sum of their individual effects. [1]

The simplest way is to mix two surfactants with the same head group. This leads to a non-interaction between the head group. When two surfactants of different types, for instance a nonionic and an anionic, are mixed a small net interaction between them is obtained. This is

because the nonionic surfactants protect the repulsion between the head groups of the anionic surfactants. [1]

One example of when a synergetic effect is obtained is when mixing the anionic surfactant sodium dodecyl sulfate (SDS) and the nonionic surfactant NP10EO. The CMC of this mixture shows a dramatic decrease when already low fractions of NP10EO are used. The decrease takes place due to the preferable absorption of NP10EO in the SDS micelle, illustrated in figure 5. The preferable absorption depends on the higher hydrophobic effect for the nonionic surfactant, revealed by its lower CMC compared with the anionic SDS. [1]

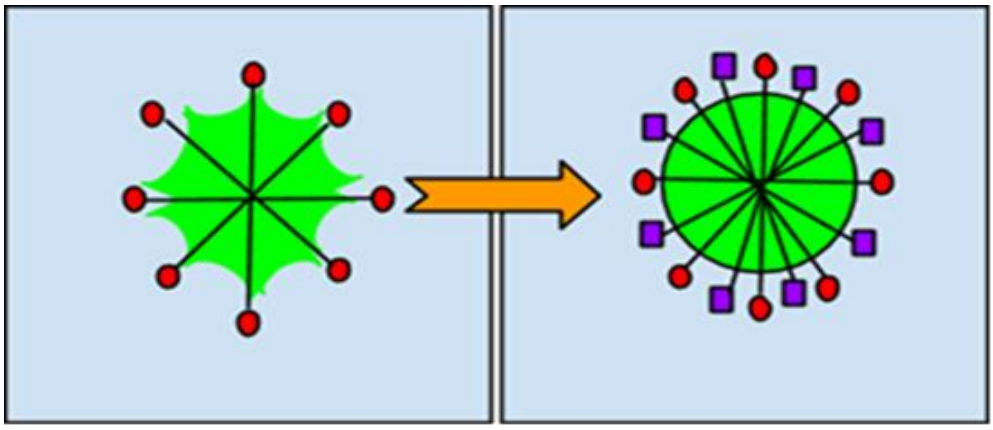


Figure 5 The hydrophobic effect is improved by adding the nonionic surfactant, which facilitate the formation of micelles.

2.4 NMR

Nuclear Magnetic Resonance spectroscopy (NMR) is an analytical method for determining the structure and composition of chemical substances. NMR diffusometry can be used for studying micellar solutions. This is performed by observing the diffusion properties of surfactants, inside and outside of micellar aggregates. The surfactants which are inside the micellar aggregates possess a much more restricted diffusion whereas the surfactants which are outside the micelles, within the water solution, diffuse much faster.[8]

2.4.1 NMR-spectroscopy

In an external magnetic field nuclei of different atoms possess a nuclear magnetic spin which is parallel to the external magnetic field and originating from the magnetic moment of the charged protons. The spinning frequency υ_0 in Hz is proportional to the external magnetic field B_0 according to the Larmor equation, see equation 2.

$$v_0 = -\gamma B_0/2\pi \qquad (2)$$

where

γ = the gyromagnetic ratio and dependant on the composition of the nuclei
B_0 = the external magnetic field

In order to analyse different nuclei, the NMR sample is exposed to an electro- magnetic radiofrequency (RF) pulse with a radiofrequency equivalent to the spinning frequency of the nuclei to be observed. In an external magnetic field the magnetic spins are in the lowest energy level when they are parallel to it. [8] The NMR sample has therefore a magnetization along that direction which can be defined as being along the Z-axis in an orthogonal coordinate system. As the RF pulse has an alternating magnetic field it can turn the magnetic spins away from the external field along the Z-axis if it is sent through the sample orthogonally from that Z-axis from what could be defined as the XY-plane.[8]

After a certain amount of time a pulse with a certain strength can turn the direction of the magnetic spins of the nuclei from the external magnetic field B_0 along the Z-axis to the perpendicular XY plane. This is called, a 90º-pulse.[8][9] After the RF-pulse is turned off the magnetic spins revert back to the lowest energy level of the magnetic spins of the nuclei in the external magnetic field. This is called relaxation and can be expressed in relaxation times T_1 and T_2, where T_1 is the longitudinal relaxation time and T_2 is the transverse relaxation time (loss of magnetization along the XY-plane). [8]

After the nuclei have been exposed to the magnetic pulses, the NMR signal can be obtained by the spectrometer, usually referred to as the free induction decay (FID) were the alteration of the induction signal of the nuclei is showed versus time. The induction signal is decreasing with the time due to the relaxation. If a sample contains nuclei with different resonance frequencies, interference between the frequencies, of the different nuclei, will occur. [8] It is very complex to obtain the frequencies of the individual magnetic spins by only observing the FIDs. Therefore, a mathematical operation called the Fourier transformation can be done.

This operation provides a spectrum, were the time scale has been converted to a frequency scale (in ppm). [8]

When a magnetic field is applied on a sample, the atoms will be affected and an internal magnetic field will be created. This internal field is also referred to as the effective field, which can vary depending on the electronically surroundings of each nucleus.[9] In molecules different nuclear shielding by the surrounding electrons will occur. The shielding increases with the number of electrons surrounding each atom. This will affect the obtained frequency from the nuclei, in a way that atoms which are more electronically shielded will receive a lower frequency. Atoms with electron withdrawing groups will receive a higher frequency, they will be shifted towards higher frequencies compared to the shielded nuclei of the selected references substance like tetramethyl silane (TMS) which has strong shielding of the nuclei by the surrounding electrons. This shifting of the frequency due to the chemical surroundings of nuclei is called the chemical shift. This difference is expressed relatively to the reference (TMS) in terms of ppm which means part per million higher frequency compared to that of TMS [9] In this way, nuclei with different nuclear shielding appear as separated signals in the final spectrum. [8]

Different types of electron withdrawing groups like oxygen's or amines or chemical double bonds are examples of parameters that can affect the surroundings and therefore, the effective field and the chemical shift. This phenomenon is called the chemical shift and it represents the difference between the frequencies of the nuclei and a standard reference.

2.4.2 NMR diffusometry

In NMR diffusometry, the diffusion rate of the different molecules in the NMR sample is studied. The diffusion rate is depending on the size and shape of the molecules in the sample and of the solvent. Large molecules will show a slower diffusion rate. In order to perform a diffusometry measurement, a series of ^{1}H-NMR are conducted where increasing gradient pulses are transmitted through the sample. The increasing gradient pulses cause the signals to disappear more with measurement time. The signal strength can be plotted as a function of the increasing pulse field gradients, which can be used to calculate the diffusion rate. [10]

3. MATERIALS

Following products and chemicals were used for the experimental part of this diploma work.

Table 1 Chemicals used in this diploma work.

Chemical	Molecular formula	Purity	M_{w} , g/mol (theoretical)	Comment	Source
Ethanol	C_2H_5OH	95%	46.07	-	-
Methanol	CH_3OH	-	32.04	For analysis	Merck
Pyridine reagent	-	-		Reagent mixture	-
Sodium hydroxide	NaOH	-	39.99	1M	-
Potassium hydroxid in ethanol	KOH	-	56.10	0.5015M	-
Glacial acetic acid	CH_3COOH	100%	60.05	-	Merck
Buffer pH 11.5	-	-	-	pH=11.5	Labservice
Chloroform	$CHCl_3$	-	119.48	For analysis	
DDMICI	-	-	-	0.00392M	
Deuteriumoxide	D_2O	≥99%	20.02	-	Deutero GmbH
Methanol, deuterated	CD_3OD	≥99%	36.07	-	Deutero GmbH
Sodium hydroxide, deuterated	NaOD	≥99%	41.00	-	Deutero GmbH
Perchloric acid	$HClO_4$	-	100.46	0.1M	-
Acetic anhydride	$C_4H_6O_3$	-	102.09	For analysis	-
DS100	-	-	400.00	Akzo Nobel product	-
NP1EO	-	-	264.4	Akzo Nobel product	-
NP 2EO	-	-	308.5	Akzo Nobel product	-
NP3EO	-	-	352.5	Akzo Nobel product	-
NP4EO	-	-	396.6	Akzo Nobel product	-
NP9EO	-	-	616.8	Akzo Nobel product	-
Methanol	CH_3OH	≥99%	32.04	For analysis	-
Karl Fisher reagent	-	-	-	For analysis	Fluka

4. METHODS AND EXPERIMENTAL

4.1 Gas Chromatography

A flame ionization detector (FID) was used in the analyses and evaluated with the computer program EzChrom Elite. The GC used was a Hewlett Packard 5890 series 2.

4.1.1 Distribution of nonylphenol ethoxylate homologues

Two drops of each sample were transferred to a corresponding 2 ml vial and diluted with ethanol. Then the samples were injected by a split injector and heated to 320 °C rising the temperature stepwise during 35 minutes

4.1.2 Determination of ethanol content in DS100

0, 35 g of DS100 were diluted in 10 ml methanol. Thereafter, the solution was left at 40°C oven for 15 minutes in order to homogenize the solution. The homogenized solution was transferred to a 2 ml vial.

In order to determine the ethanol content two standards, A and B, with known ethanol concentrations were also prepared. For standard A, 0. 09 g of ethanol was diluted in 10 ml methanol. For standard B, 1 ml of standard A was diluted in 10 ml methanol.

The standards were transferred to a corresponding 2 ml vial. The solutions were injected by a split injector and heated to 300 °C with the temperature rising stepwise during 30 minutes.

4.2 Wet chemistry methods

4.2.1 Determination of water content in DS100 according to Karl-Fischer

Water content was determined by titration according to Karl-Fischer [Arvidsson Rolf, Analytical Methods for Production AB46-1208, 2004 Akzo Nobel Surfactants]. Titrations were performed with a Karl Fischer solution, Combi Titrant 5 on a 701 KF Titrino Metrohm together with 703 Ti Stand and 701 KF Titrino keyboard all from Metrohm.

4.2.2 Determination of the molecular weight of nonylphenol ethoxylate by potentiometric titration

0.05 – 1.00 g of a sample were weighed into a 250mL Erlenmeyer flask. (An additional flask without any sample was used as a blank). 25mL of pyridine reagent solution were added to each flask. The flasks were sealed with caps, followed by swirling to ensure good mixing.

The Erlenmeyer flasks were left in an incubator at 40°C for 20 minutes. Then 25mL of 0.1M NaOH was added to each flask.

All of the sample solutions, including the blank, were titrated with 0,5M KOH in ethanol. The OH-value (mgKOH/g) is calculated for all of the samples according to following equation:

$$OH - value = \frac{(b-a)*c*56.1}{\text{g}} \quad (3)$$

Where a= amount of KOH solution consumed by the sample, (mL)
b= amount of KOH solution consumed by the blank, (mL)
c= concentration of the KOH solution, (M)
g= amount of sample, (g)

The molecular weight for each substance was calculated as follows:

$$M_w = \frac{1}{OH-value*56.1} * 1000 \quad (4)$$

4.2.3 Determination of the molecular weight of DS100 by the use of the total amine method.

0.1g of DS100 was weighed into a beaker, and dissolved in 50mL of glacial acetic acid. Thereafter, the solution was titrated by 0.1M perchloric acid.

The amount of total amine (meq/g) was calculated, see equation 5.

$$Ntot = \frac{\text{a}*\text{c}}{g} \quad (5)$$

Where, a= amount of perchloric acid consumed by the sample, (mL)
c= concentration of perchloric acid, (M)
g= amount of sample, (g)

The molecular weight of DS100 was calculated as follows:

$$Mw = \frac{2}{Ntot} * 1000 \quad (6)$$

4.2.4 Determination of the molecular weight of DS100 by the use of anionic content.

5mL of 0.3% DS100 aqueous solution was transferred to a black painted beaker containing 5mL of buffer, 5mL of chloroform and ~15mL of distilled water. To ensure a good emulsion, the sample solution was left with heavily stirred for approximately 1 min. A photosond was put into the solution and the solution was titrated with 0.004 M DDMICI.

Amount of anionic surfactant (meq/g) was calculated as follows:

$$meq/g = \frac{\text{a}*\text{c}*100}{g*5} \quad (7)$$

Where, a= amount of DDMICI consumed by the sample, (mL)
c= concentration of DDMICI, (M)
g= amount of sample, (g)

The molecular weight of DS100 was calculated according to the following equation:

$$Mw = \frac{1}{meq/g} * 1000 \quad (8)$$

4.3 Static surface tension

4.3.1 Determination of CMC by du Noüy ring method

Principle: amount of the test sample is continuously added into a flat beaker filled with 50 ml of distilled water. After each addition the equilibrium surface tension is determined by the use of a du Noüy ring: the force that is required to pull the ring through the surface is measured. The CMC is obtained when the surface tension is constant. This is performed by interpolating a CMC curve, where the intersect equals the CMC value.

300 g of 2g/l solutions containing DS100 and NPEO at a molar ratio 1:1 were prepared according to the table 2.

Table 2 Amounts of DS100 and NPEO that was used for the CMC measurements, 2g/l.

Solutions	Amount of DS100 (g)	Amount of NP+XEO (g)
Na-DS100	0.60	0.00
DS100 +NP1EO	0.40	0.20
DS100 +NP2EO	0.39	0.21
DS100 +NP3EO	0.36	0.24
DS100 +NP4EO	0.35	0.25
DS100 +NP9EO	0.27	0.33
NP9EO	0.00	0.60

4.3.2. Determination of CMC by conductivity method

This method is applied for ionic surfactants only. The electrical conductance is measured at different concentrations of the test sample and CMC is obtained as an abrupt change of the slope, due to the change in electrical conductance. The change depends on that the surfactant unimers behaves as strong electrolytes and that the micelles in turn are partially ionized. Therefore, the micelles act as weak electrolytes. [7]

100 g of 10g/l solutions containing DS100 and NPEO at a molar ratio 1:1 were prepared according to the table 3. The solutions were diluted to different concentrations, see table 4.

Table 3 Amounts of DS100 and NPEO that was used for the CMC measurements, 10 g/L.

Solutions	Amount of DS100 (g)	Amount of NP+XEO (g)
DS100	1.00	0.0
DS100 +NP1EO	0.67	0.33
DS100 +NP2EO	0.65	0.35
DS100 +NP3EO	0.61	0.39
DS100 +NP4EO	0.57	0.43
DS100 +NP9EO	0.44	0.56

Table 4 The chosen concentrations for the conductivity method, in order to determine CMC.

DS100 [g/l]	DS100 + NP9EO [g/l]
3	3
2	2
1.5	1
1	0.75
0.75	0.6
0.5	0.45
0.25	0.3
0.1	0.2
3	0.15
-	0.125
-	0.1
-	0.075
-	0.05
-	0.025
-	0.01
-	0.005

4.4 Dynamic surface tension

Bubble pressure method is a common method to determine the dynamic surface tension and measures how fast the surfactant reduces the surface tension. Gas bubbles are produced in the sample liquid in a capillary, with known radius, at an exactly defined bubble generation rate. The pressure to form the bubble is inversely proportional to the radius which in turn is proportional to the surface tension of the liquid. [1][6]

4.4.1 Determination of dynamic surface tension

2 ml from each of the solutions for the measurements of CMC, see table 3, were diluted to 40 ml with distilled water.

4.4.2 Determination of CMC by the use of dynamic surface tension

Stock solutions at a concentration of 10g/l, see table 3, were further diluted according to table 5. Also, a 1g/l solution with NP9EO was prepared.

Table 5 The chosen concentrations for the dynamic surface tension method, in order to determine CMC.

DS100 [g/l]	DS100 + NP1EO [g/l]	DS100 + NP2EO [g/l]	DS100 + NP3EO [g/l]	DS100 + NP4EO [g/l]	DS100 + NP9EO [g/l]	NP9EO [g/l]
0	0	0	0	0	0	0
0.01	0.01	0.01	0.01	0.005	0.01	0.01
0.1	0,05	0,05	0,05	0,01	0,05	0,025
0.2	0.075	0.075	0.075	0.05	0.075	0.05
0.3	0.1	0.1	0.1	0.1	0.1	0.075
0.5	0.15	0.15	0.2	0.2	0.25	0.1
1	0.25	0.29	0.3	0.5	0.48	0.25
-	0.49	0.49	0.5	-	1	1
-	0.8	0.8	0.58	-	-	-

4.5 NMR

NMR spectroscopy was used in order to determine the molecular weight for the six different products, by the use of ^{1}H-NMR (complementary to the titrations). Also DOSY was used to determine the diffusion rate for mixed solutions, see table 6. For these measurements a Varian 400MHz NMR spectrometer was used.

4.5.1 Determination of molecular weights of NPEO by ^{1}H-NMR

~3 drops of product were transferred into an NMR tube and diluted by 0,8-1 ml of CD_3OD. The sample solution was properly dissolved by turning the tube up and down a couple of times.

In order to interpret the ^{1}H-NMR spectra, see figure 6, following calculations were performed:

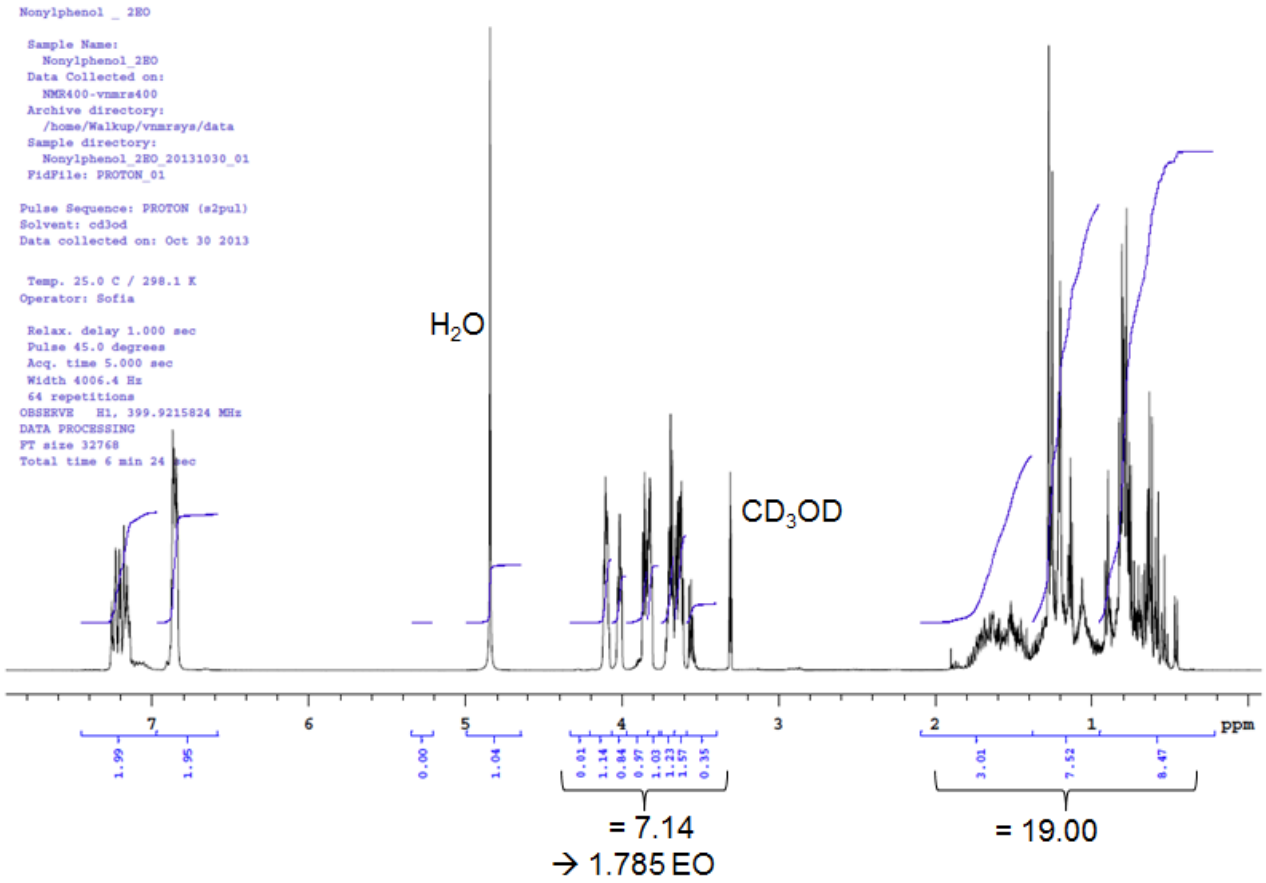


Figure 6. ^{1}H-NMR spectra obtained from measurements.

The hydrophobic nonyl group of the NPEO was set to 19 since this part has 19 hydrogen atoms. Integral of all peaks at 3,4-4,2ppm correspond to the amount of hydrogens in the EO chain. Therefore the peaks at 3,4-4,2ppm, were summed and used for further calculations:

$$\boldsymbol{EO = \frac{integral\ of\ the\ peaks\ at\ 3{,}4-4{,}2ppm}{4}} \qquad (9)$$

Where

4 = Number of hydrogen atoms in each EO unit

The molecular weight could then be calculated according to following:

$$\boldsymbol{Mw = 220.354 + EO * 44.053} \qquad (10)$$

Where

220.354 = the molecular weight of nonyl phenol

44.053 = the molecular weight of one EO unit

The distribution could also be calculated by means of values from the spectra:

Example) Nonyl phenol + 2EO

Different peaks in the spectra were corresponding to the different homologues of nonyl phenol ethoxylates. By the use of these peak values the distribution of three different homologues (in mol-%) could be calculated i.e. the homologues with 1, 2 and ≥3 units of EO, as seen below.

1.14+0.84=1.98

NP-1EO: 0.84/1.98 = 42.4 mol-%

NP-≥3EO: 0.35/1.98 = 17.7 mol-%

NP-2EO: 100-(42.4+17.7) = 39.9 mol-%

This method was used to determine the distribution and molecular weight for all of the spectra with nonyl phenol ethoxylate (diluted in CD_3OD)

4.5.2 Determination of diffusion rate with DOSY

Several sample solutions were prepared according to table 6. 2g/l solutions were prepared at a molar ratio 1:1, diluted in D_2O. All of the solutions, used for DOSY, were prepared in a 10mL beaker. When properly dissolved into D_2O, a small amount was transferred into an NMR tube.

Table 6 Sample solutions prepared at 2g/L (1:1), diluted in D_2O.

Solutions	Amount of DS100 (mg)	Amount of NP+XEO (mg)	Total amount of the solution, ml
DS100 + NP1EO	1.3	0.65	1
DS100 + NP2EO	1.3	0.7	1
DS100 + NP3EO	2.4	1.7	2
DS100 + NP4EO	1.2	0.8	1
DS100 + NP9EO	1.8	2.2	2

Solutions with varying concentrations and ratio of DS100 and NP3 were also prepared, see table 7.

Table 7 Sample solutions, with DS100 and NP3, dissolved in D_2O with varying concentrations and molar ratio (Total amount of the solution 2 ml).

Solutions:	**Concentration g/l**	**Molar ratio (NP3: Sarc.)**	**Amount of DS100 (mg)**	**Amount of NP3EO (mg)**
DS100 + NP3EO	10	(1:1)	7.8	13.2
DS100 + NP3EO	1	(1:1)	1.3	0.9
DS100 + NP3EO	5	(1:1)	3.9	6.1
NP3EO	2	(1:0)	4.1	-
DS100	2	(0:1)	-	4.2
DS100 + NP3EO	2	(3:1)	1.5	2.5
DS100 + NP3EO	2	(1:3)	0.6	3.3

Some solutions were also prepared at a lower concentration, 0.13g/l. These were prepared according to table 8.

Table 8 Sample solutions at 0.13g/L, dissolved in D_2O (Total amount of the solution 2 ml).

Solutions:	**Molar ratio (NPX: Sarc.)**	**Amount of DS100 (mg)**	**Amount of NPXEO (mg)**
DS100	(0:1)	0.3	-
DS100 + NP1EO	(1:1)	0.2	0.1
DS100 + NP2EO	(1:1)	0.2	0.1
DS100 + NP3EO	(1:1)	0.2	0.1
DS100 + NP4EO	(1:1)	0.2	0.1
DS100 + NP9EO	(1:1)	0.1	0.2

The DOSY diffusion NMR experiments were done on a 400MHz Brucker instrument with a diffusion probe. The diffusion rate was determined with a DOSY pulse sequence using Gradient stimulated echo with spin lock. The gradient strength (G) was linearly increased from 75 to 1200G/cm in 16 subsequent steps with 128 iterations per step. Small δ was set to 0,5 ms and big Δ was 75 ms. In order to determine the diffusion rate, the integrals (I) of interesting peaks were measured for each gradient and compared to the initial integral value (I_0) for the first gradient. The natural logarithm of the attenuation $LN(I/I_0)$ was plotted against $\gamma^2\delta^2(2\pi)^{-1}G^2(\Delta-(\delta/3))$ were γ is the magnetogyric ratio for a proton. Linear regression was done on the obtained dots in the diagram and the negative slope of the obtained line is equivalent of the diffusion rate. The peaks at the chemical shifts of δ 2,3-2,5 for the DS100 and at the chemical shifts of δ 6,6-7,1 for the nonyl phenol ethoxylate were used for the evaluation.

5. RESULTS AND DISCUSSION

This study is focused on surface chemistry measurements for mixed surfactant systems used for the beneficiation of complex phosphorus containing ores. The research is performed in order to gain a deeper understanding on surfactant interactions at the water-air interphase for zwitterionic / non-ionic surfactant mixtures. In the field of Mining industry surface dynamics are of great importance, since beneficiation usually is a very fast process.

5.1 Analysis of surfactants used in the study

Since only industrial samples of the surfactants were used in the study a complete analysis of all the surfactants was conducted prior to the physical-chemical measurements.

5.1.1 Evaluation of the molecular weight of the surfactants

Molecular weight of the zwitterionic surfactant DS100 was identified by two titrimetric methods (total amine content and anion content). The results are presented in table 9. A theoretical molecular weight for the zwitterionic is around 400 g/mol. Both practically evaluated values are not in an agreement with the theoretical value; hence that can be explained by the following reasons:

1.) Molecular weight determination from the total amine value is not accurate, since there is some unreacted N-methyl-glycine present in the industrial surfactant. A presence of unreacted N-methyl-glycine affects molecular weight value.

2.) The molecular weight from the anionic titration showed a higher molecular weight, due to the fact that there are some ethanol (0,4 w%), water (4 w%), unreacted N-methyl-glycine and some other by-products present, but fits much better with the theoretical calculations

Due to the reasons above the molecular weight of 499 g/mol was regarded as being actual for the zwitterionic.

Table 9 Molecular weight of DS100 by diffrent analytical methods

Analytical method	**Evaluated M_w(g/mol)**
Total amine	363,6
Anionic content	499,00

Molecular weight of used nonylphenol ethoxylates was calculated by two techniques as well. As one can see the results are similar independently on the evaluation method, see table 10.

Table 10 Molecular weight of NPEO determined by different analytical methods.

Product sample	M_w (g/mol) evaluated		
	Theoretically	**By titration**	**By ^{1}H-NMR**
NP1EO	264.4	249.89	265.18
NP 2EO	308.5	273.71	298.99
NP3EO	352.5	321.96	348.77
NP4EO	396.6	368.10	388.64
NP9EO	616.8	625.27	619.03

As seen in table 10, the molecular weights obtained by ^{1}H-NMR are in an agreement with the results from the titrations and theoretical values.

5.1.2 Distribution of nonylphenol ethoxylate homologues

The distribution of the homologs of the industrial nonylphenol ethoxylate products was obtained by the GC and ^{1}H-NMR methods.

GC is a common analytical method for compounds that can be vaporized without decomposition. The principle of the method is to separate the compounds according to its vapour pressure at elevated temperature. As a result the substances with the lowest molecular weight will remain in GC column the shortest time. The first peak corresponds therefore, to the unreacted nonylphenol, the second correspond to the homolog with 1EO etc., see table 11 and appendix 1. The area of the peaks is equivalent to the amount of the homologs in the samples.

The ^{1}H-NMR technique allows measuring a magnetic spin frequency, which depends on the chemical environment of the proton nuclei. Results are recorded as a ^{1}H-NMR spectrum (See fig 6, in the experimental part, for information needed for the calculation of the chemical composition of the analyzed substance).

Table 11 Homolog distribution of ethoxylated nonylphenol, obtained by the GC and NMR methods. (N.D= Not Detectable.)

Name	NP1EO		NP2EO		NP3EO		NP4EO		NP9EO	
	GC Area%	NMR Mol%	GC Area%	NMR Mol%	GC Area%	NMR Mol%	GC Area%	NMR Mol%	GC Area%	NMR Mol%
0 EO	1.4	-	0.1	-	-	-	0.1	-	2.9	-
1 EO	94.6	95.9	41.7	42.4	10	9.6	3.3	3.5	1.6	N.D
2 EO	3.8	4.1	39.9	39.9	32	32.8	18.7	14.16	1.6	N.D
≥3EO	-	-	-	17.7	-	57.6	-	81.8	-	100
3 EO	-	-	13.3	-	29.2	-	27.4	-	3.1	-
4 EO	-	-	2.9	-	16.3	-	22.9	-	6.7	-
5 EO	-	-	0.4	-	7	-	14.1	-	11.7	-
6 EO	-	-	-	-	2.8	-	7.6	-	16.5	-
7 EO	-	-	-	-	1.1	-	3.7	-	19.1	-
8 EO	-	-	-	-	0.3	-	1.2	-	16.6	-
9 EO	-	-	-	-	0	-	0.1	-	11.1	-
10 EO	-	-	-	-	-	-	-	-	6.2	-
11 EO	-	-	-	-	-	-	-	-	0.8	-

As seen in table 11, the molecular weights obtained by ^{1}H-NMR correspond well with the GC results.

5.2 CMC and surface tension

As it was discussed in the theoretical part, CMC and surface tension are important characteristics of the surfactants, which give us information about distribution and packing of the surfactants in the micelles.

Seven different samples were analyzed. These were DS100, DS100+NP1EO, DS100+NP2EO, DS100+NP3EO, DS100+NP4EO, DS100+NP9EOand NP9EO. Three different methods were used for measurement of surface tension and calculation of CMC: conductivity, static and dynamic surface tension.

5.2.1. Static surface tension

Surprisingly it was found that the CMC of DS100 was lower, compared to the rest of the mixed solutions and even for non-ionic as such, see table 12 and figure in appendix 2. It is not in an agreement with theoretical expectations: it is well known that ionic surfactants have higher CMC values than non-ionic surfactants [1]. The obtained behavior of the DS100 alone and the DS100+NPEO mixtures are not fully understood and should therefore be investigated further.

Table 12 CMC values for the different mixtures of DS100 and NPEO determines by the use of static surface tension measurement.

Solution	CMC [g/L]	pH	CMC, mol/l	Surface tension above CMC, mN/m
DS100	0.0025	10.2	$0,5*10^{-5}$	28
DS100 +NP1EO	0.0025	10.3	-	25
DS100 +NP2EO	0.0038	10.7	-	25
DS100 +NP3EO	0.0045	9.3	-	25
DS100 +NP4EO	0.0045	9.5	-	26
DS100+NP9EO	0.006	8.5	-	30
NP9EO	0.03	8.6	$4,9*10^{-5}$	30

Due to the questionable results from the static surface tension method, the conductivity method was tested as well (see figure 7 and 8 and table 13). This method could only be used for ionic surfactants, since the principle of the measurement lies in the slower increase of conductivity of the measured solution at the concentration higher than CMC.

Two measurements were performed, in which DS100 and DS100+NP9EO were used. There was no problem measuring on the DS100 solution (though the CMC was much higher compared with the results obtained from the static surface measurements). Unfortunately, no CMC could be obtained for the mixed solution (Fig 8). This phenomenon can be explained by very low CMC values for mixed micelles and by uneven distribution of the surfactants in the mixed micelles. It is known that around CMC the mixed micelles consist mainly from non-ionic surfactants.

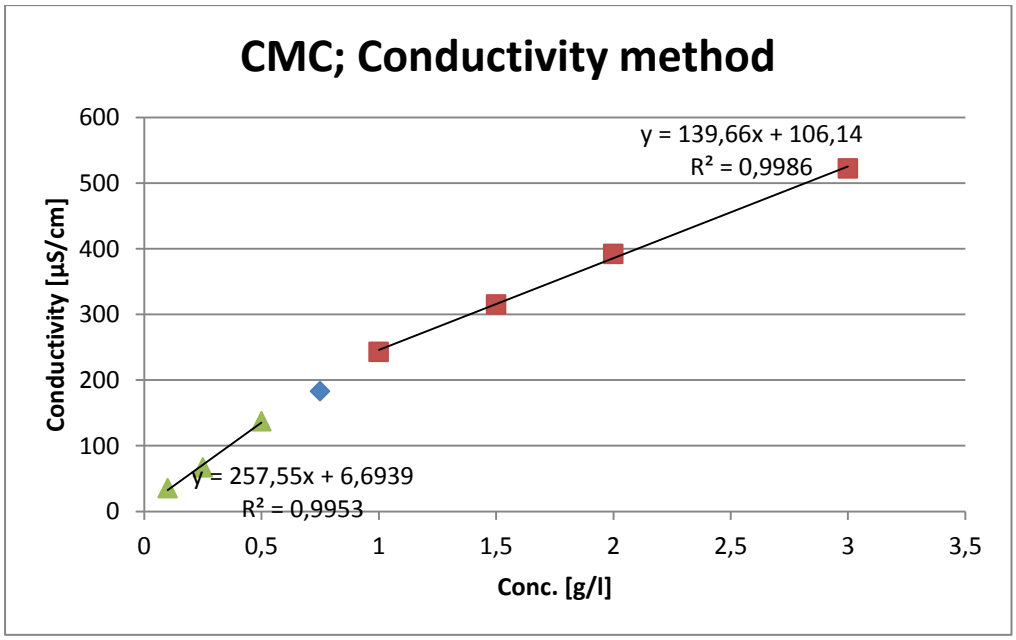


Figure 7 Obtained results for DS100 using the conductivity method.

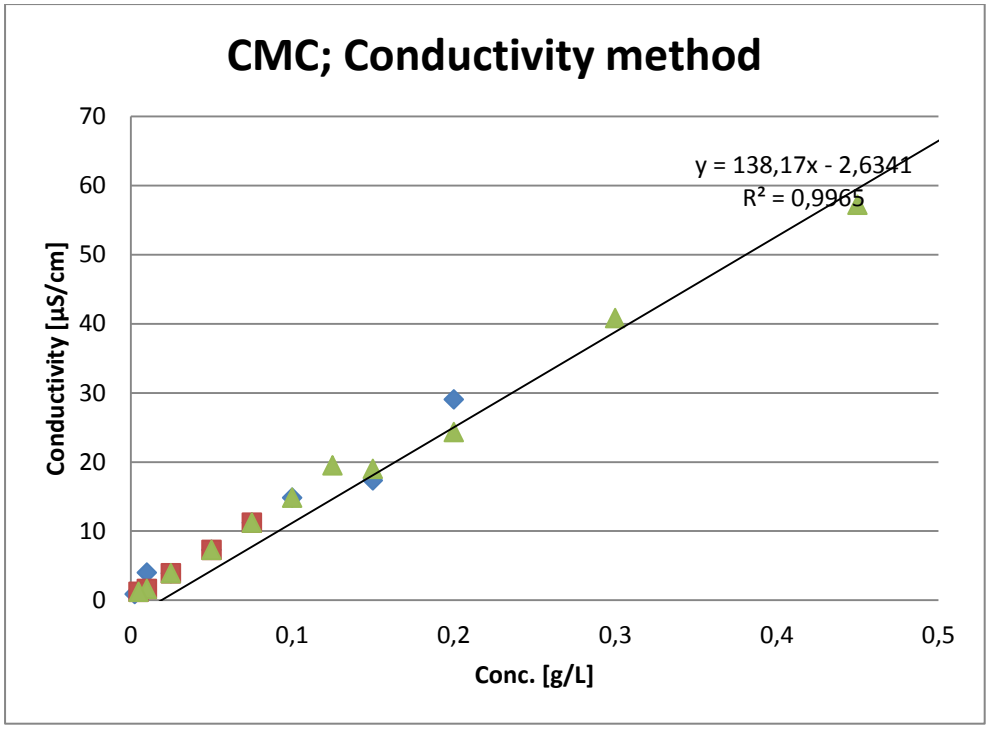


Figure 8 Obtained results for DS100 and DS100+NP9EO using the conductivity method.

Table 13 CMC values for DS100 and DS100/NP9EO.

Solution	CMC [g/l]
DS100 pH 10.7	0.843
DS100+ NP9EO pH 9,5	-

5.2.2. Dynamic surface tension

Usually the method for dynamic surface tension measurement is not used for the evaluation of the CMC. However, as it was mentioned previously, it is also of a great interest for different industrial applications to find out what kind of changes take place in dynamic systems during the short time (less or around 1 min). Therefore the surface tension measurements were taken not after the system approached equilibrium, but after a fixed time (bubble life time of ~50sec).

Several concentrations (from 0 to 1 g/l) of the surfactants and their mixtures were used. The obtained results are presented in the graph, see appendix 2 and evaluated CMC values are shown in table 14. The results from this measurement must only be considered as approximate, but can be used in a comparative study. It is important to note that the results obtained by the use of dynamic surface tension are most in agreement with the theoretical expectations (DS100 obtained the highest CMC value and NP9 the lowest). CMC decreased with the increasing amount of EO for the mixed solutions.

Table 14 CMC by the use of dynamic surface tension.

Solution	CMC [g/l]	CMC mol/l
DS100	0.15	$3*10^{-4}$
DS100 +NP1EO	0.14	-
DS100 +NP2EO	0.10	-
DS100 +NP3EO	0.07	-
DS100 +NP4EO	0.065	-
DS100+NP9EO	0.062	-
NP9EO	0.05	$0,8*10^{-4}$

5.3 Dynamic surface tension

Dynamic surface tension was measured for all seven solutions. The concentration of all analyzed samples was 0,1g/l. This value is related to the surfactant concentration that is used during the beneficiation process. The results of the dynamic surface tension show that sodium DS100 has the slowest reduction of the surface tension and nonylphenol with 9EO on the other hand has the fastest reduction see figure 9. These results can mean that NPEO improve efficiency of the surfactants at least in the applications where the surfactants have to act rapidly, as an example is a beneficiation of ores where the surfactants are expected to perform during very short time.

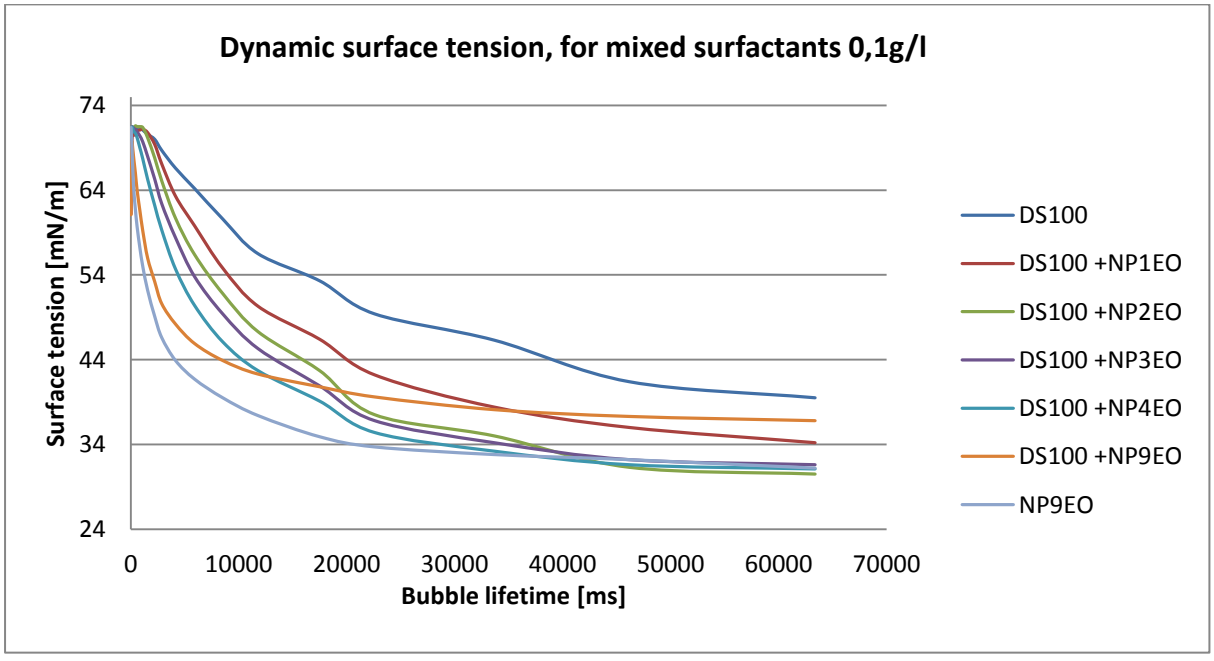


Figure 9 Obtained results of the dynamic surface tension method.

As one can see from the results, not all of the NPEOs are equally efficient when mixed with DS100: NP9EO do not decrease the surface tension as much as the other NPEOs used in this study and NP1EO provides a slowest reduction of the surface tension.

All above mean, that there is an optimum for the degree of ethoxylation (DE) for nonylphenol in the mixtures with DS100. This DE optimum is >1 - <9.

5.4 NMR

5.4.1 NMR Diffusiometry

According to the results from the diffusometry measurements, DS100 had a moderately fast diffusion rate, which were affected by its molecular size, see table 15.

Table 15 Diffusion coefficients of DS100.

Samples (2g/l 1:1 mol-%)	D (1e-11 m2/s)	
	1	2
DS100	3.76 ± 0.11	3.79 ± 0.09

However, when measuring on mixed solutions different results were obtained. The first measurement, using mixed surfactants at a concentration of 2g/l, no significant difference in diffusion rate of the different signals could be detected, see table 16. Most probable reason to this is that the surfactants, at this high concentration, mainly are present in micelles and that no separate unimers can be observed. However, the spectra indicated that the solutions contained a low molecular substance, sodium sarcosine, which could be confirmed by spiking. According to these results DS100 + NP9EO had a higher diffusion rate than DS100 + NP3EO, see table 16. This is due to the size and shape of the mixed micelles, i.e. DS100 + NP3EO> DS100 + NP9EO in a respect of micelles size, as illustrated in figure 10.

The results show that at the concentration of 2g/l the surfactants distribute in the micelles evenly (Table 16).

Table 16 Diffusion coefficients of mixtures DS100/NPXEO.

Samples (2g/l 1:1 mol-%)	D (1e-11 m2/s)	
	NPX	DS100
DS100 + NP3EO	2.13 ± 0.10	1.91 ± 0.03
DS100 + NP9EO	7.25 ± 0.19	7.89 ± 0.21

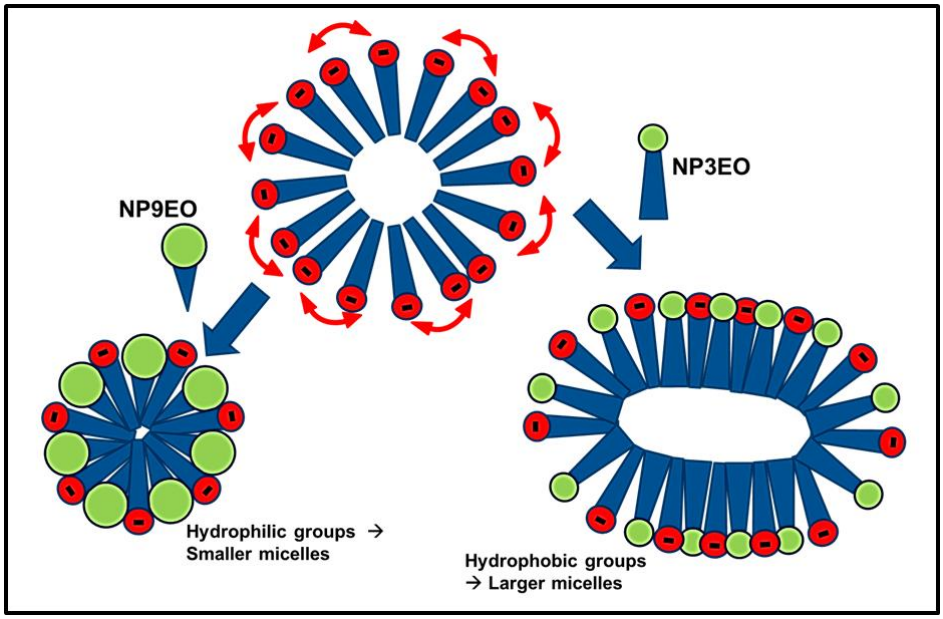


Figure 10. Illustration of micelle size.

The measurements performed on formulations at lower concentration, 0.13g/l, were hard to evaluate due to low signals and a low sensitivity. Further tests were done for some of the formulations with the concentrations of 2g/l, containing more scans to increase sensitivity. However, there was still no significant difference in the diffusion rate of the different signals originating from the NP3 and DS100 for the mixed micelles, see table 17.

Table 17 Diffusion coefficients of DS100/NP3EO.

Samples (0.13g/l 1:1 mol-%)	**D (1e-11 m2/s)**	
	NP3	**DS100**
DS100 + NP3EO	3.32 ± 0.48	2.25 ± 0.12

When comparing the results for both concentrations (2g/l and 0.13g/l), it is also shown that there was no significant difference in diffusion rate, between the different concentrations. The compounds, nonyl phenol + 3EO and DS100, were diffusing at approximately the same rate. Therefore, the surfactant concentration in the sample solution that is being measured does not change the diffusion rates markedly.

6. CONCLUSIONS

Results of the static surface tension measurements showed that the CMC of the DS100 was lower, compared to the CMC of all mixed surfactant solutions and even of non-ionic NP9EO as such. However the obtained behavior is not in agreement with the established theoretical expectations, it is not fully understood and should therefore be investigated further.

CMC determinations by conductivity measurements cannot be used for DS100+NPEO mixtures. The phenomenon can be explained by very low CMC values where accurate conductivity measurements are problematic.

Results obtained by the use of dynamic surface tension indicate that nonionic surfactants increase the efficiency of the zwitterionic. Surface tension decreases more rapidly when mixed micelles are formed. That is a demonstration of a synergetic effect.

The CMC of all surfactants and their solutions was determined by dynamic surface tension measurements as well. All measurements were done at a time referred to as 50 s bubble life time. It was found that the nonionic surfactants decrease the surface tension of the zwitterionic.

Results showed that there is an optimum for the degree of ethoxylation (DE=>1 - <9) for nonylphenol in case of DS100. These NPEOs reduced the surface tension fastest and more efficient.

Results of the diffusion NMR indicated that the size of the micelles follows bellow order: DS100 + NP3EO>DS100>DS100 + NP9EO. The results show that at the concentration of 2g/l the surfactants distribute in the micelles evenly.

6.1 Recommendations for further work

- Investigate the reliability of static surface tension measurement (du Noüy ring) for zwitterionics (DS100).

- Investigate dynamic surface tension of the mixed surfactants at a different ratio of zwitterionic/NPEO.

- Further diffusometry measurements on AkzoNobel NMR instrument in order to determine diffusion coefficients (D) for other 2g/l concentrations of DS100+NPEO formulations in D_2O.

- Further evaluations of other molar ratio and concentrations for DS100 + NPEO formulations in D_2O.

- Further evaluation at different concentrations of NP3EO +DS100 formulations in D_2O.

7. REFERENCES

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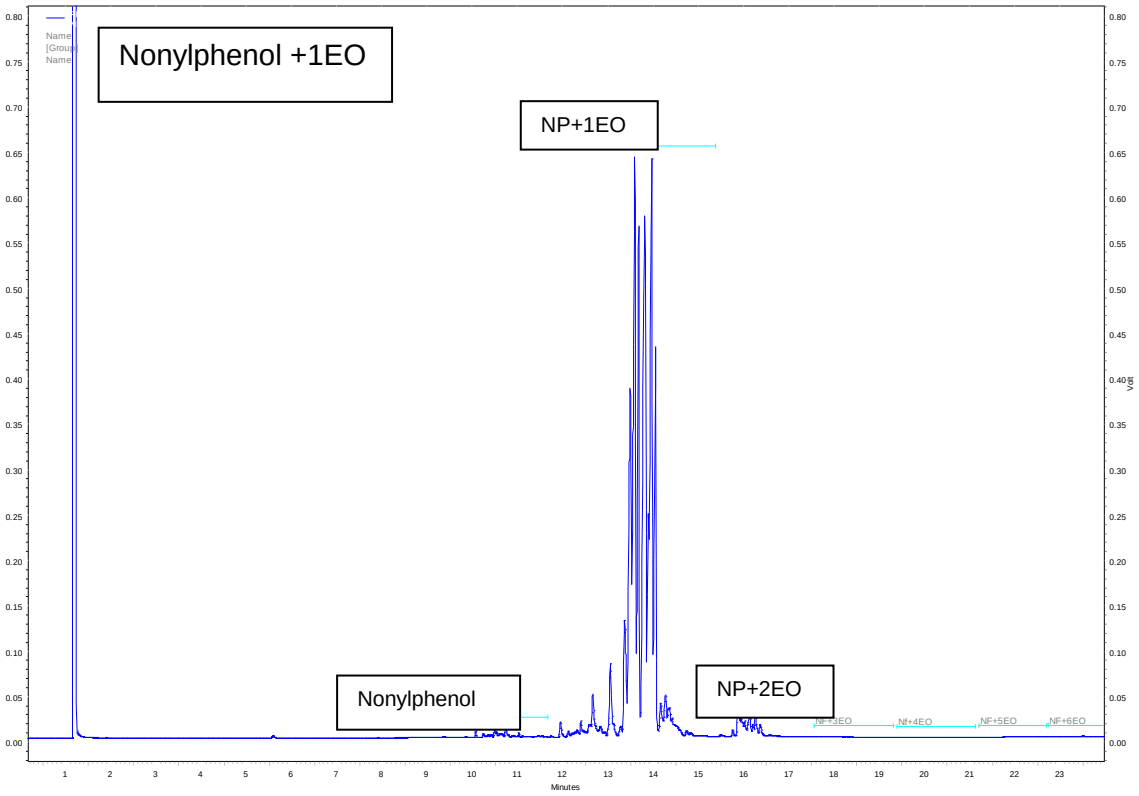
APPENDIX 1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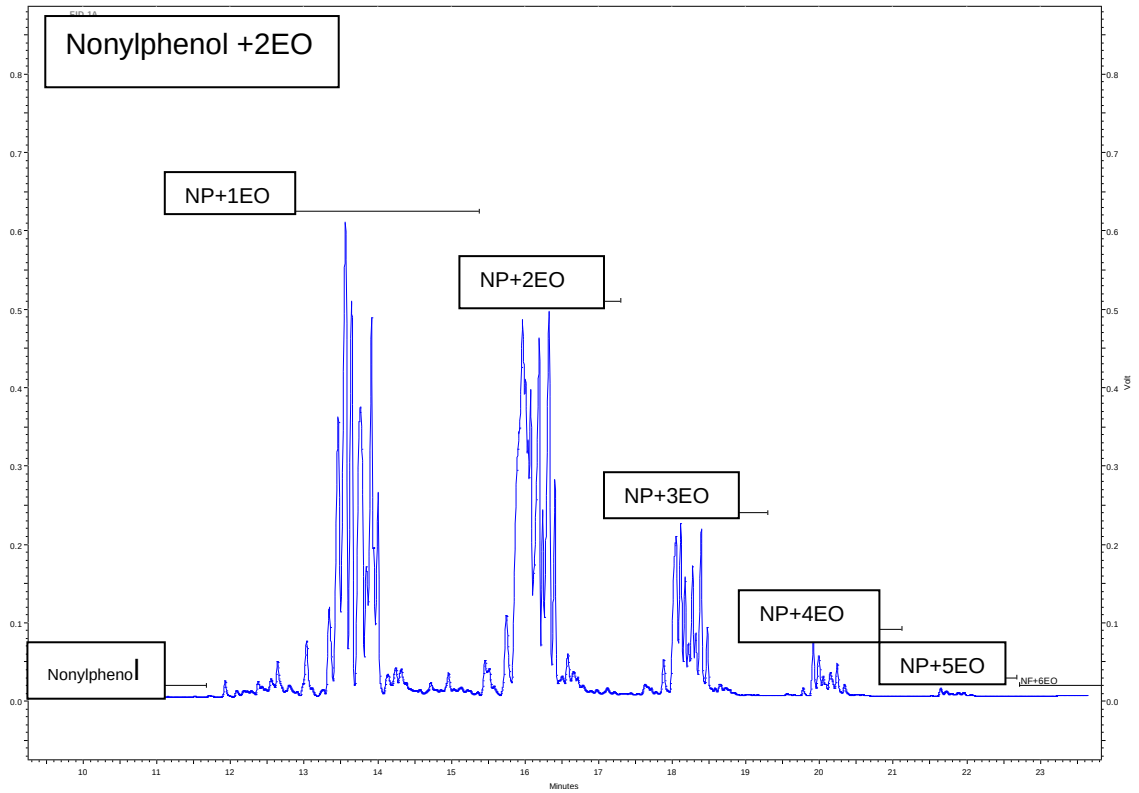
Minutes
Volt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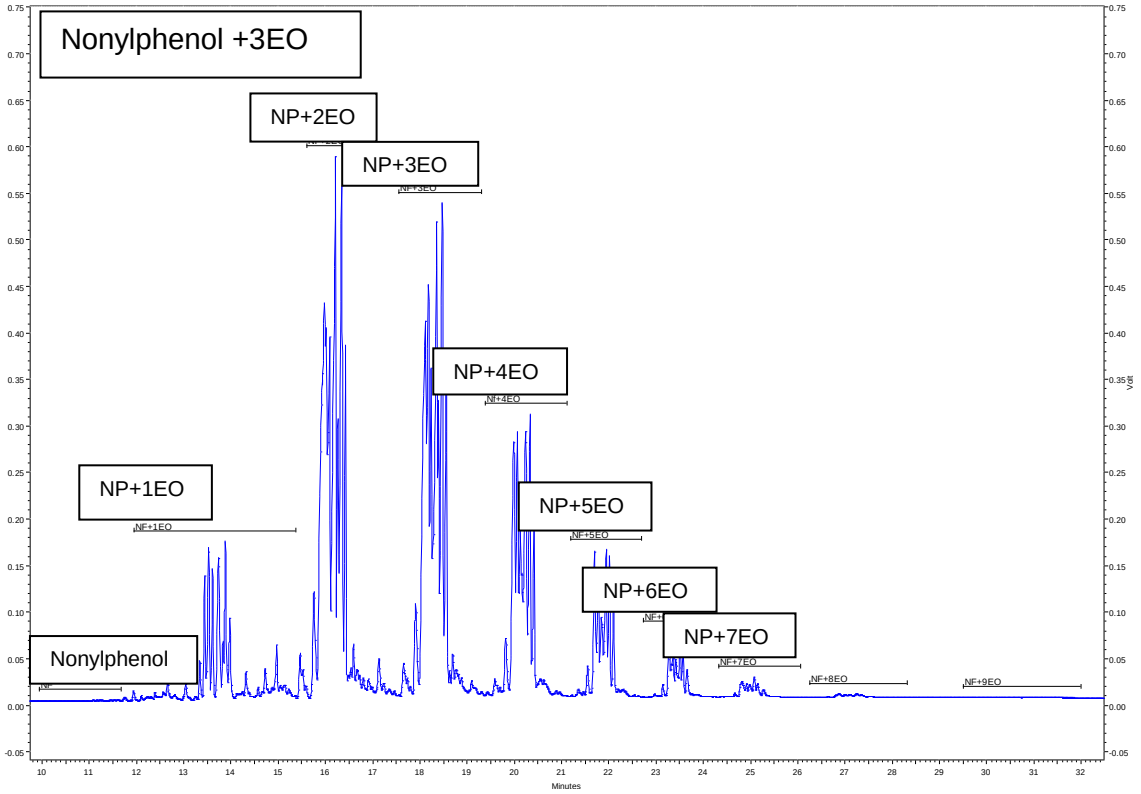
Minutes
Volt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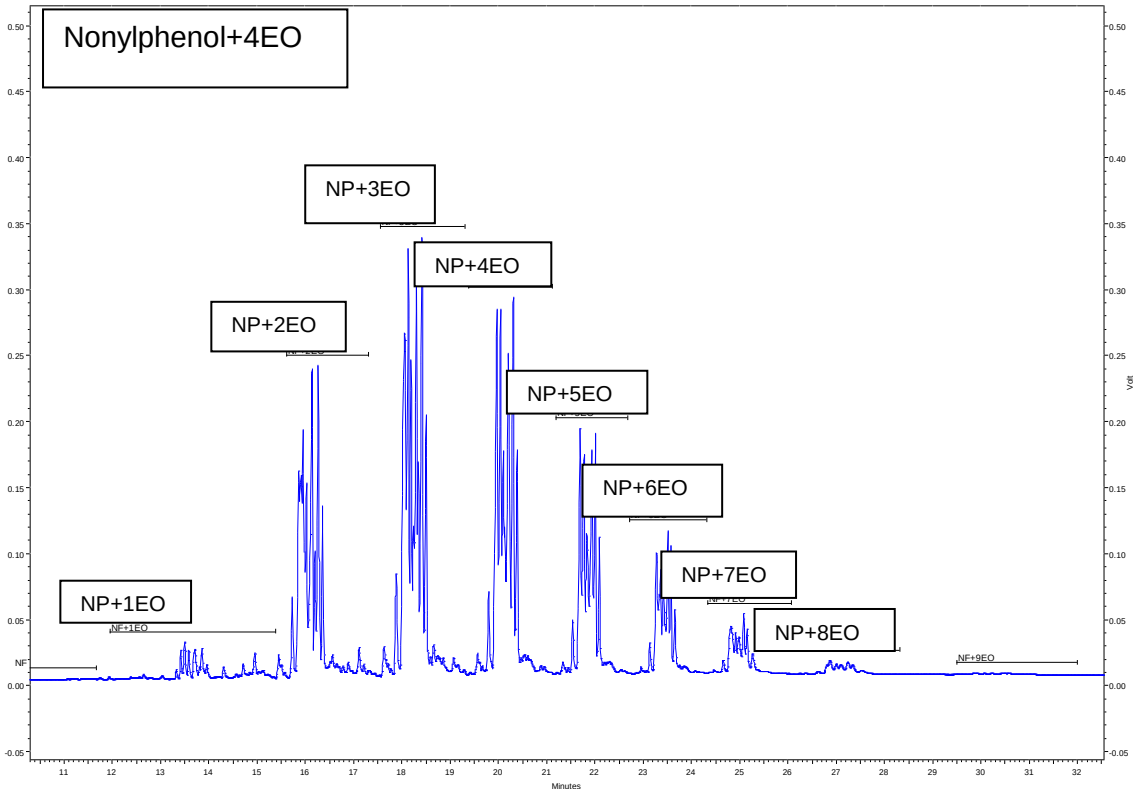
Minutes
Volt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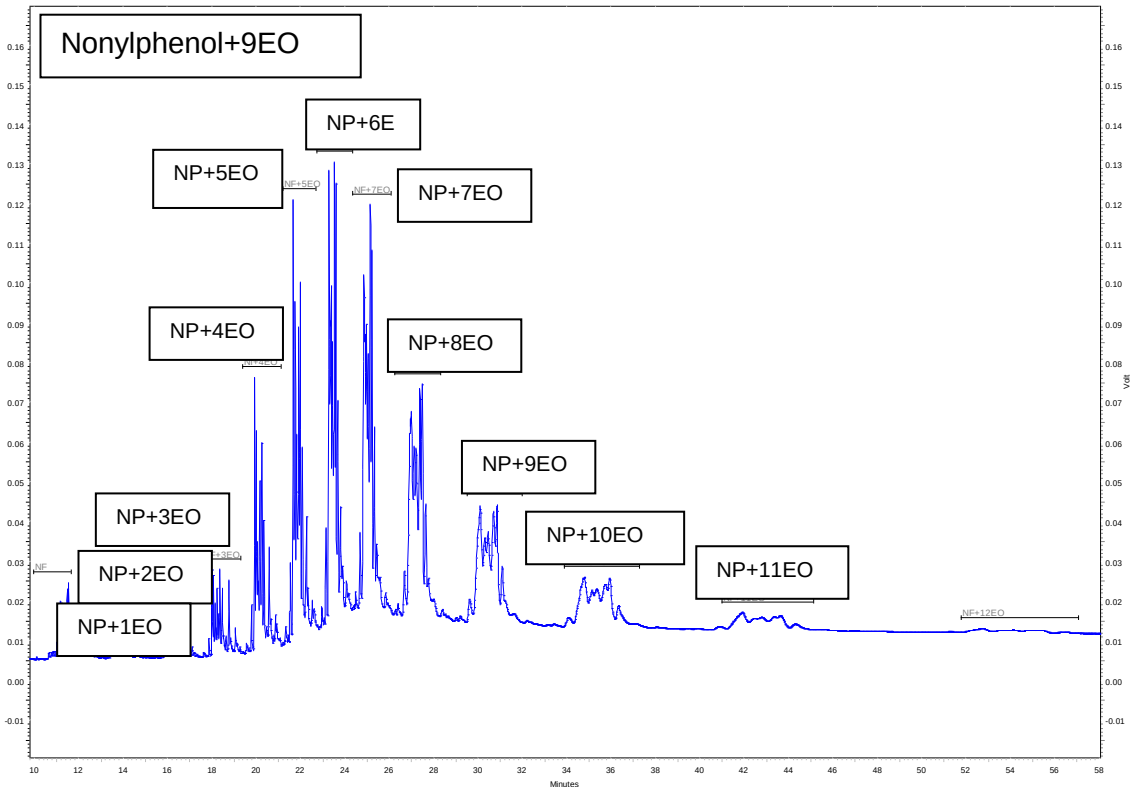
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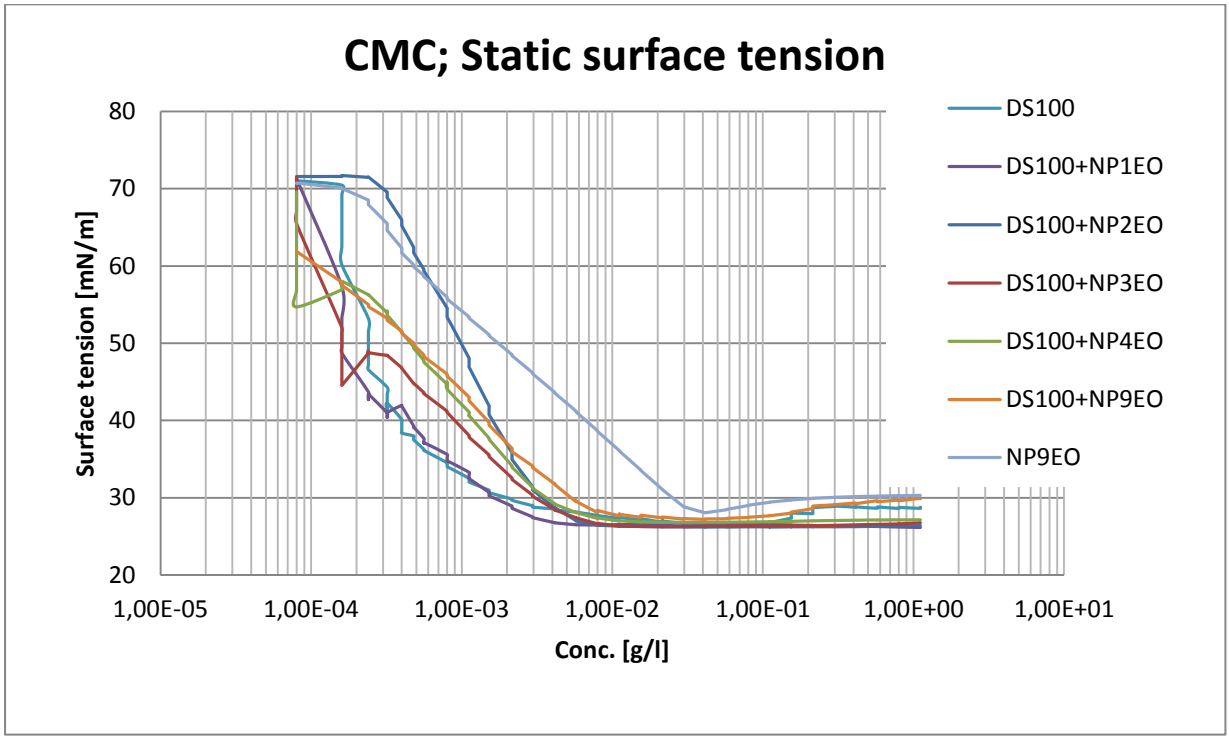
NP+1EO
Minutes
Volt

APPENDIX 2


CMC; Static surface tension
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70
60
50
40
30
20
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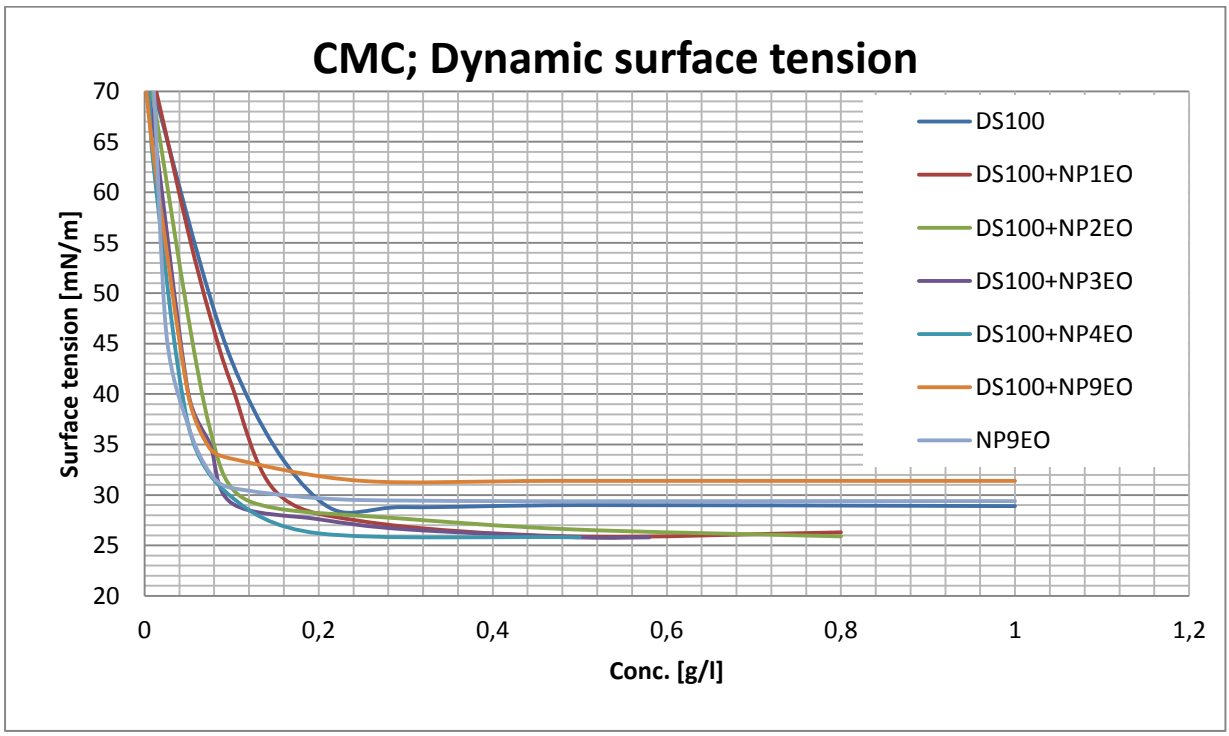
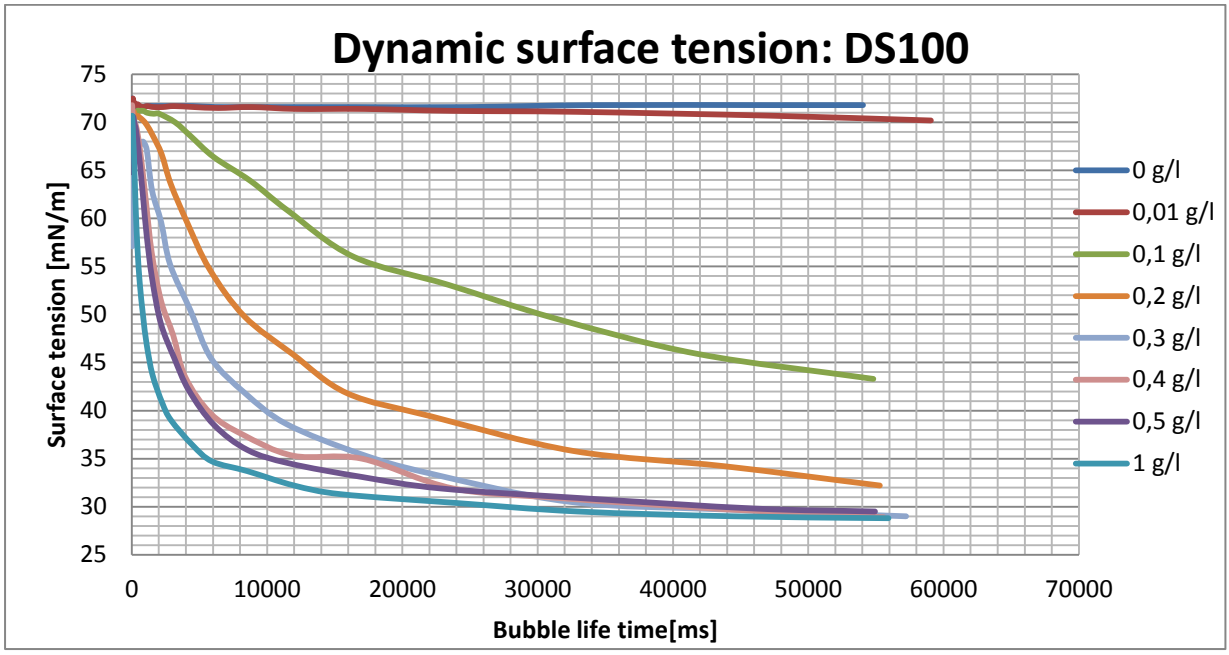
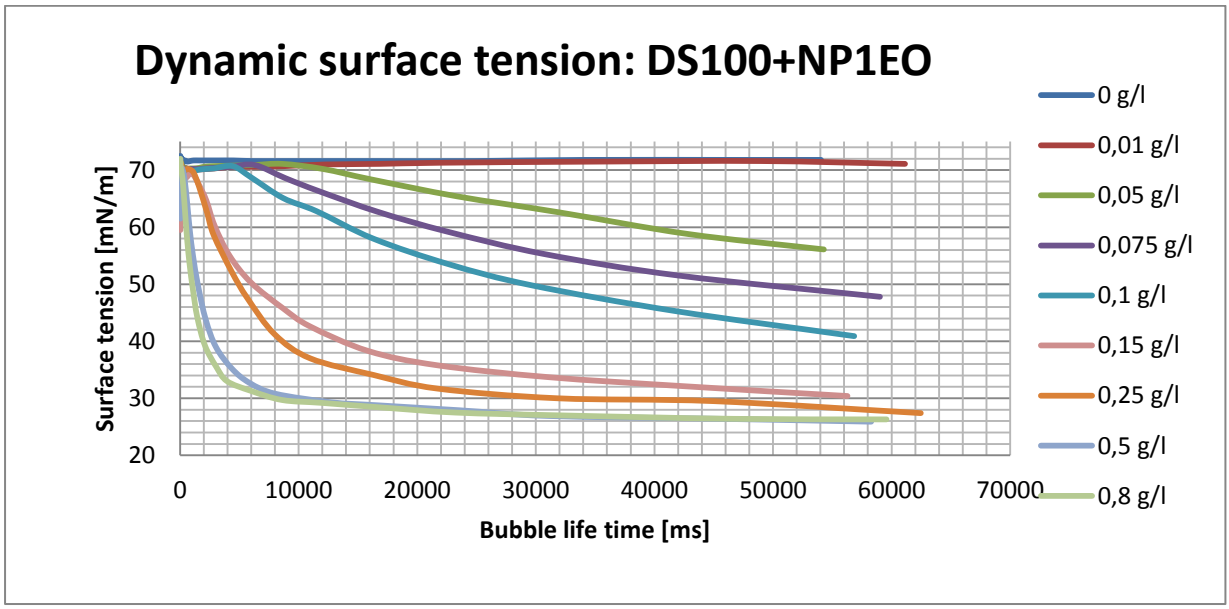
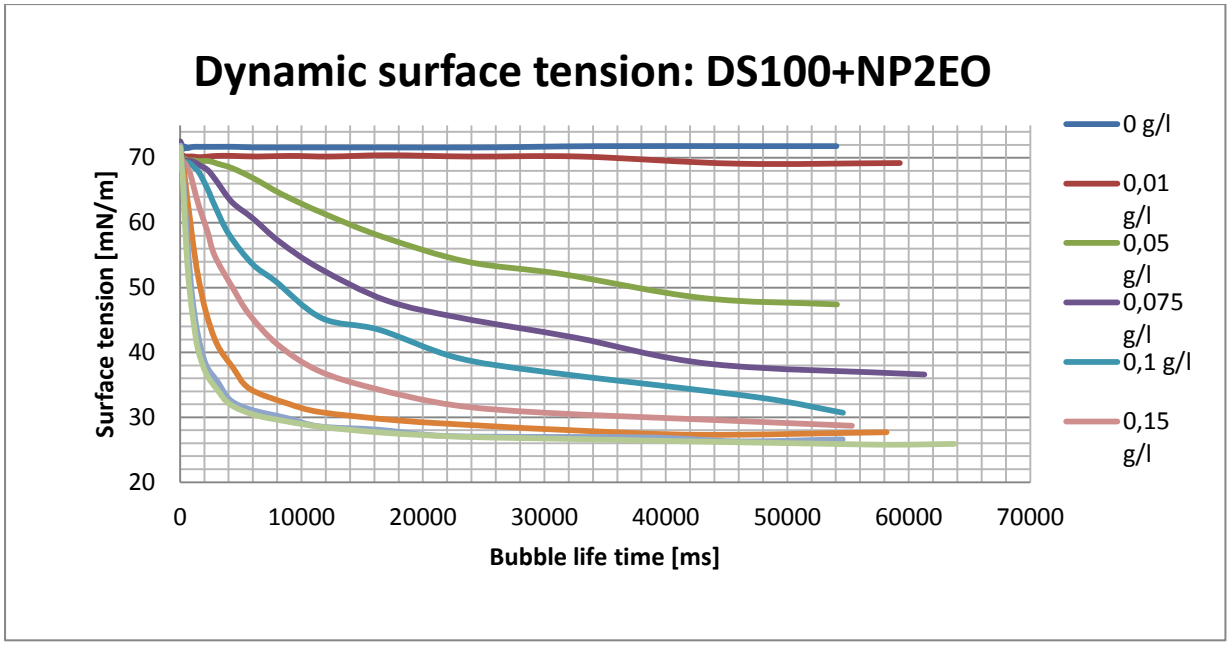
1,00E-04
1,00E-03
1,00E-02
1,00E-01
1,00E+00
1,00E+01
Conc. [g/l]
DS100
DS100+NP1EO
DS100+NP2EO
DS100+NP3EO
DS100+NP4EO
DS100+NP9EO
NP9EO

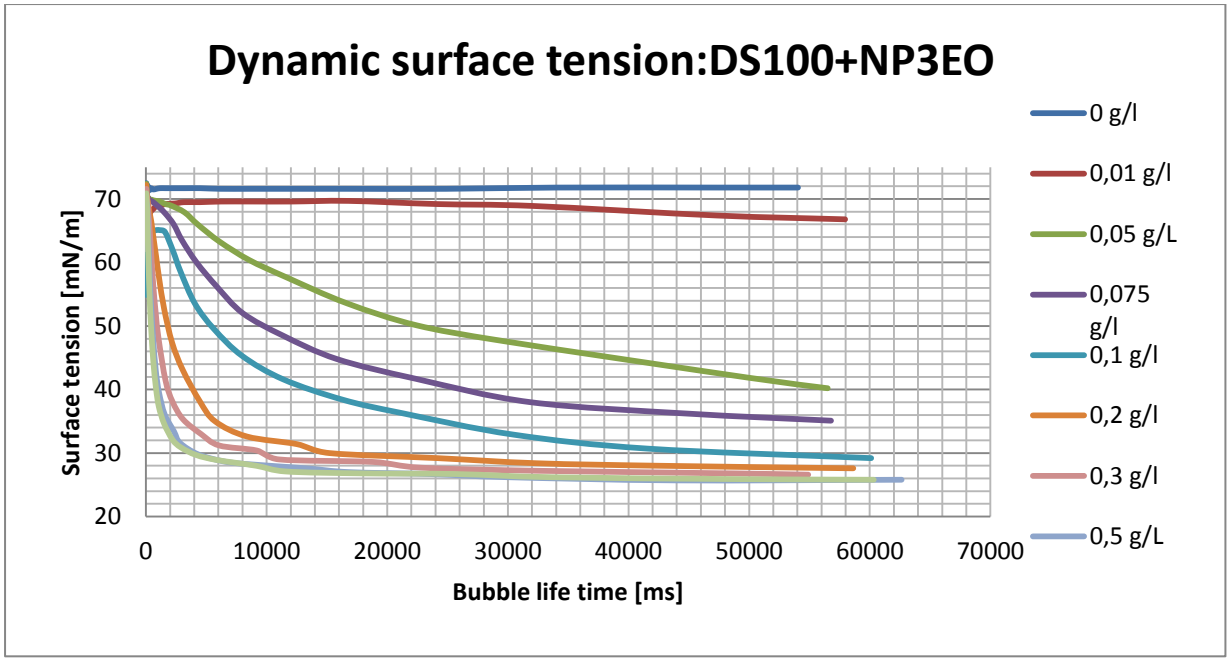

CMC; Dynamic surface tension
Surface tension [mN/m]
70
65
60
55
50
45
40
35
30
25
20
0
0,2
0,4
0,6
0,8
1
1,2
Conc. [g/l]
DS100
DS100+NP1EO
DS100+NP2EO
DS100+NP3EO
DS100+NP4EO
DS100+NP9EO
NP9EO

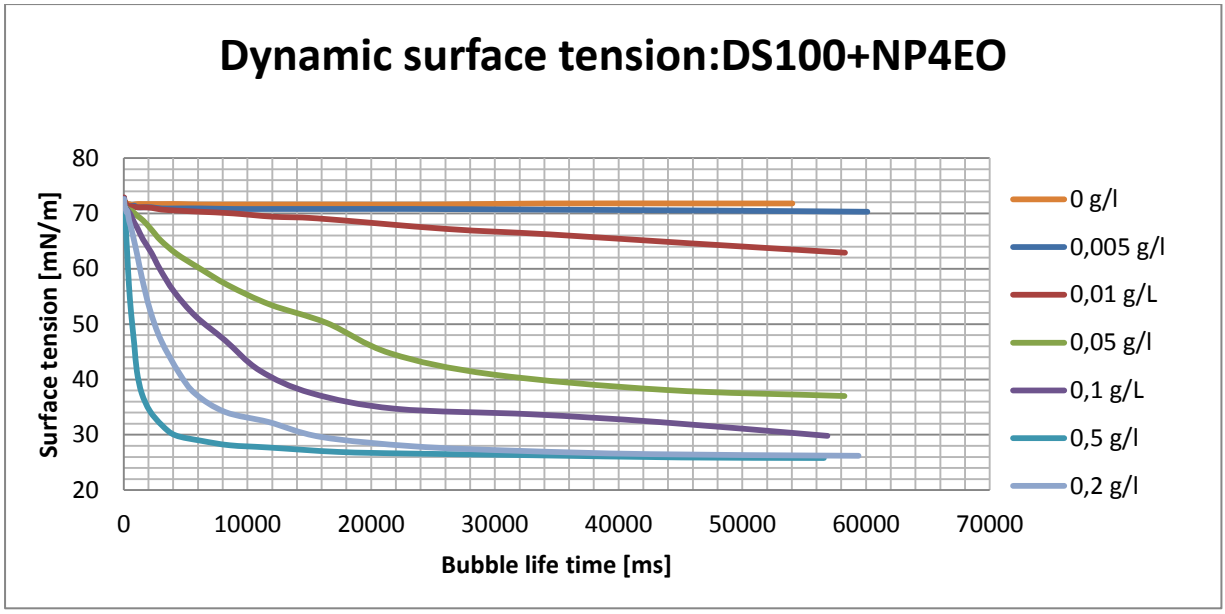
APPENDIX 3

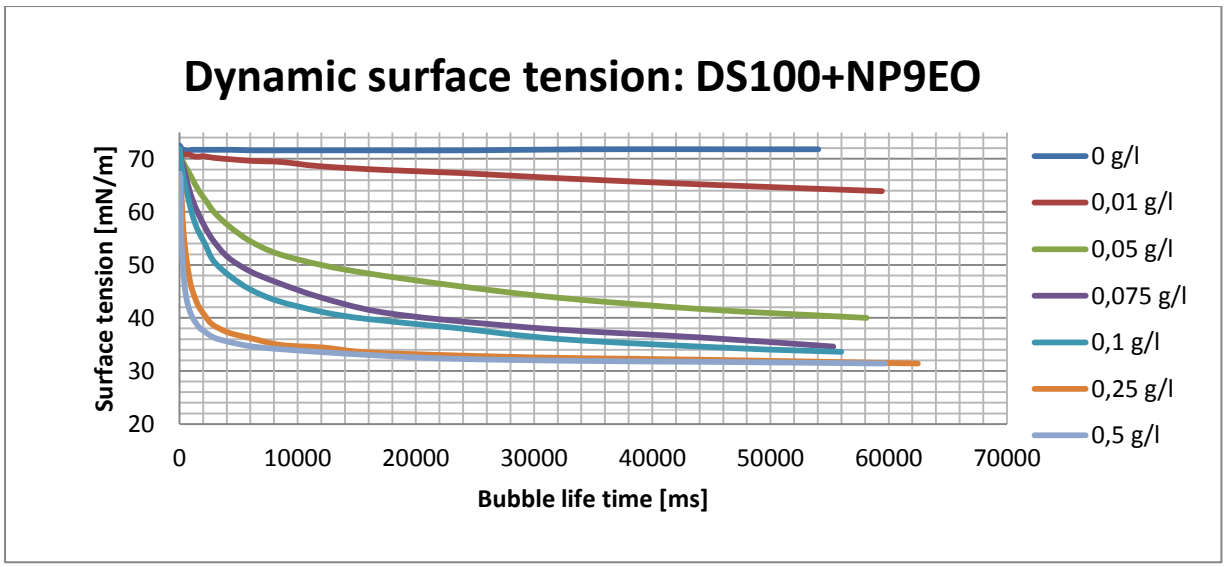

Dynamic surface tension: DS100
Surface tension [mN/m]
75
70
65
60
55
50
45
40
35
30
25
0
10000
20000
30000
40000
50000
60000
70000
Bubble life time[ms]
0 g/l
0,01 g/l
0,1 g/l
0,2 g/l
0,3 g/l
0,4 g/l
0,5 g/l
1 g/l

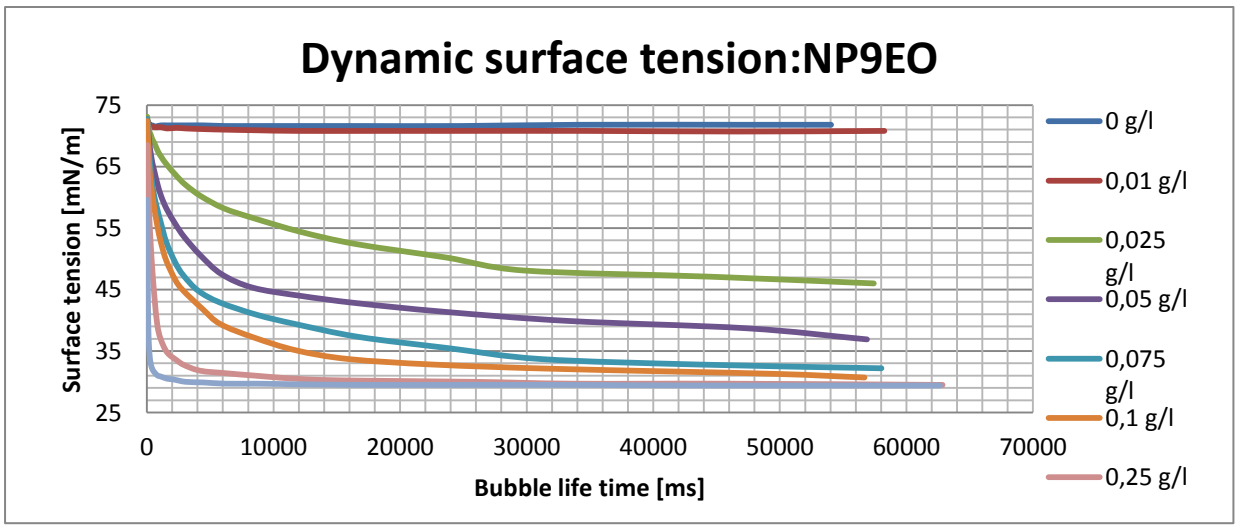

Dynamic surface tension: DS100+NP1EO
Surface tension [mN/m]
70
60
50
40
30
20
0
10000
20000
30000
40000
50000
60000
70000
Bubble life time [ms]
0 g/l
0,01 g/l
0,05 g/l
0,075 g/l
0,1 g/l
0,15 g/l
0,25 g/l
0,5 g/l
0,8 g/l


Dynamic surface tension: DS100+NP2EO
Surface tension [mN/m]
70
60
50
40
30
20
0
10000
20000
30000
40000
50000
60000
70000
Bubble life time [ms]
0 g/l
0,01 g/l
0,05 g/l
0,075 g/l
0,1 g/l
0,15 g/l

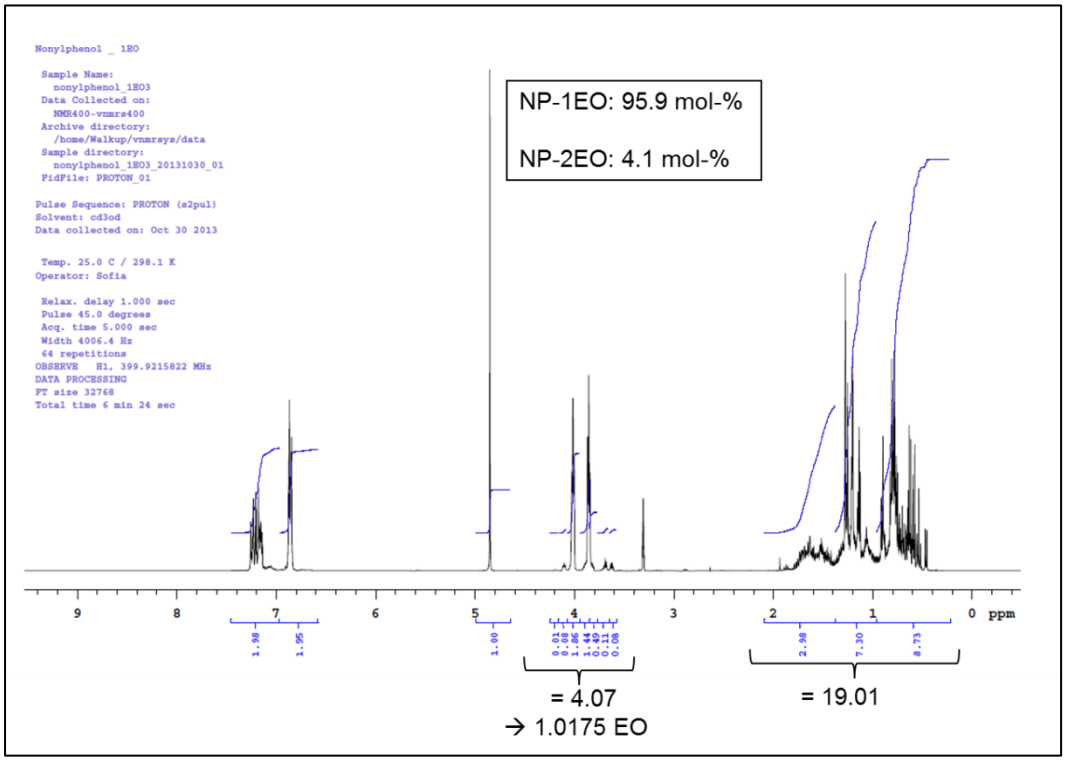

Dynamic surface tension:DS100+NP3EO
Surface tension [mN/m]
70
60
50
40
30
20
0
10000
20000
30000
40000
50000
60000
70000
Bubble life time [ms]
0 g/l
0,01 g/l
0,05 g/L
0,075 g/l
0,1 g/l
0,2 g/l
0,3 g/l
0,5 g/L

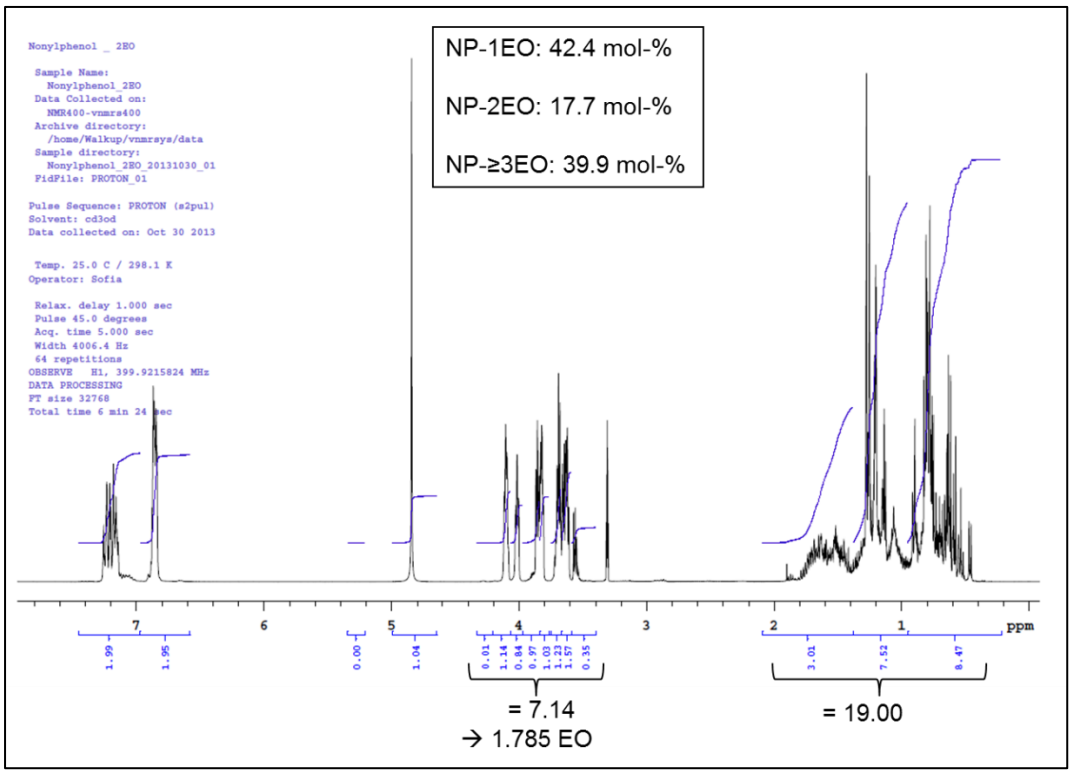

Dynamic surface tension:DS100+NP4EO
Surface tension [mN/m]
80
70
60
50
40
30
20
0
10000
20000
30000
40000
50000
60000
70000
Bubble life time [ms]
0 g/l
0,005 g/l
0,01 g/L
0,05 g/l
0,1 g/L
0,5 g/l
0,2 g/l

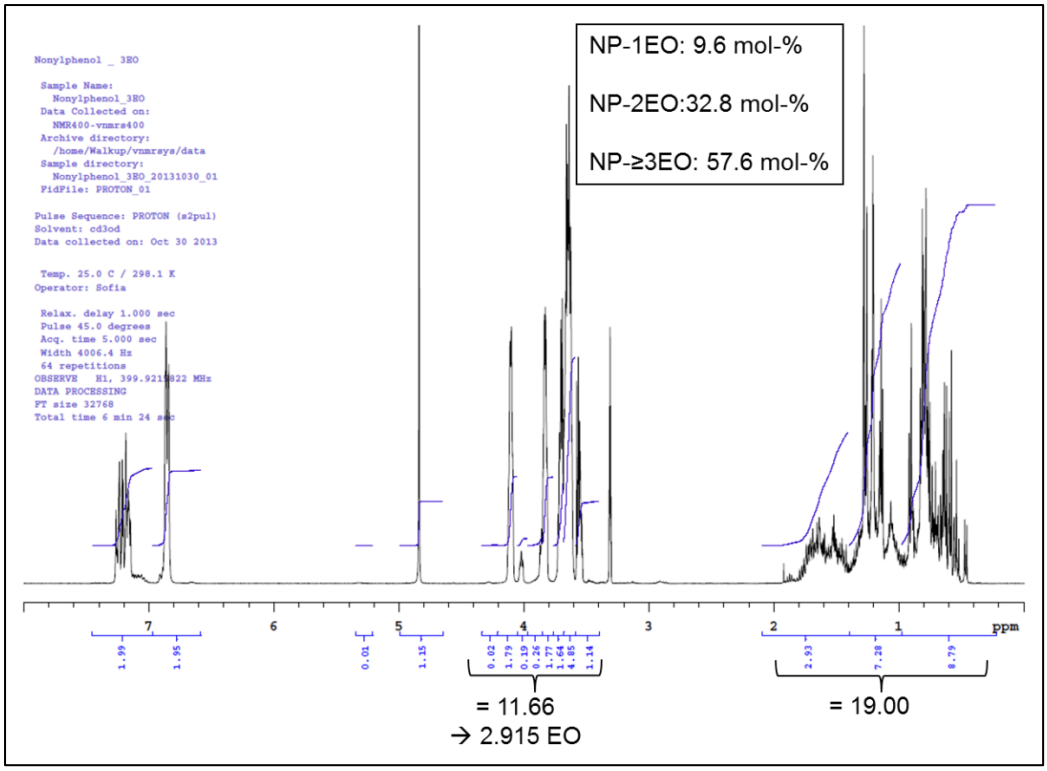

Dynamic surface tension: DS100+NP9EO
Surface tension [mN/m]
70
60
50
40
30
20
0
10000
20000
30000
40000
50000
60000
70000
Bubble life time [ms]
0 g/l
0,01 g/l
0,05 g/l
0,075 g/l
0,1 g/l
0,25 g/l
0,5 g/l

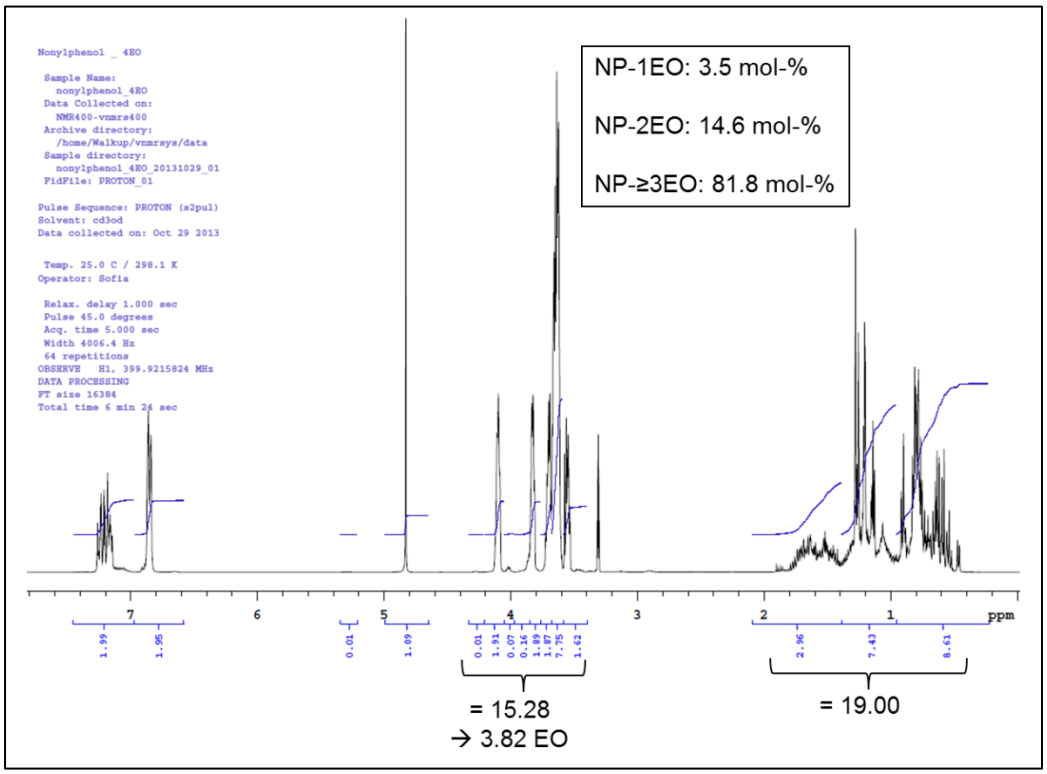

Dynamic surface tension:NP9EO
Surface tension [mN/m]
75
65
55
45
35
25
0
10000
20000
30000
40000
50000
60000
70000
Bubble life time [ms]
0 g/l
0,01 g/l
0,025 g/l
0,05 g/l
0,075 g/l
0,1 g/l
0,25 g/l

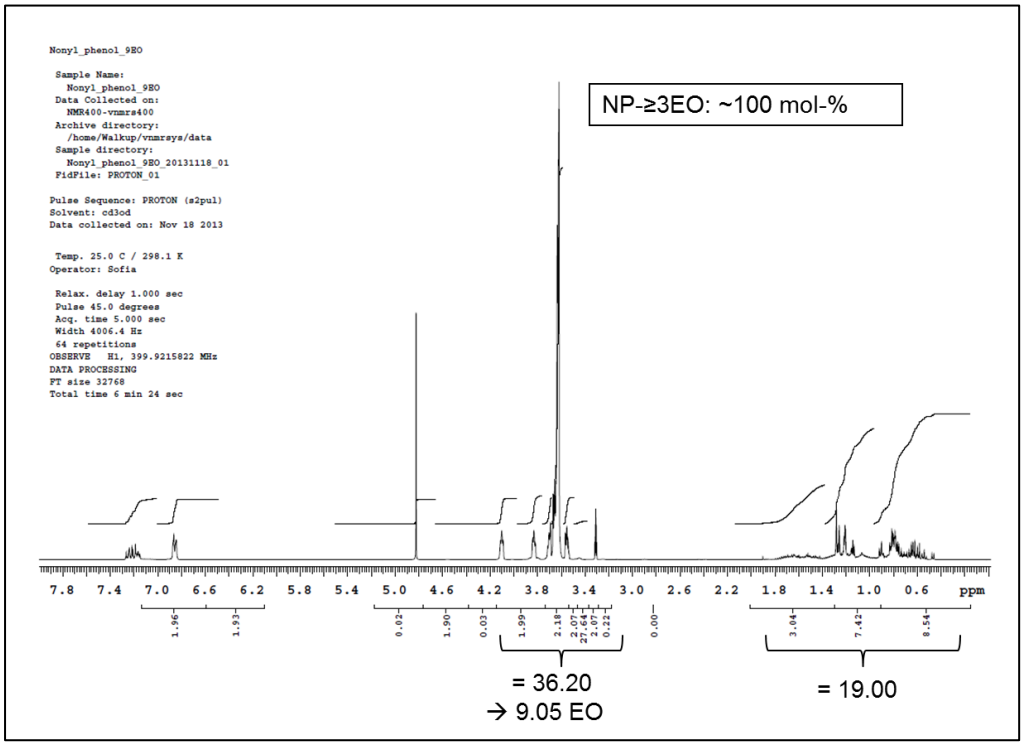
APPENDIX 4


Nonylphenol _ 1EO
Sample Name:
nonylphenol_1EO3
Data Collected on:
NMR400-vnmrs400
Archive directory:
/home/Walkup/vnmrsys/data
Sample directory:
nonylphenol_1EO3_20131030_01
FidFile: PROTON_01
Pulse Sequence: PROTON (s2pul)
Solvent: cd3od
Data collected on: Oct 30 2013
Temp. 25.0 C / 298.1 K
Operator: Sofia
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 5.000 sec
Width 4006.4 Hz
64 repetitions
OBSERVE H1, 399.9215822 MHz
DATA PROCESSING
FT size 32768
Total time 6 min 24 sec
NP-1EO: 95.9 mol-%
NP-2EO: 4.1 mol-%
ppm
= 4.07
→ 1.0175 EO
= 19.01

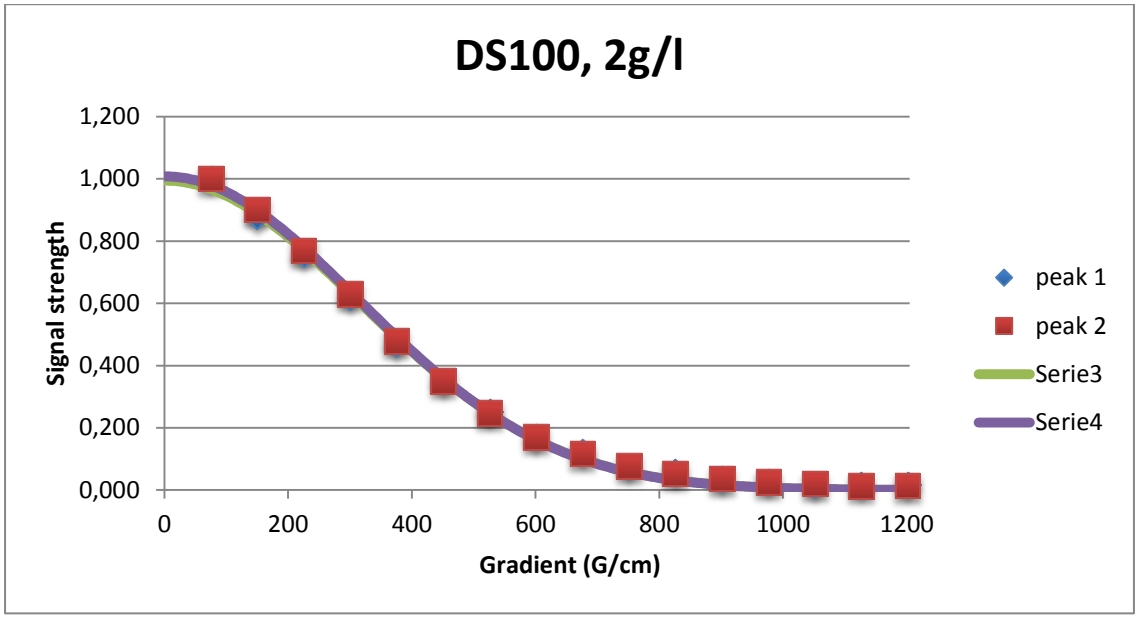

Nonylphenol _ 2EO
Sample Name:
Nonylphenol_2EO
Data Collected on:
NMR400-vnmrs400
Archive directory:
/home/Walkup/vnmrsys/data
Sample directory:
Nonylphenol_2EO_20131030_01
FidFile: PROTON_01
Pulse Sequence: PROTON (s2pul)
Solvent: cd3od
Data collected on: Oct 30 2013
Temp. 25.0 C / 298.1 K
Operator: Sofia
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 5.000 sec
Width 4006.4 Hz
64 repetitions
OBSERVE H1, 399.9215824 MHz
DATA PROCESSING
FT size 32768
Total time 6 min 24 sec
NP-1EO: 42.4 mol-%
NP-2EO: 17.7 mol-%
NP-≥3EO: 39.9 mol-%
ppm
= 7.14
→ 1.785 EO
= 19.00

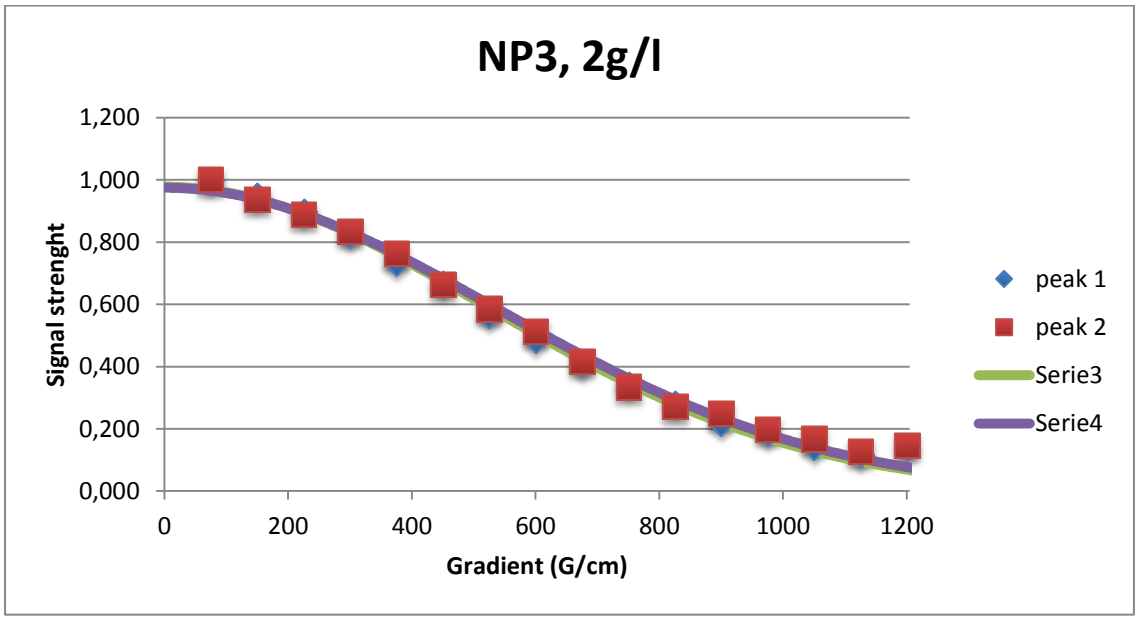

Nonylphenol _ 3EO
Sample Name:
Nonylphenol_3EO
Data Collected on:
NMR400-vnmrs400
Archive directory:
/home/Walkup/vnmrsys/data
Sample directory:
Nonylphenol_3EO_20131030_01
FidFile: PROTON_01
Pulse Sequence: PROTON (s2pul)
Solvent: cd3od
Data collected on: Oct 30 2013
Temp. 25.0 C / 298.1 K
Operator: Sofia
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 5.000 sec
Width 4006.4 Hz
64 repetitions
OBSERVE H1, 399.9215822 MHz
DATA PROCESSING
FT size 32768
Total time 6 min 24 sec
NP-1EO: 9.6 mol-%
NP-2EO:32.8 mol-%
NP-≥3EO: 57.6 mol-%
ppm
= 11.66
→ 2.915 EO
= 19.00

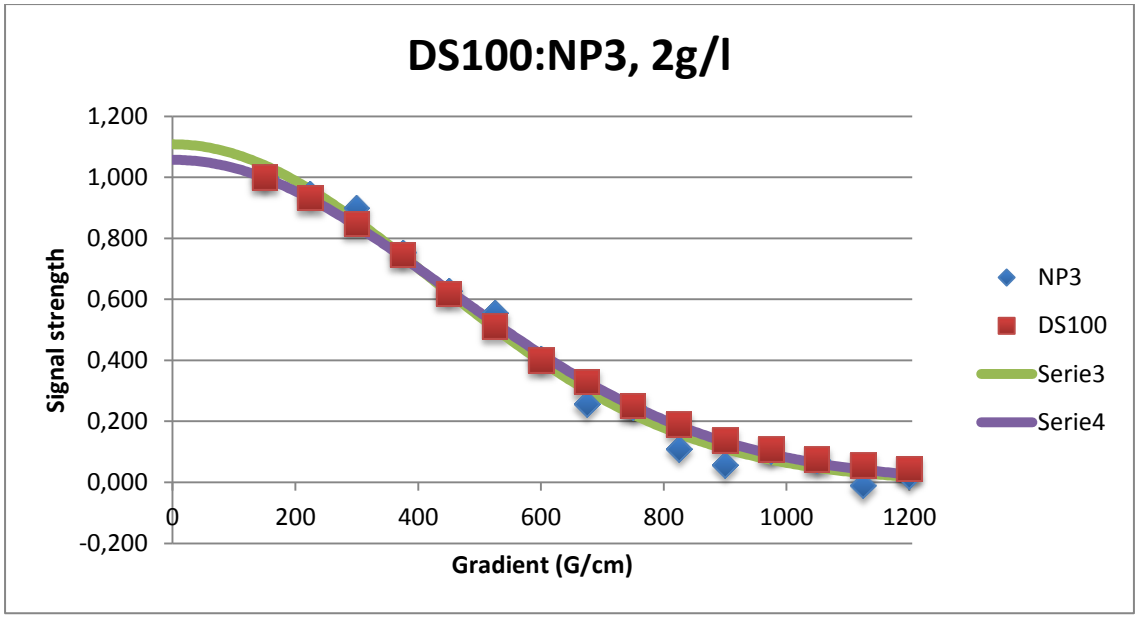

Nonylphenol _ 4EO
Sample Name:
nonylphenol_4EO
Data Collected on:
NMR400-vnmrs400
Archive directory:
/home/Walkup/vnmrsys/data
Sample directory:
nonylphenol_4EO_20131029_01
FidFile: PROTON_01
Pulse Sequence: PROTON (s2pul)
Solvent: cd3od
Data collected on: Oct 29 2013
Temp. 25.0 C / 298.1 K
Operator: Sofia
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 5.000 sec
Width 4006.4 Hz
64 repetitions
OBSERVE H1, 399.9215824 MHz
DATA PROCESSING
FT size 16384
Total time 6 min 24 sec
NP-1EO: 3.5 mol-%
NP-2EO: 14.6 mol-%
NP-≥3EO: 81.8 mol-%
ppm
= 15.28
→ 3.82 EO
= 19.00

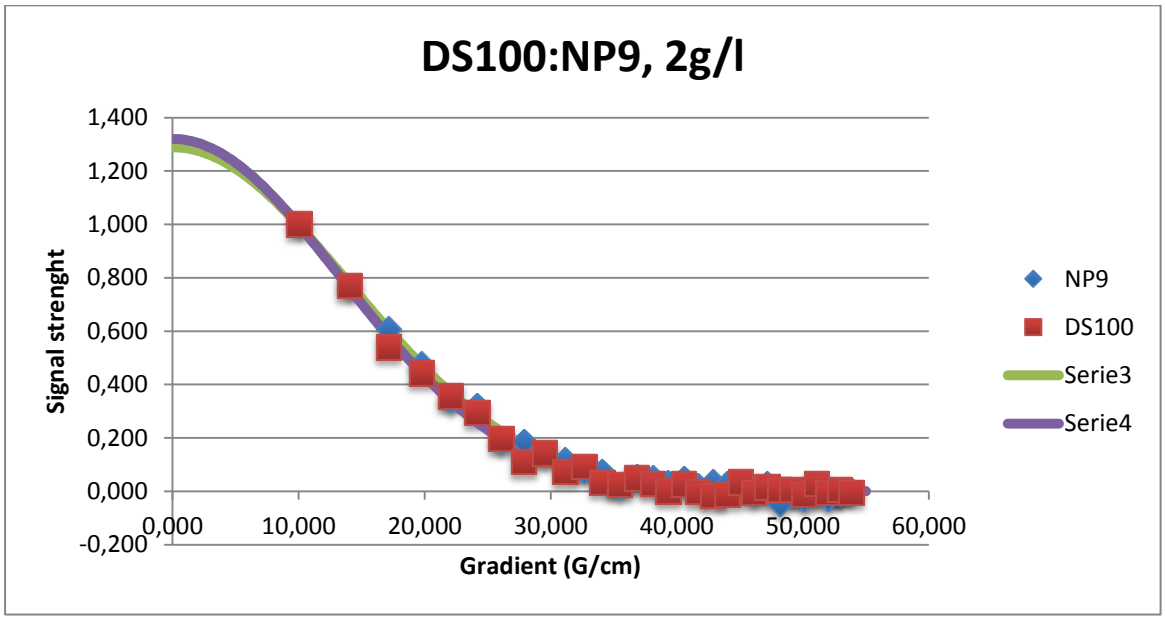

Nonyl_phenol_9EO
Sample Name:
Nonyl_phenol_9EO
Data Collected on:
NMR400-vnmrs400
Archive directory:
/home/Walkup/vnmrsys/data
Sample directory:
Nonyl_phenol_9EO_20131118_01
FidFile: PROTON_01
Pulse Sequence: PROTON (s2pul)
Solvent: cd3od
Data collected on: Nov 18 2013
Temp. 25.0 C / 298.1 K
Operator: Sofia
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 5.000 sec
Width 4006.4 Hz
64 repetitions
OBSERVE H1, 399.9215822 MHz
DATA PROCESSING
FT size 32768
Total time 6 min 24 sec
NP-≥3EO: ~100 mol-%
7.8 7.4 7.0 6.6 6.2 5.8 5.4 5.0 4.6 4.2 3.8 3.4 3.0 2.6 2.2 1.8 1.4 1.0 0.6 ppm
1.96 1.93 0.02 1.90 0.03 1.99 2.18 2.07 27.64 2.17 0.22 0.00 3.04 7.42 8.54
= 36.20
→ 9.05 EO
= 19.00

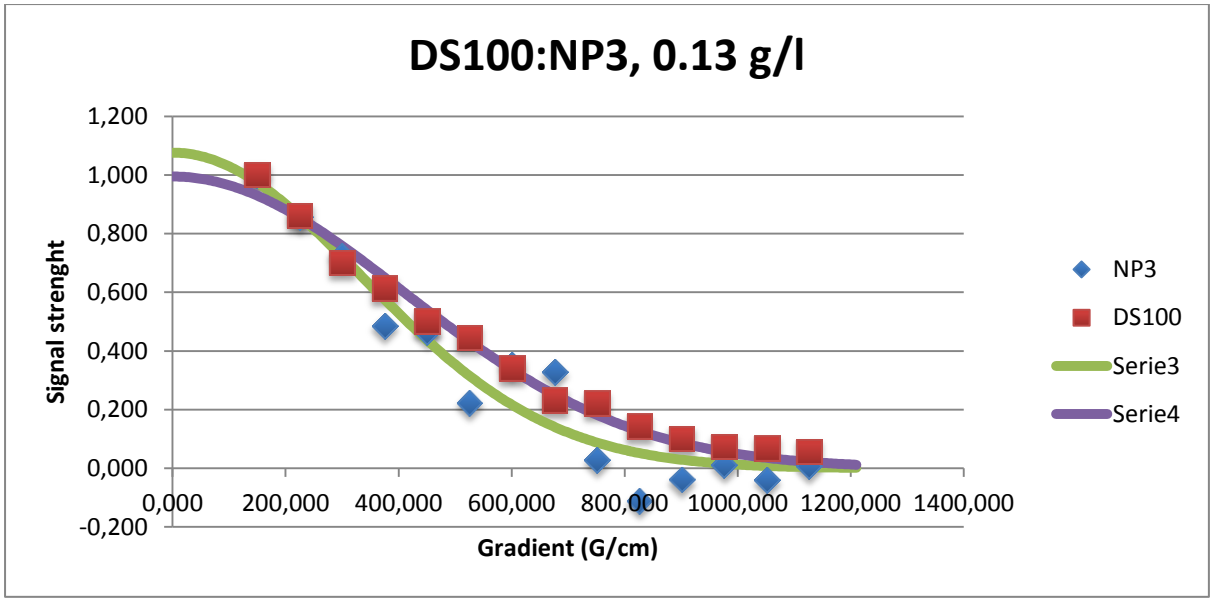
APPENDIX 5


DS100, 2g/l
Signal strength
1,200
1,000
0,800
0,600
0,400
0,200
0,000
0
200
400
600
800
1000
1200
Gradient (G/cm)
peak 1
peak 2
Serie3
Serie4


NP3, 2g/l
Signal strenght
1,200
1,000
0,800
0,600
0,400
0,200
0,000
0
200
400
600
800
1000
1200
Gradient (G/cm)
peak 1
peak 2
Serie3
Serie4


DS100:NP3, 2g/l
1,200
1,000
0,800
0,600
0,400
0,200
0,000
-0,200
Signal strength
0
200
400
600
800
1000
1200
Gradient (G/cm)
NP3
DS100
Serie3
Serie4


DS100:NP9, 2g/l
1,400
1,200
1,000
0,800
0,600
0,400
0,200
0,000
-0,200
Signal strenght
0,000
10,000
20,000
30,000
40,000
50,000
60,000
Gradient (G/cm)
NP9
DS100
Serie3
Serie4


DS100:NP3, 0.13 g/l
Signal strenght
1,200
1,000
0,800
0,600
0,400
0,200
0,000
-0,200
0,000
200,000
400,000
600,000
800,000
1000,000
1200,000
1400,000
Gradient (G/cm)
NP3
DS100
Serie3
Serie4