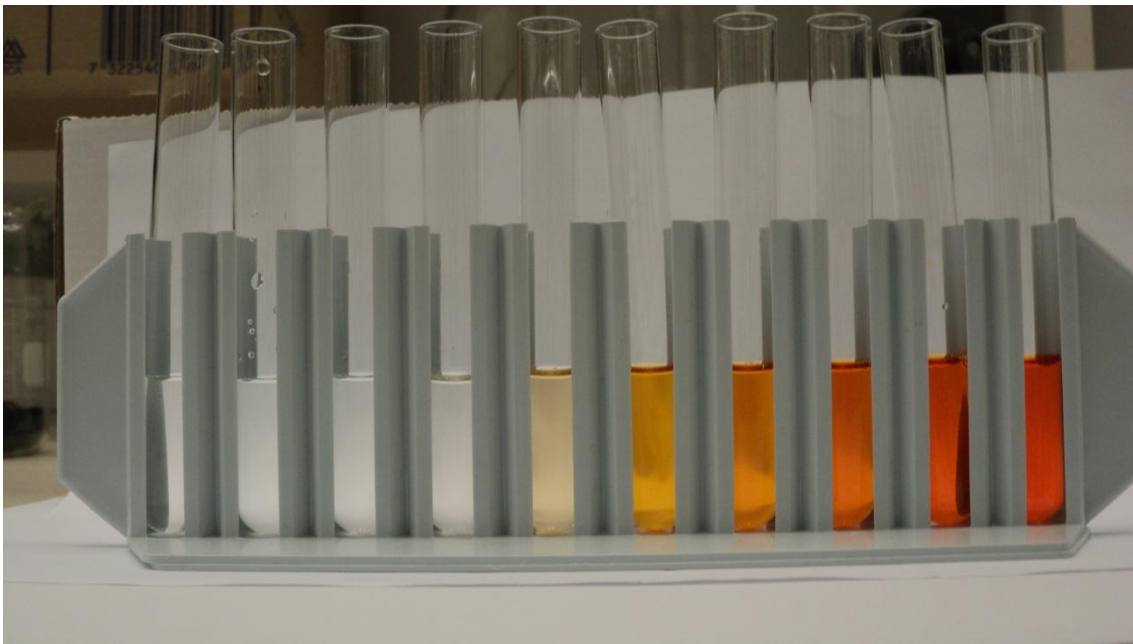


# CHALMERS



## Solubilization of Organic Dyes in Surfactant Micelles

*Master of Science Thesis in the Master Degree Programme Materials and Nanotechnology*

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Gothenburg, Sweden, 2012

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Cover: The effect of surfactant concentration on dye solubilization (left to right). The solubilization starts at around critical micelle concentration of each surfactant and increases almost linearly at higher concentrations.

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## ABSTRACT

In this study, the solubilization of two organic dyes, Sudan I (1-Phenylazo-2-naphthol) and Quinizarin (1,4-Dihydroxyanthraquinone), was studied in the presence of different types of surfactants (2 polymeric, 2 nonionics, 2 anionic, and one cationic) using UV-Vis spectroscopy. The effects of temperature, pH and addition of different electrolytes (NaCl, Na<sub>2</sub>CO<sub>3</sub>, NaI, NaOH, NaSCN) on dye solubilization were investigated mainly for Berol 535 (C<sub>11</sub>EO<sub>5</sub>), DTAB (C<sub>12</sub> quaternary ammonium bromide) and SDS (C<sub>12</sub> sodium sulphate). The effect of mixed micelles of different surfactants (DTAB:Berol 535 and SDS:Berol 535) on dye solubilization at different concentrations of NaCl was also studied. No synergy effect was observed for the solubilization of dyes in the binary mixture of surfactant micelles. The results showed that the solubilization of both dyes in the surfactant micelles increased with the temperature and addition of salt. However, the anionic surfactant (SDS) precipitated in the solution at high salt concentration (>20 g/l) and room temperature due to its high Krafft point and this had an adverse effect on dye solubilization. This was overcome by adding a nonionic surfactant to the solution or increasing the temperature. The absorbance spectrum of both dyes in surfactant micelles was similar to that obtained in ethanol and water/ethanol. This suggested that both dyes are located in rather polar region of the micelles (palisade region) and close to the surfactants head groups.

Keywords: Solubilization, organic dye, surfactants (cationic, anionic, nonionic, and polymeric), micelle, mixed micelle

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## 1. Introduction

Solubilization of water-insoluble materials in the surfactant aqueous solution is important in many industrial applications such as detergency, emulsion polymerization, enhanced oil recovery, drug delivery and textile dyeing [1-3]. The surfactant aggregates known as micelles are responsible for the solubilization of the hydrophobic substances in water [4]. Therefore, surfactants that start to aggregate into micelles at low concentrations, are good candidates for this purpose.

Among different effective parameters, the effect of temperature and electrolyte concentration on solubilization is very high. An increase in temperature and addition of electrolytes increases the solubilization [1].

### 1.1 Objective

The aim of this project was to study the effects of the surfactant chemical structure (anionic, cationic or nonionic), surfactant concentration, surfactant mixture, temperature, pH and addition of salt on the solubilization of the two organic dyes in aqueous solution.

The main objective of this work was to make a systematic study on solubilization of two organic dyes (Quinizarin with anthraquinone structure and Sudan I with azo structure) in surfactant micellar solution. For this reason, a series of surfactants with different types of polar head groups were investigated. The solubilization of dyes in the mixed micelles of ionic surfactants with a nonionic surfactant at different salt concentrations was determined.

A minor part of this study deals with the location of the dye molecule in a surfactant micelle and kinetics of solubilization.

## 2. Background

In this section some background is given regarding surfactants, solubilization, dyes and instrumental techniques.

### 2.1 Surfactants

Surface active agents, also known as surfactants, refer to molecules that are active at surfaces. A surfactant is characterized by its tendency to adsorb at surfaces and interfaces. An interface is a boundary between any two immiscible phases whereas a surface is an interface where one phase is a gas [1,5].

There are five different interfaces:

- Solid-vapour surface
- Solid-liquid
- Solid-solid
- Liquid-vapour surface
- Liquid-liquid

Since nature always favors lower free energy, one can guess why surfactants adsorb at interfaces. The driving force for a surfactant to adsorb at an interface is of course to reduce the free energy of that specific phase boundary [5].

Surfactants are amphiphilic molecules consisting of a non-polar, hydrophobic tail and a polar, hydrophilic head group (Figure 2.1). The hydrophobic tail is usually a branched or linear long-chain hydrocarbon residue with a chain length in the range of 8-18 carbon atoms. The polar head group can be either ionic or non-ionic [1,4,5].

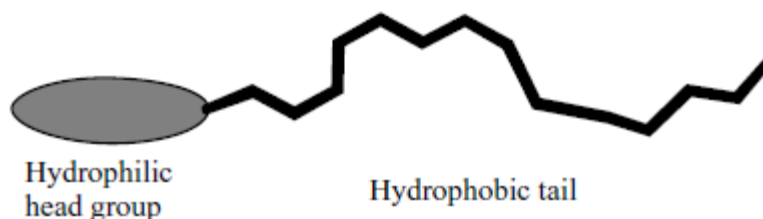


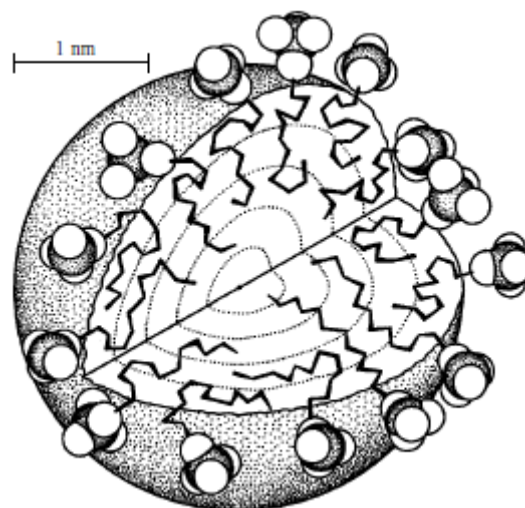
Figure 2.1 A typical illustration of a surfactant molecule [5]

Depending on the charge of the polar head group, surfactants are classified as anionic (negatively charged), cationic (positively charged), zwitterionic (both positively and negatively charged groups) or nonionic (non-charged) [1,4,5].

When a surfactant is dissolved in an aqueous environment, the hydrophobic tail interacts weakly with the water molecules using van der Waals forces. On the other hand, the hydrophilic head interacts strongly with the water molecules using dipole-dipole or ion-dipole forces. Surfactants are water soluble because of this strong interaction with the water molecules [4]. However, the much weaker van der Waals forces breaks the much stronger hydrogen bonds between water molecules. The surfactants are therefore forced to the interfaces of the system, where the hydrophobic tails get oriented in a way to keep minimum contact with water [1,4].

### 2.1.1 Micelle formation

Surfactants have limits to how much they can lower the surface and interfacial tension. At a certain surfactant concentration in a system when all interfaces and surfaces are occupied by surfactant unimers (free surfactant), the surfactant unimers in the bulk start to aggregate into micelles. This specific concentration is called the critical micelle concentration (CMC). They start to aggregate since they do not want the hydrophobic tails to be in contact with water. So instead micelles are formed with the hydrophobic tails pointing inwards and the hydrophilic head groups pointing outwards towards the water, as can be seen in Figure 2.2. In that way the free energy of the system is reduced. Surfactants behave differently depending on if they are present in micelles or as surfactant unimers in the solution. Surfactant unimers are the only surface active of the two, so they are the one responsible of decreasing the interfacial and surface tension. Micelles are not surface active. They just act as reservoirs for the surface active surfactant unimers [5].



*Figure 2.2 A typical illustration of a spherical micelle [5]*



Micelles are not necessarily spherical as they are usually portrayed. They can also be cylindrical, just a bilayer, reversed etc. It is the critical packing parameter (CPP) that governs the shape of the micelles. CPP is a dimensionless number defined as:

$$CPP = \frac{v}{al} \quad \text{Eq. (1)}$$

Where  $v$  is the volume of the hydrophobic tail,  $a$  is the area of the hydrophobic head and  $l$  being the length of the hydrophobic tail. An illustration of CPP can be seen in Figure 2.3 [5].

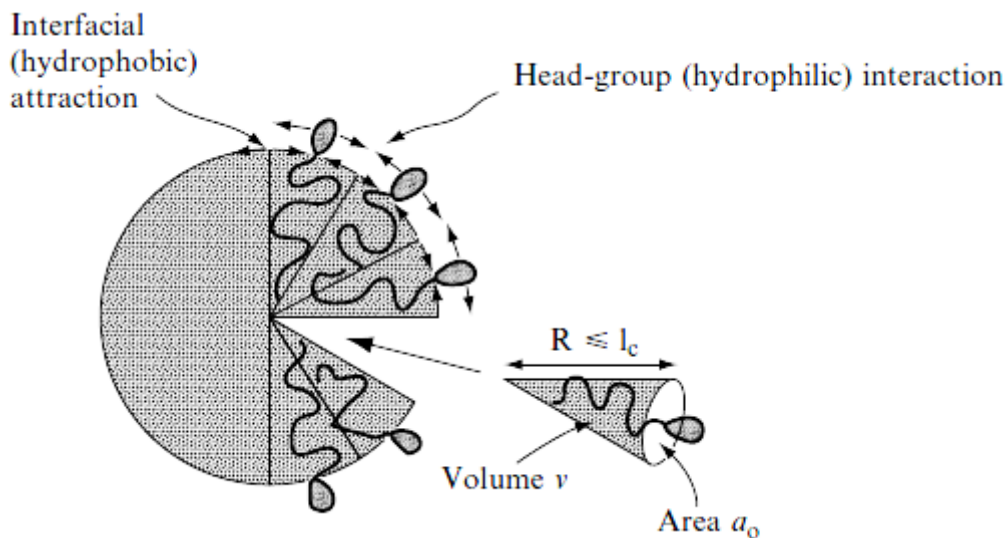


Figure 2.3 The concept of CPP [5]

Spherical micelles will be formed as long as CPP is not higher than  $1/3$  [4,5]. Figure 2.4 illustrates how the aggregate structures depend on the CPP.

This explains why surfactants with

- 1) straight hydrophobic tails tend to form spherical micelles
- 2) branched hydrophobic tails tend to form cylindrical micelles which aggregates further into hexagonal structures
- 3) double hydrophobic tails tend to form lamellar phases and reversed structures

Simply the volume of the hydrophobic tails gets larger which leads to a higher CPP [5].

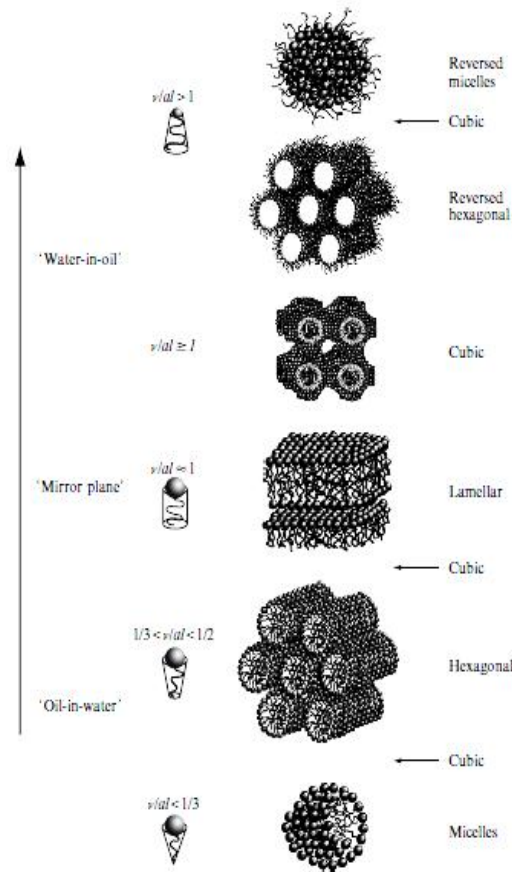


Figure 2.4 The CPP of different structures [5]

### 2.1.2 Krafft temperature

The Krafft temperature, or Krafft point, is the temperature at which the solubility of a surfactant starts to increase dramatically. At this temperature, the solubility of the surfactant unimers becomes high enough to start to form micelles. Below this temperature, no micelles will form, no matter how much surfactant unimers are added. The Krafft temperature depends very much on the head group and counter ion of the surfactant. Adding salt usually increases the Krafft temperature [5]. Figure 2.5 illustrates the phenomenon.

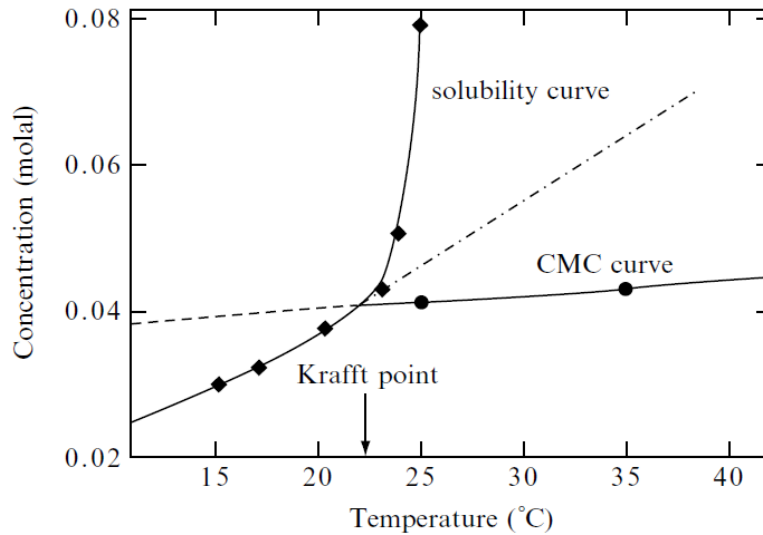


Figure 2.5 Krafft temperature [5]

### 2.1.3 Cloud point

Nonionic surfactants containing oxyethylene groups are very much affected by the temperature. While heating a nonionic surfactant solution, it becomes turbid at a specific temperature range. The solution becomes “cloudy”. The temperature range is called the cloud point, or cloud temperature. Clouding is really a phase separation into two micellous solutions; one with a high concentration of surfactants, and one with a low concentration of surfactants. The cloud point depends very much on the polyoxyethylene chain length of the surfactant, a longer chain corresponds to a higher cloud point [5].

### 2.1.4 Solubilization of surfactants

Solubilization is defined as the spontaneous dissolving of an insoluble substance in a solvent to form a thermodynamically stable isotropic solution with the help of surfactants [1]. In other words, a substance (e.g. hydrophobic compound) that is usually insoluble in a solvent (e.g. water) becomes soluble with the help of surfactants. Below the CMC of the surfactant, the solubility (amount of substance that is incorporated in the solution) is slightly higher than in the pure insoluble solvent. However, just above the CMC, the solubility increases dramatically. And by adding even more surfactant, the solubility increases in a linear fashion, which can be seen in Figure 2.6. This is because micelles are formed which can accommodate the insoluble substance [4].

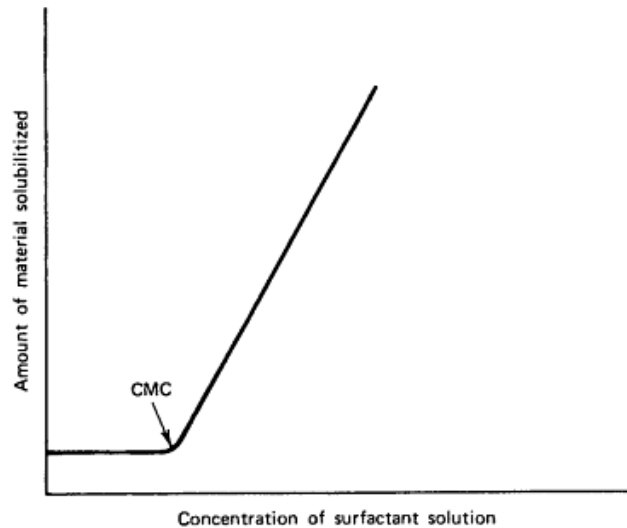


Figure 2.6 Amount of material solubilized as a function of concentration of surfactant solution [1]

### 2.1.5 Mixed micelles

Surfactant mixtures form micelles consisting of all surfactant species present. The CMC value of the mixture depends on how the CMC values of the single surfactants differs. When there is no net interaction between the surfactants the CMC value of the mixture can be calculated with Eq. (2).

$$CMC = \frac{1}{\frac{x_1}{CMC_1} + \frac{x_2}{CMC_2}} \quad \text{Eq. (2)}$$

where  $x_1$  is the mole fraction of surfactant 1,  $x_2$  is the mole fraction of surfactant 2,  $CMC_1$  is the CMC value of surfactant 1,  $CMC_2$  is the CMC value of surfactant 2. If there is a big difference ( $CMC_2/CMC_1=0.01$ ), where 2 represents a very hydrophobic surfactant, only a small amount of the very hydrophobic surfactant is needed for the CMC value to be decreased significantly (synergy). This is consistent with Eq. (2) and shown in Figure 2.7 [5].

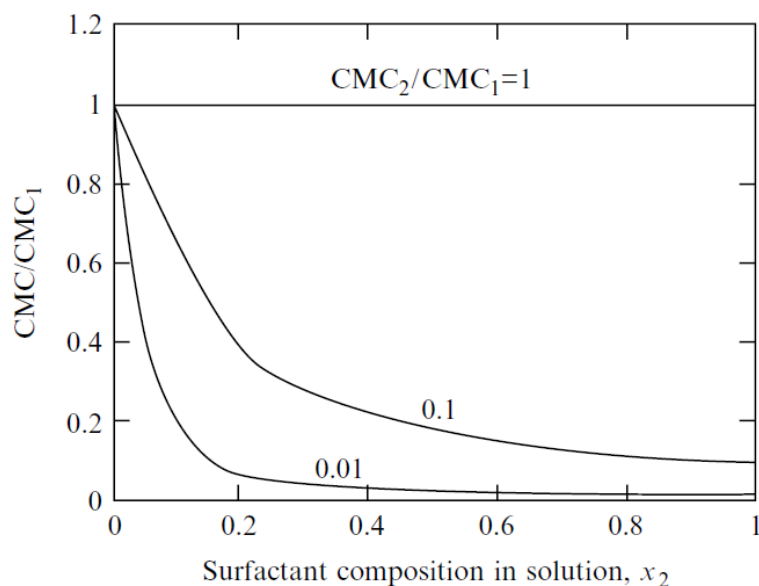


Figure 2.7 CMC value of the mixture as a function of surfactant composition depending on the difference in CMC of the single surfactants [5]

The simple explanation for this behavior is that the more surface active material, hydrophobic surfactant, will as it literally says be more surface active and consequently to a higher extent adsorb at the interfaces. In other words, the interfaces will be occupied by the hydrophobic surfactant to a higher extent which lowers the CMC. To have single hydrophobic surfactants in the water is not good regarding the free energy of the system. That is why micelles start to form earlier than when less hydrophobic surfactants are in the system [5].

However, in many systems, surfactants of different kinds are mixed, for example mixtures of anionic and nonionic surfactants; anionic and cationic surfactants. In the former, the nonionic surfactants shield the repulsion between the anionic head groups in the micelle and so there is a net charge between the different surfactants, whereas in the latter, the anionic and cationic surfactants interact because of their opposite charges. In the mentioned examples, there is an attraction between the surfactants and basically the higher the attraction, the lower the CMC value of the system [4,5]. Mixing of surfactants in a formulation may also have some other advantages, such as lowering the Krafft temperature and increasing the cloud point of the system [6].

Detergents consist of a mixture of ionic and nonionic surfactants. Ionic surfactants are usually too hydrophilic to give efficient soil removal, unlike nonionic surfactants that are usually too hydrophobic. So by mixing the different surfactants an optimum in soil removal is reached around equal amounts of the two surfactants. This is shown in Figure 2.8 [5].

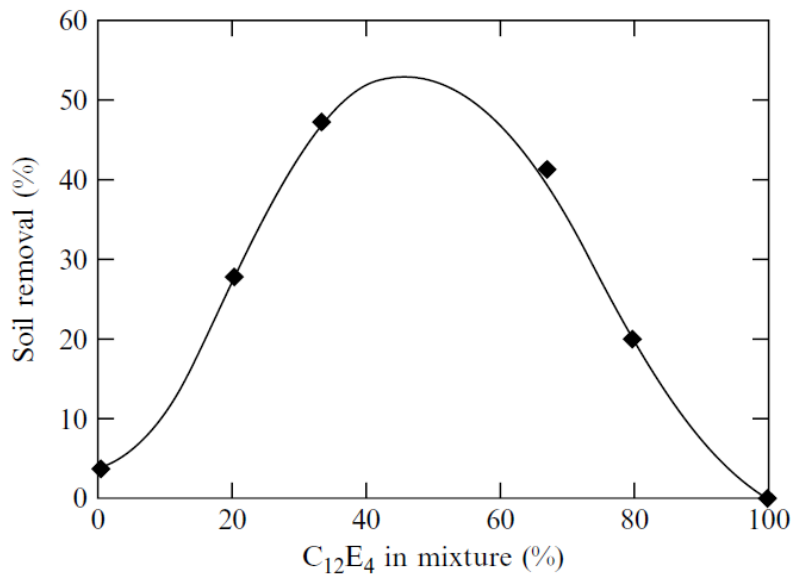


Figure 2.8 Oily soil removal as a function of  $C_{12}E_4$  content in a mixture with the hydrophilic anionic surfactant sodium octylbenzene sulfonate [5]

### 2.1.6 Physical-chemical properties

Many physical-chemical properties change drastically at the CMC. Figure 2.9 illustrates how some of the physical-chemical properties behave around the CMC for an ionic surfactant.

At low concentrations of surfactant, most properties are similar to that of an electrolyte with one big exception, the surface tension. The surface tension decreases as surfactant concentration increases until the CMC is reached. As illustrated in Figure 2.9, the osmotic pressure and surface tension stay constant after the CMC. The turbidity (light scattering) and solubilization are examples of two properties that increase after CMC [4,5].

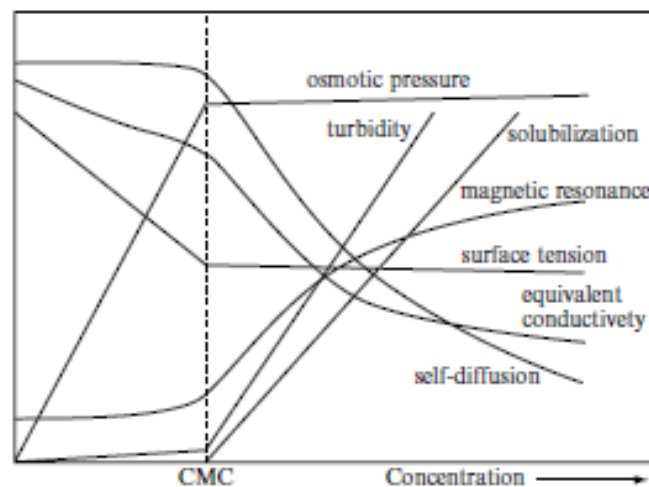


Figure 2.9 The change in physical-chemical properties of the aqueous solution by increasing the concentration of surfactant in the solution [5]

The physical-chemical properties of ionic surfactants can be very much affected by electrolytes. Strong electrolytes virtually completely dissociate into ions. The charge of head groups is neutralized by the adsorption of oppositely charged ions. Thus, the repulsion between the head groups is reduced. This leads to a denser packing of the surfactants in the interfaces.

There are several different methods to measure the CMC. The two most widely used are the surface tension and conductometry measurements. Solubilization of a dye and fluorescence spectroscopy can also be used in this regards. The conductivity can be measured only for ionic surfactant in the absence of electrolytes [4,5].

## 2.2 Dyes

A dye is usually a colored organic compound that is used to color a substrate, e.g. fabric, paper or plastic in a permanent way. Thus, it should be able to resist outer forces which can be caused by washing, rubbing etc. The dye must have some specific groups that create bonds to the substrate. The dye has an affinity to the substrate to which it is applied to and is applied in an aqueous solution [7].

Pigments are usually mistaken for dyes. Both are colorants, however, the difference is that pigments consist of small particles that are insoluble in the media they are applied, whereas dyes are applied in the form of a solution where they are soluble [7,8]. So, pigments need additional compounds to attach to the substrate [8]. More information can be found in the books *Synthetic Dyes* [7] and *Color Chemistry* [8].

### 3. Experimental (Materials and methods)

#### 3.1 Materials

Acetone (>99.5%), chloroform (99%), cyclohexane (99%), dichloromethane (>99.5%), diethyl ether (99%), hexane (99%), methanol (99%), toluene (99%), Sudan I (97%), Quinizarin (>98%), citric acid (99%), sodium bicarbonate (99%), sodium carbonate (99%), sodium chloride (99%), sodium hydroxide (97%), sodium iodide (99.5%), sodium phosphate dibasic (99%), sodium thiocyanate (98%), 4-dodecylsulfonic acid (technical grade), dodecyltrimethylammonium bromide (99%), nonylphenyl etoxylate 9, pluronic F127, pluronic P123, propylene glycol monopropyl ether (99%) and sodium dodecyl sulphate (99%) were all purchased from Sigma-Aldrich. Ethanol (99.5%) was provided by Kemetyl. The chemical structure of the surfactants is shown in Table 1. DTAB, IGEPAL CO-630, SDBS and SDS were also purchased from Sigma and nonionic surfactant, Berol 535, was obtained from Akzo Nobel.

Table 1. Used surface active species

Abbreviation	Name	Structure
Berol 535	Penta(ethylene glycol) monoundecyl ether	
DTAB	Dodecyltrimethylammonium bromide	
IGEPAL CO-630	Nonylphenyl etoxylate 9 (NP-EO <sub>9</sub> )	
SDBS	4-Dodecylsulfonic acid	
SDS	Sodium dodecyl sulphate	
Pluronic F127	Pluronic F127 (EO <sub>100</sub> PO <sub>64</sub> EO <sub>100</sub> )	
Pluronic P123	Pluronic P123 (EO <sub>20</sub> PO <sub>70</sub> EO <sub>20</sub> )	

#### 3.1.1 Sudan I (1-Phenylazo-2-naphthol)

Sudan I is a synthetic organic red azo dye mainly used in the industry as a colorant (coloring products such as textiles, waxes, polishes and oils) [9]. Azo dyes contains the functional



group  $R_1-N=N-R_2$ . The solubility of Sudan I in water (21 °C) at room temperature was around 0.16 mg/l. The chemical structure of Sudan I is shown in Figure 3.1. Sudan I exists as a mixture of two tautomers that are in equilibrium, the azo form and the hydrazone form (Figure 3.2). The ratio of the tautomers depends on the properties of the solvent in which has been used for the solubilization of the dye [10].

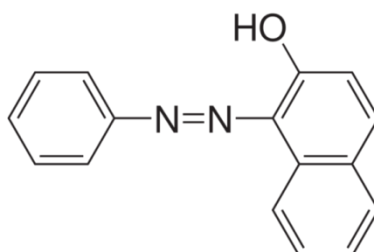


Figure 3.1 Chemical structure of Sudan I

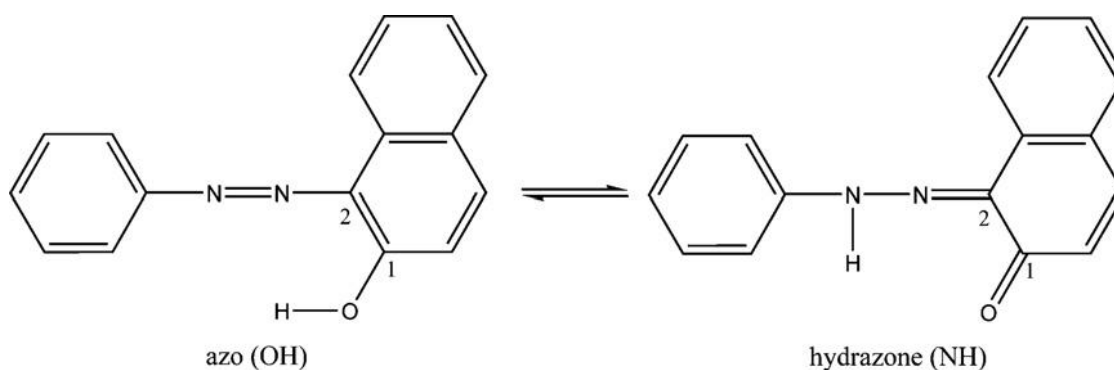


Figure 3.2 The azo-hydrazone equilibrium of Sudan I [10]

### 3.1.2 Quinizarin (1,4-Dihydroxyanthraquinone)

Quinizarin is a red anthraquinone derivative used for dyeing of textiles [11,12]. The solubility of Quinizarin in water (21 °C) at room temperature was around 0.2 mg/l. The chemical structure of Quinizarin is shown in Figure 3.3. Quinizarin also exist as a mixture of two tautomers that are in equilibrium, 1,4-Dihydroxy-9,10-antraquinone and 9,10-Dihydroxy-1,4-antraquinone (Figure 3.4) [11].

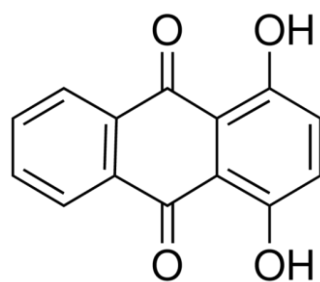


Figure 3.3 Chemical structure of Quinizarin

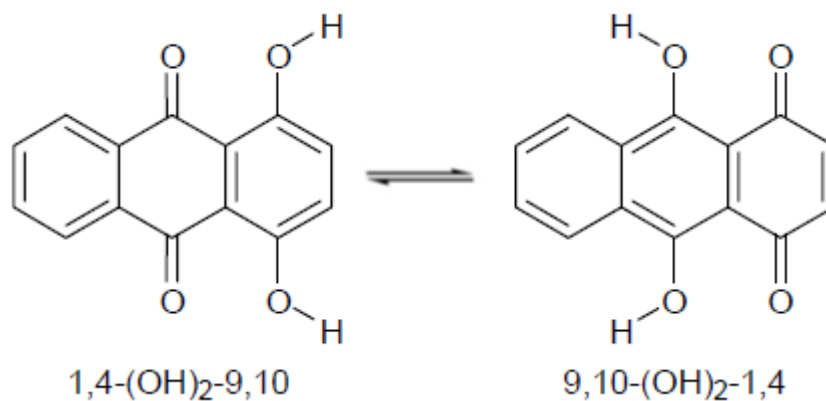


Figure 3.4 The tautomer equilibrium of Quinizarin

## 3.2 Experimental methods

### 3.2.1 Absorption measurement

The absorption spectra of the solutions were recorded using a double beam UV-Vis spectrophotometer (GBC 920, Australia) with a matched pair of quartz cuvettes (1 cm in optical path length).

In a UV-Vis Spectrophotometer, light from the near ultraviolet (UV) and visible (vis) range of the spectrum (200-800 nm) interacts with the molecules. The light excites electrons from a ground state to an excited state. The light loses intensity as it goes through the sample and the absorbance of the sample is defined as

$$A = \log \left( \frac{I_0}{I} \right) \quad \text{Eq. (3)}$$

where  $I_0$  is the intensity before passing through the sample and  $I$  is the intensity after passing through the sample.

The absorbance is important because it is directly proportional to the concentration,  $c$ , of the light absorbing compound in the sample according to Lambert-Beer's law (Eq. (4))

$$A = \epsilon cl \quad \text{Eq. (4)}$$

where  $\epsilon$  is the molar absorptivity (or extinction coefficient),  $c$  is the concentration and  $l$  is the optical path-length [13].

### 3.2.2 Solubilization measurements

High concentrated dye solution in acetone was transferred to the glass vials and acetone was evaporated. Aqueous solutions of a specific surfactant covering a range of concentrations below and above its critical micelle concentration (CMC) were prepared using Milli-Q water and added to the vials containing the excess amount of dye. The samples were then shaken for at least 16 hours at room temperature (21 °C) on a RS 10 basic shaker (210 rpm from Skafta Medlab). The non-solubilized dye was filtered off using Millipore Millex Syringe Filters with a PVDF Membrane (pore size of 0.22  $\mu\text{m}$ ). The first 2 ml of filtrate was discarded in order to avoid the dilution effect as a result of adsorption on the membrane. The filtrate was finally diluted with an equal volume of ethanol and an appropriate volume of 50% aqueous ethanol solution. The concentrations of solubilized dye were determined from the absorbance of the solutions at the wavelength of maximum absorption,  $\lambda_{\text{max}}$ , with the help of each dye calibration curve in 50% aqueous ethanol solution.

The solubilization power,  $S_e$ , of a surfactant is defined as the number of moles of solubilized dye per mole of micellar surfactant (Eq. (5)).

$$S_e = \frac{S_w - S_{CMC}}{C_{surf} - CMC} \quad \text{Eq. (5)}$$

where  $S_w$  is the molar solubility of the dye in the aqueous system,  $S_{CMC}$  is the molar solubility of the dye at CMC,  $C_{surf}$  is the molar concentration of the surfactant [1,14]. The solubilization power of a specific surfactant can thus be determined by calculating the slope of its solubility curve after CMC.

### 3.2.3 Determine the excess amount of dye

To determine the amount of dye that would be considered as excess in the solubilization measurements, different amounts of dye was added to different series of aqueous DTAB solutions covering a broad range of concentrations below and above its CMC. An excess amount of dye was considered as dye concentration above which there would not be any changes in the slope of straight line in solubilization curve after CMC.

### 3.2.4 CMC measurements

The CMC measurements were conducted using the Du Noüy ring method on a Sigma 70 tensiometer. Known concentrations of specific surfactant solutions were added until the surface tension of the liquid did not decrease anymore (the surfactant unimers start to aggregate into micelles). Most of the measurements were carried out at room temperature. The platinum ring was washed with ethanol and cleaned before each new series of measurements by flaming (Bunsen burner) in order to get rid of any residual deposits [15]. The vials were washed several times with ethanol and water before each new series of measurements.

### 3.2.5 Krafft temperature

An aqueous surfactant solution (1 wt%) was heated to form a clear solution. The solution was placed in a refrigerator for 24 h. The temperature of the precipitated systems was slowly increased under constant stirring. The conductance was monitored by a CDM 210 conductometer (Radiometer, France) equipped with a thermocouple that was immersed in the solution. The Krafft temperature was taken as the temperature at which the conductance vs. temperature plot showed an abrupt change in slope. The Krafft temperature of surfactant solutions with high amount of NaCl salt (10, 20 g/l) was determined by the naked eye as conductance vs. temperature plot did not show an abrupt change in slope.

### 3.2.6 Cloud point

The cloud point is the temperature at which a nonionic surfactant solution turns turbid due to the separation into one more concentrated micellar phase and one more dilute surfactant solution [5]. An aqueous solution of the nonionic surfactants (1 wt.%) was first heated in an oil bath under stirring until the solution turned completely cloudy. The system then slowly cooled down under stirring and the temperature was monitored. When the cloud point temperature is reached, the turbid solution dramatically turns clear which was observed by the naked eye.

### 3.2.7 Temperature effect

An excess amount of dye was put in a flask with 100 ml of the surfactant solution (1wt.%). The flask was put in an oil bath under stirring at 25 °C for 16 h. The sample (around 3 ml) was extracted and the solubilization was measured. The temperature of the system was then increased. This procedure was repeated at different temperature (35, 45, 55, 65 and 75 °C).

### 3.2.8 The effect of pH on solubilization

To investigate the pH effect on the solubilization of the two dyes, six different buffer solutions were prepared and used for making the surfactant solutions. The pH was in the range of 3.07-11.77. The composition of these buffers has been summarized in Table 2.

*Table 2. Preparation of the different buffer solutions*

Buffer solution	pH
Citric acid (0.0077M) - Na <sub>2</sub> HPO <sub>4</sub> (0.004M)	3.07
Citric acid (0.0047M) - Na <sub>2</sub> HPO <sub>4</sub> (0.01M)	5.27
Citric acid (0.0017M) - Na <sub>2</sub> HPO <sub>4</sub> (0.016M)	7.14
NaHCO <sub>3</sub> (0.01M)	8.23
Na <sub>2</sub> CO <sub>3</sub> (0.01M)	10.85
NaOH (0.01M)	11.77

## 4. Results and Discussion

In this section the different results from the experimental work are presented and discussed.

### 4.1. Physical-chemical properties of surfactants

The CMC value of all surfactants used is reported in Table 3. The Krafft temperature and cloud point are also reported for ionic and nonionic surfactants, respectively. Some of the values are from the literatures.

Table 3. Physical-chemical properties of surfactants

Surfactant	Molecular weight	CMC (mM) at 22°C	Krafft temp.*	Cloud point*
	g/mol		°C	°C
Berol 535	392.57	0.28, 0.25 [29]	-	28, 27 [16]
DTAB	308.34	13, 14 [20]	20 [24]	-
IGEPAL CO-630	617	0.1, 0.08 [18]	-	53, 52-56 [17]
SDBS	348.48	3, 3 [19]	12, 27.6 [25,26]	-
SDS	288.38	6.4, 8-9 [21]	12, 14-15 [22,23]	-
Pluronic F127	12600	4-11 [28]	-	-
Pluronic P123	5750	0.07 [27]	-	-

\* The range of uncertainty was  $\pm 0.5^\circ\text{C}$

As can be seen from Table 3, the CMC values of nonionic surfactants (Berol 535 and IGEPAL CO-630) were much lower than CMC values of ionic surfactants (DTAB, SDS, SDBS). The CMC of Berol 535 at room temperature was in good agreement with the value given by the manufacturer (0.1 g/l). The CMC of IGEPAL CO-630 was slightly higher than the reported value in literature (0.05-0.08 mM) [18]. We should not put so much emphasis on the obtained values for DTAB and SDS, since we had a minimum in the surface tension curve. This minimum is caused by some surface active impurities in the surfactant, e.g. dodecanol in the case of SDS. When the CMC is reached, surfactant micelles start to solubilize the surface active impurities and they leave the interfaces. Therefore, the surface tension increases a bit until all impurities have left the interfaces [5]. However, the obtained values for SDS and DTAB are quite close to the reported values (8-9 mM and 14 mM, respectively) [20,21].

The Krafft temperature of both anionic surfactants (SDS and SDBS) was around 12 °C. The effect of salt concentration on Krafft temperature of SDS, SDBS and a mixture of SDS and Berol 535 was shown in Table 4.

*Table 4. The effect of salt concentration on the Krafft temperature of anionic surfactants*

Solution	Added NaCl [g/l]	Krafft temp. [°C]
SDS(10g/l)	0	11.5-12.5
	10	19.5-20.5
	20	22.5-23.5
	50	30
SDS(10g/l)80:20Berol 535 (10g/l)	0	<0
	10	14.5-15.5
	20	18-19
	50	23-24
SDBS(10g/l)	0	11-12
	10	21-22
	20	36-37
	50	-

The obtained Krafft temperature for SDS was somewhat lower than the reported value in the literature (14-15 °C) [22,23]. The Krafft temperature increased when salt was present in the solutions as mentioned in the literature [5]. As can be seen in Table 4, the Krafft temperature of SDBS was more sensitive to salt content than that of SDS which can be due to the presence of one aromatic ring in its chemical structure. However, the Krafft temperature measurement was not performed for SDBS at 50g/l of NaCl.

The CMC values of Berol 535 were also determined at higher temperatures. The CMC values were decreased by increasing the temperature as nonionic surfactant becomes more hydrophobic due to a conformational change in the ethylene oxide groups from a large to a low dipole moment [5]. However, since the cloud point of this surfactant was around 28 °C, the obtained results could not be trusted and considered as the true values and we preferred not to report them here.

The effect of salt concentration on cloud point of Berol 535 and IGEPAL CO-630 was shown in Figure 4.1.

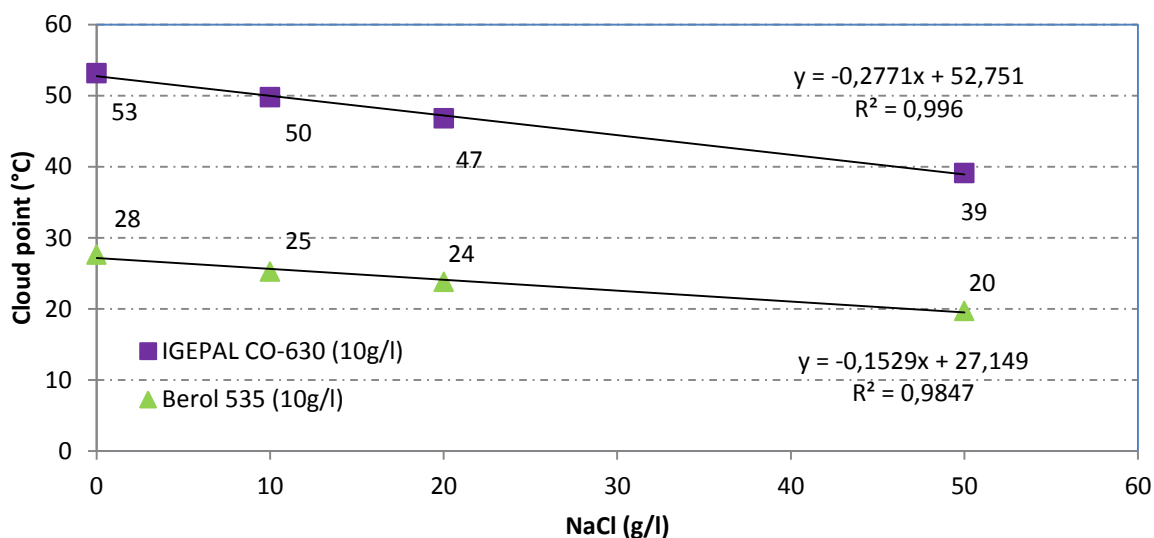


Figure 4.1 The effect of salt concentration on the cloud point of two nonionic surfactants

The obtained cloud points of Berol 535 (28 °C) and IGEPAL CO-630 (53°C), were in good agreement with the reported value in the literature [16,17]. As shown in Figure 4.1, the cloud point of Berol 535 was much lower than the cloud point of IGEPAL CO-630. This was consistent with the polyoxyethylene chain length in Berol 535 (~5) and in IGEPAL CO-630 (~9). As mentioned in the background, a longer polyoxyethylene chain means a higher cloud point. The addition of salt to the solutions depressed the cloud point in a linear fashion which was also illustrated in Figure 4.1. IGEPAL CO-630 was more sensitive to salt (almost twice as sensitive as Berol 535). This might also have to do with the polyoxyethylene chain length.

## 4.2 Excess amount of dye

The effect of dye initial concentration on solubilization of Sudan I in the presence of DTAB was shown in Figure 4.2. The onset of solubilization of dye was at CMC of the surfactant and this clearly showed that surfactant micelles were responsible for dye solubilization. When the initial dye concentration was as low as 0.01 g/l, the solubilized amount of dye in surfactant micelles reached to a plateau at surfactant concentration above the CMC. By increasing the dye initial concentration the solubilization curve became more linear after CMC. Therefore, the dye initial concentration greater than 0.4 g/l of Sudan I can be considered as excess amount of dye. This value for Quinizarin was also determined and it was 0.02 g/l. Obviously, Sudan I had higher solubilization in surfactant micelles than that of Quinizarin which can be explained by their different chemical structures.



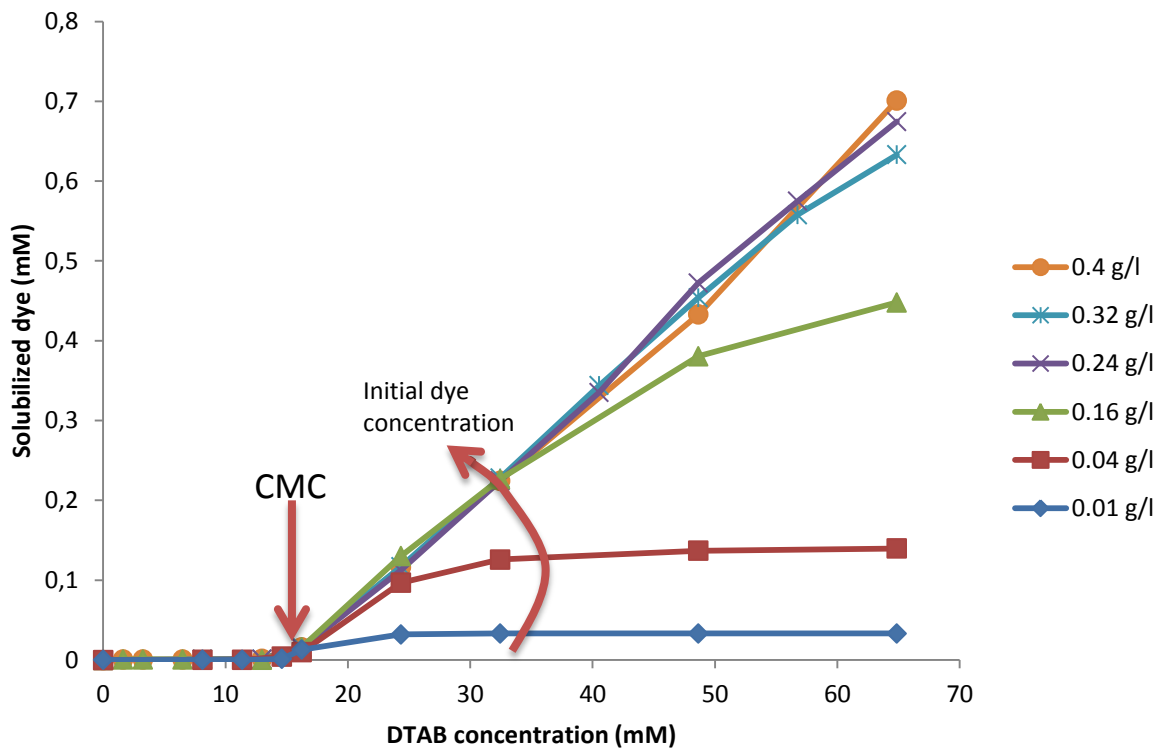


Figure 4.2 Amount of solubilized dye as a function of DTAB concentration when the initial dye concentration is increasing (Sudan I)

### 4.3 Solubilization power

The effect of surfactant concentration on solubilization of Sudan I and Quinizarin was determined for different surfactants. The solubilization curves have been provided for Sudan I and Quinizarin in Figures 4.3 and 4.4, respectively. For industrial application, expressing the surfactant concentration in g/l would be more relevant for comparison. Therefore, the same solubilization curves vs. g/l of surfactants have also been provided in Figures 4.5 and 4.6. The solubilization power ( $S_e$ ) and the regression coefficient ( $R^2$ ) of both dyes for all the surfactants were summarized in Table 5.

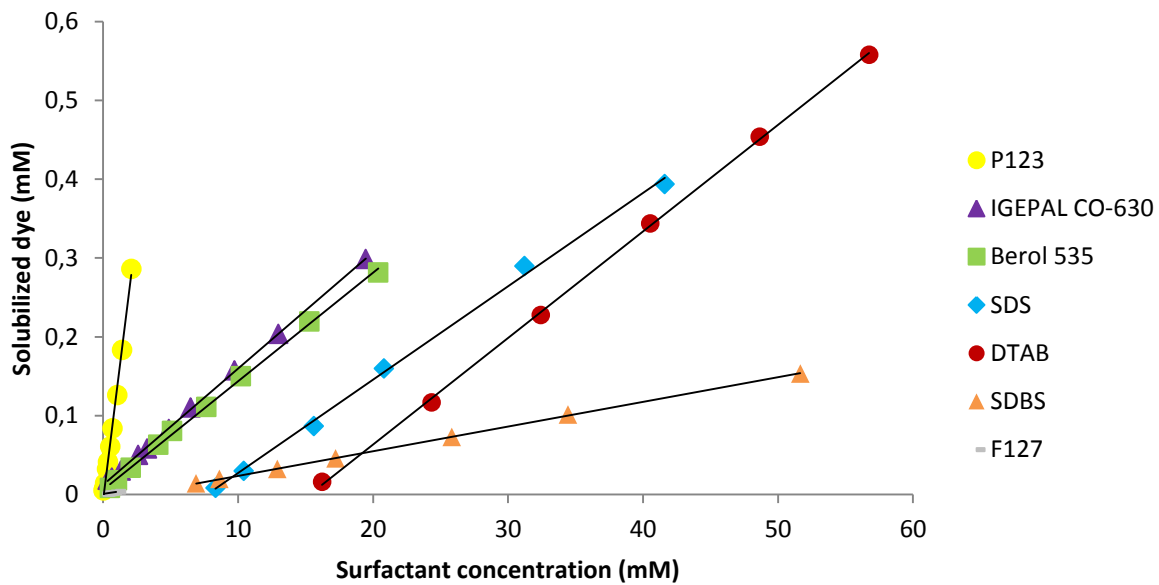


Figure 4.3 Solubility of Sudan I as a function of surfactant concentration.

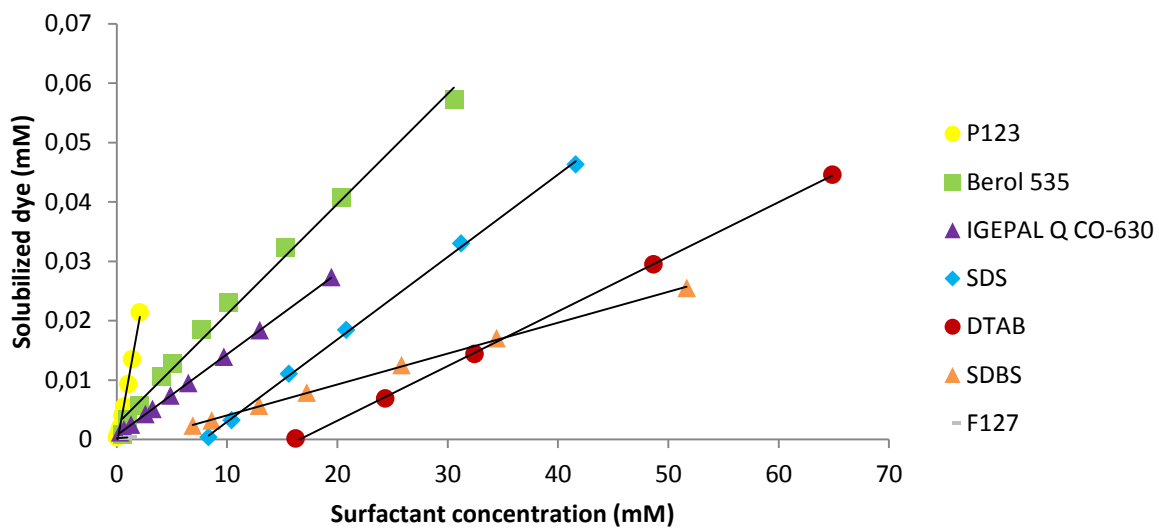


Figure 4.4 Solubility of Quinizarin as a function of surfactant concentration.

Table 5. Solubilization power of the dyes in the surfactant micelles

Surfactant	Solubilization power Sudan I		Solubilization power Quinizarin	
	$S_e$	$R^2$	$S_e$	$R^2$
Berol 535	0.0138	0.9987	0.0019	0.9926
DTAB	0.0135	0.9996	0.0009	0.9997
IGEPAL CO-630	0.0148	0.9998	0.0014	1
SDBS	0.0031	0.9998	0.0005	0.9995
SDS	0.0118	0.9977	0.0014	0.9993
Pluronic F127	0.0028	0.9912	0.0002	0.8082
Pluronic P123	0.1363	0.9963	0.0103	0.9917

The results showed that the solubility of the dyes increased with the surfactant concentration regardless of the surfactant type. The onset of solubilization of the dyes was around the CMC of each surfactant, as previously mentioned in the background. This was due to micelle formation and the accommodation of dye molecules within these micelles [4].

Table 5 showed that the solubilization power depended on both surfactant and dye chemical structures. The solubilization power of the different surfactants for Sudan I was at least 6 times higher than those values for Quinizarin. In other words, Sudan I can be accommodated in the surfactant micelles better. In a previous study, it was shown that the amount of solubilized dye decreased with the size of the dye molecule [14]. In this study, however, the dye with almost the same molecular weight showed completely different results. In this respects, the dye structure with higher flexibility for accommodating in the surfactant micelles would be solubilized more. Sudan I with an azo structure can rotate around the azo bond and has more conformational freedom than Quinizarin with its anthraquinone structure [30].

For Sudan I, the solubilization power increased in the order: Pluronic F127 < SDBS < SDS < DTAB < Berol 535 < IGEPAL CO-630 < Pluronic P123, whereas for Quinizarin it increased in the order of: Pluronic F127 < SDBS < DTAB < SDS = IGEPAL CO-630 < Berol 535 < Pluronic P123. The higher solubilization power of the nonionic surfactants (Berol 535 and IGEPAL CO-630) was not only a consequence of the interaction between the dyes and micelles, but also the fraction of surfactant in micellar form. At a specific concentration, the nonionic surfactants have a higher molar fraction in micellar form compared to ionic surfactants, due to their much lower CMC [31].

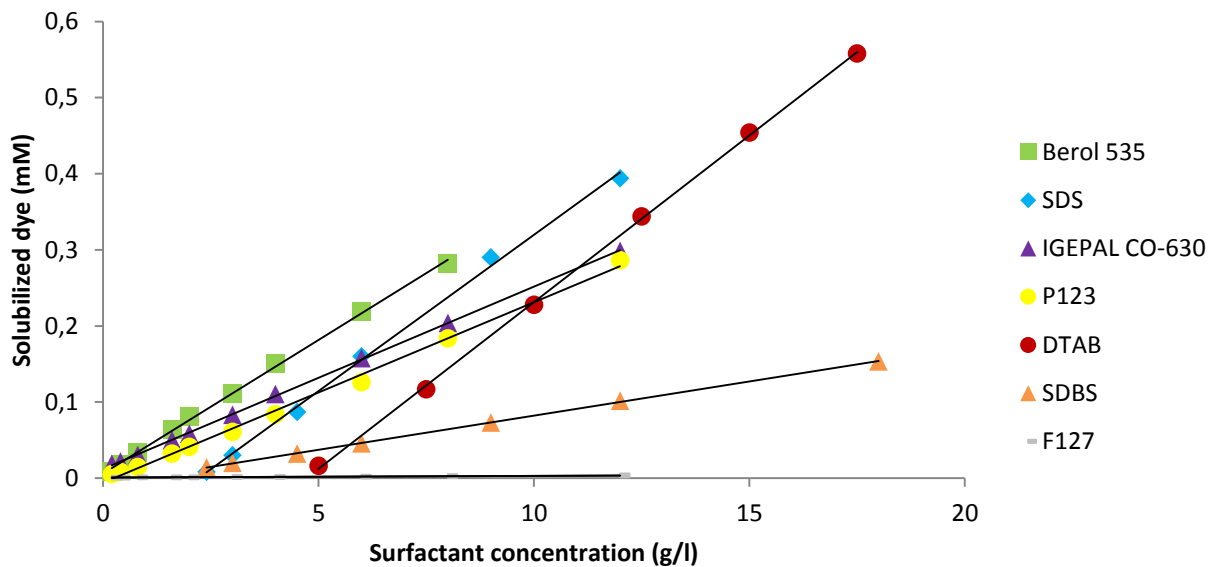


Figure 4.5 Amount of solubilized dye as a function of surfactant concentration (g/l) (Sudan I)

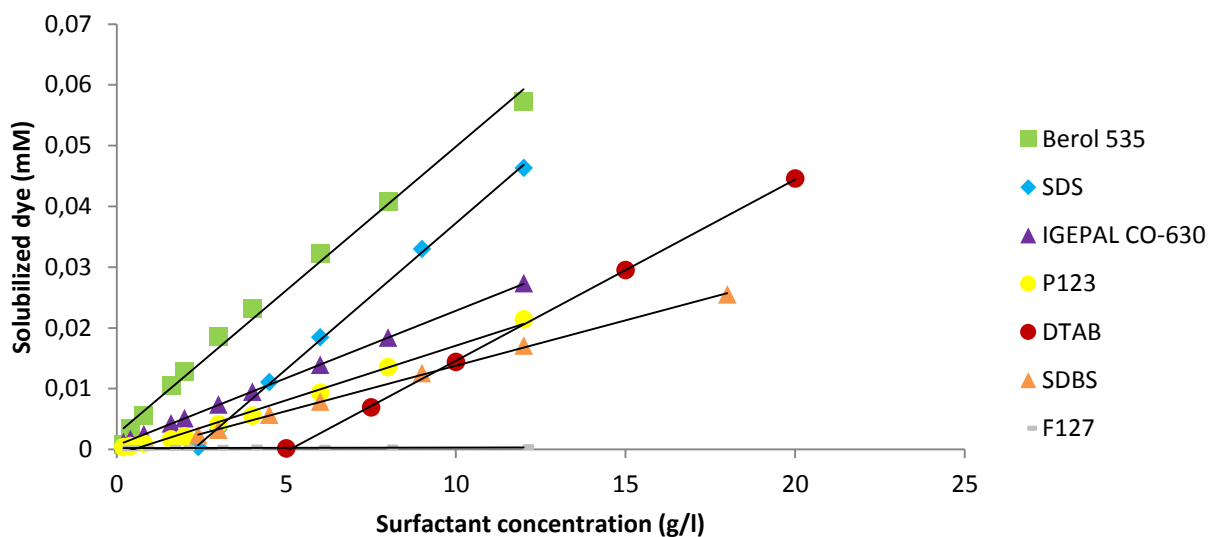


Figure 4.6 Amount of solubilized dye as a function of surfactant concentration (g/l) (Quinizarin)

Both polymeric surfactants (Pluronic P123 and F127) have very high molecular weights and therefore, there would be a big difference if solubilization power would be expressed as the solubilized dye per g/l of surfactant (Compare Figure 4.3 with 4.5 and Figure 4.4 with 4.6). In this respect, normal ionic or nonionic surfactants would have a better solubilization power.

#### 4.4 Temperature effect

The effect of temperature on dye solubilization can be seen in Figures 4.7-4.10. The amount of solubilized dye as a function of temperature showed a constant increase and nonionic surfactants (Berol 535 and IGEPAL CO-630) were affected more than other ionic surfactants. For ionic surfactants, the amount of solubilized dye was raised with the temperature basically because of an increased thermal agitation which increases the available space for solubilization in the micelle [1]. The ethylene oxide (EO) units of nonionic surfactants were dehydrated with the temperature. The area of the hydrophilic head groups is consequently decreased leading to a higher CPP. The nonionic micelles are probably getting bigger and can accommodate more dye [32]. However, the amount of solubilized dye for IGEPAL CO-630 was higher than Berol 535 at 75 °C as can be seen in Figure 4.8 and Figure 4.10. This showed that Berol 535 had almost reached its precipitation point and its solubility would then decrease to a great extent. Therefore, there would be a deviation in solubilization rate at high temperatures for nonionic surfactants with shorter polyoxyethylene chain length.

The effect of temperature on solubilization of mixture of surfactants (DTAB 50:50 Berol 535 and SDS 50:50 Berol 535) also showed the same trend.

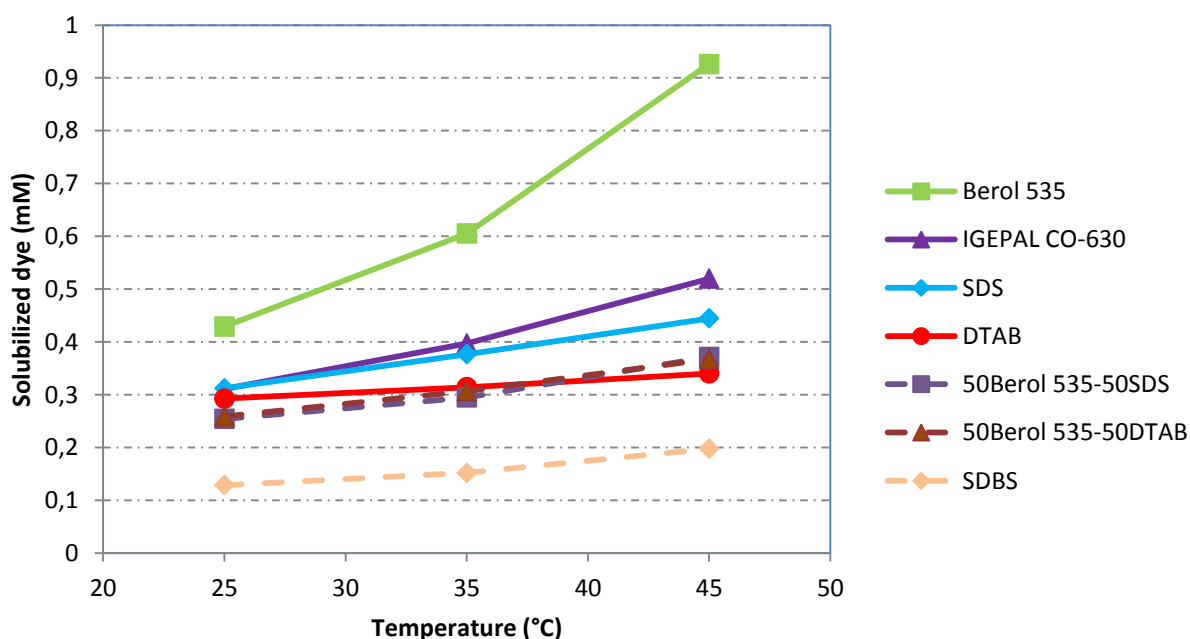


Figure 4.7 The amount of solubilized dye (Sudan I) as a function of temperature (25-45 °C) for all surfactants

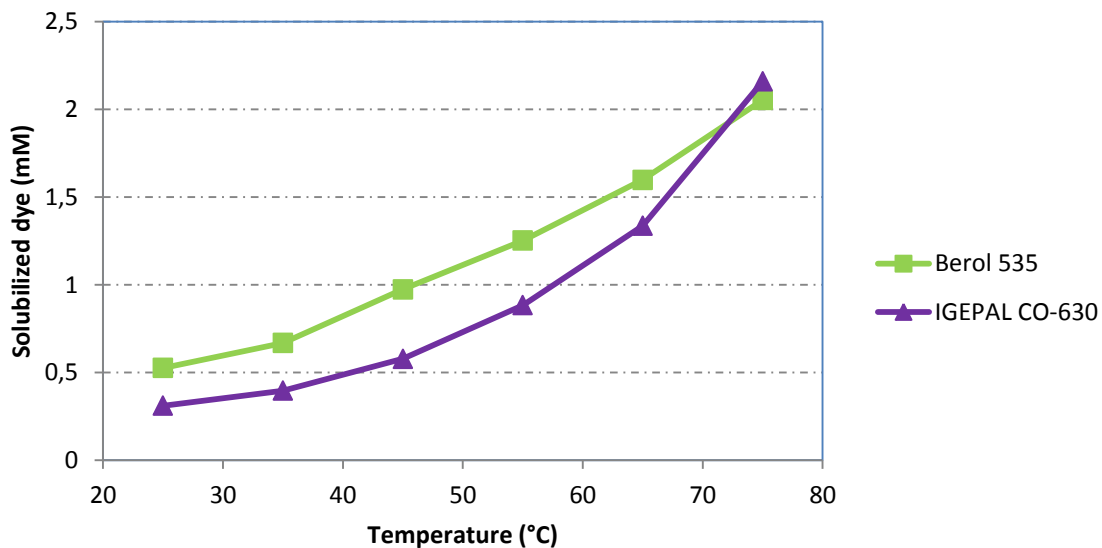


Figure 4.8 The amount of solubilized dye (Sudan I) as a function of temperature (25-75 °C) for nonionic surfactants

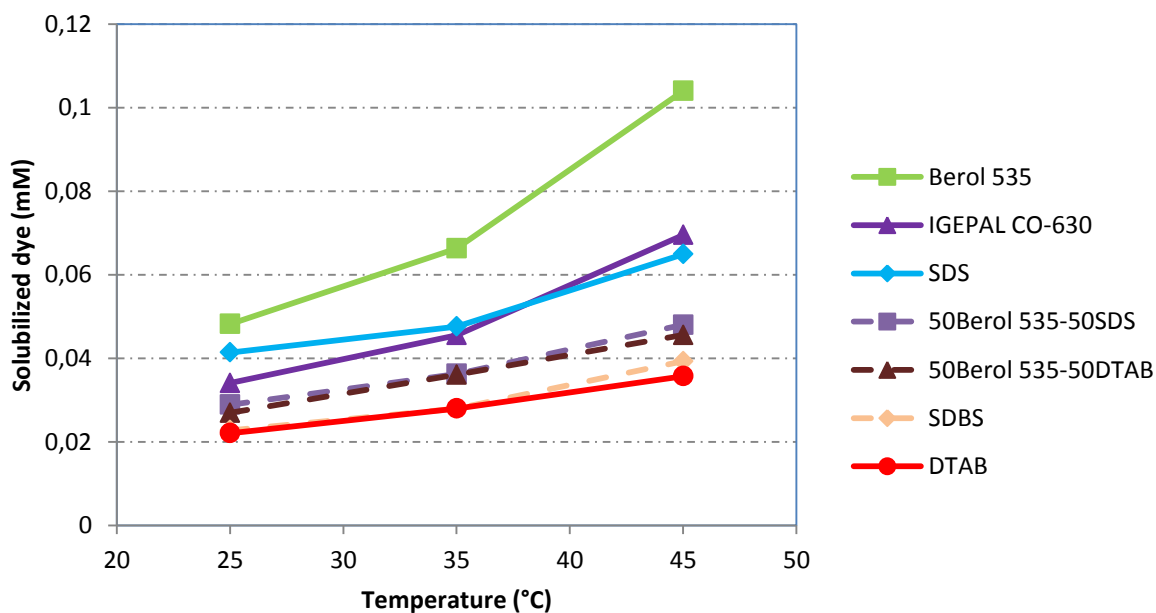


Figure 4.9 The amount of solubilized dye (Quinizarin) as a function of temperature (25-45 °C) for all surfactants

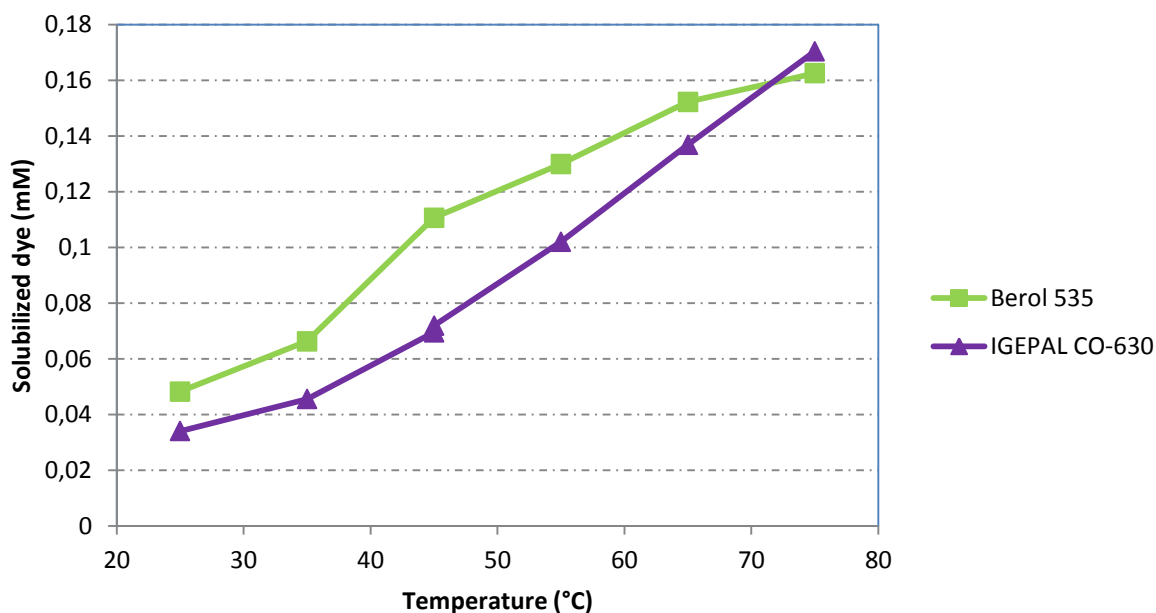


Figure 4.10 The amount of solubilized dye (Quinizarin) as a function of temperature (25-75 °C) for nonionic surfactants

#### 4.5 Kinetics

The kinetic of solubilization at room temperature has been shown for Sudan I and Quinizarin in Figure 4.11 and Figure 4.12, respectively. The rate of solubilization of both dyes in the presence of DTAB, SDS and Berol 535 was very fast and the solubilization reached to its maximum value at around 8 h for DTAB and Berol 535. However, the time 23h was considered as an equilibrium point for all three surfactants.

The amount of solubilized dye in Figure 4.11 is in agreement with Figure 4.5 for the different surfactant solutions. In case of solubilization of Quinizarin (Figure 4.12), the solubilized amount of dye in Berol 535 micellar solution was slightly less than the results of the previous experiments (see, Figure 4.6).

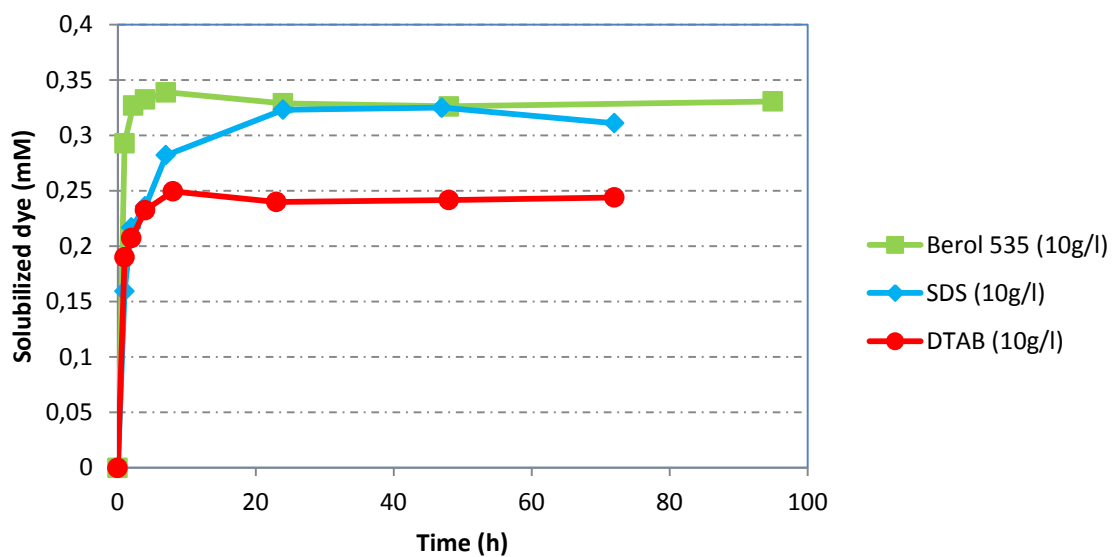


Figure 4.11 The amount of solubilized dye as a function of time (Sudan I)

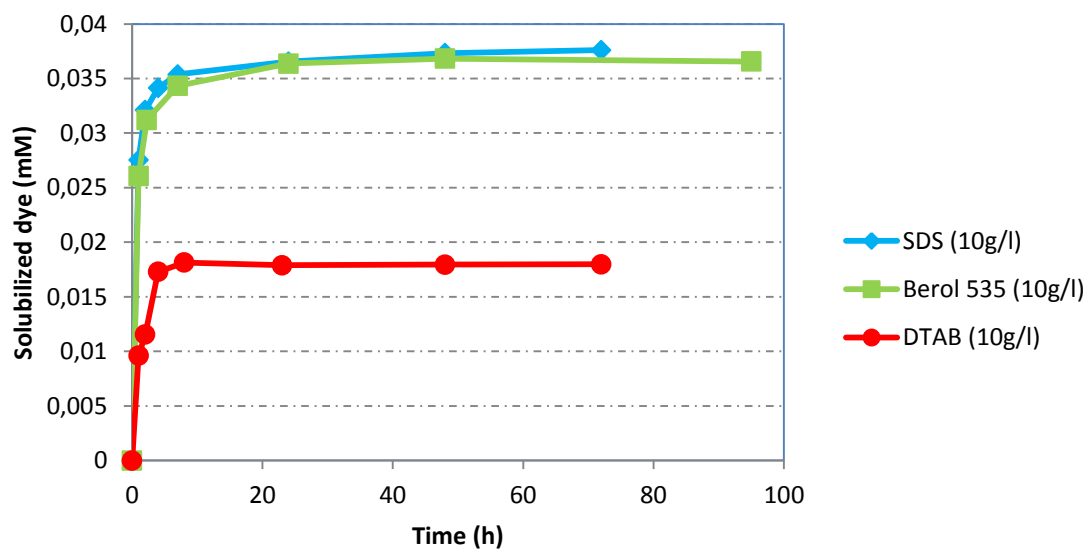


Figure 4.12 The amount of solubilized dye as a function of time (Quinizarin)

#### 4.6 Solubilization in mixed micelles

The solubilization of the mixture of surfactants in the presence and absence of salt (NaCl) and a hydrotrope (PGPE) has been investigated in this section.



#### 4.6.1 The binary mixture of Berol 535 and DTAB

The solubilization of Sudan I and Quinizarin in the binary mixture of Berol 535 and DTAB were illustrated in Figure 4.13 and Figure 4.14, respectively. The effect of addition of NaCl at different concentrations was also presented in these figures.

There is usually a synergy effect for the CMC of surfactant mixtures (mixture of nonionic and ionic surfactant) [5]. However, no synergy effect in solubilization for any of the mixtures was observed. As shown in Figure 4.13, the addition of PGPE (10 g/l) to the mixture had almost no effect at all for Sudan I, even though PGPE is a hydrotrope (substance that improve the solubility, without having any significant surface activity) [4]. Adding salt on the other hand, made a big impact on the amount of solubilized dye. As mentioned in the background, by adding salt, the electrostatic repulsion between the ionic head groups decreases (acts as counter ions). This means that the CPP increases and we can get elongated and bigger micelles that can accommodate more dye. The CMC also drops, which means that more micelles will be presented in the solution. More micelles usually improve the solubilization [5]. It was a relatively big difference in amount of solubilized dye for the DTAB solution and DTAB + NaCl (10 g/l) solution. However, by adding even more salt, the effect was not as dramatic. By adding more salt, the ionic surfactant might start to precipitate in the system. Further, salt was more effective, the higher the composition of DTAB was in the solution. This was expected, since addition of salt to a nonionic surfactant, e.g. Berol 535, had only a negligible effect on amount of solubilized dye while the solubilization in the presence of an ionic surfactant like DTAB was more sensitive to addition of salt.

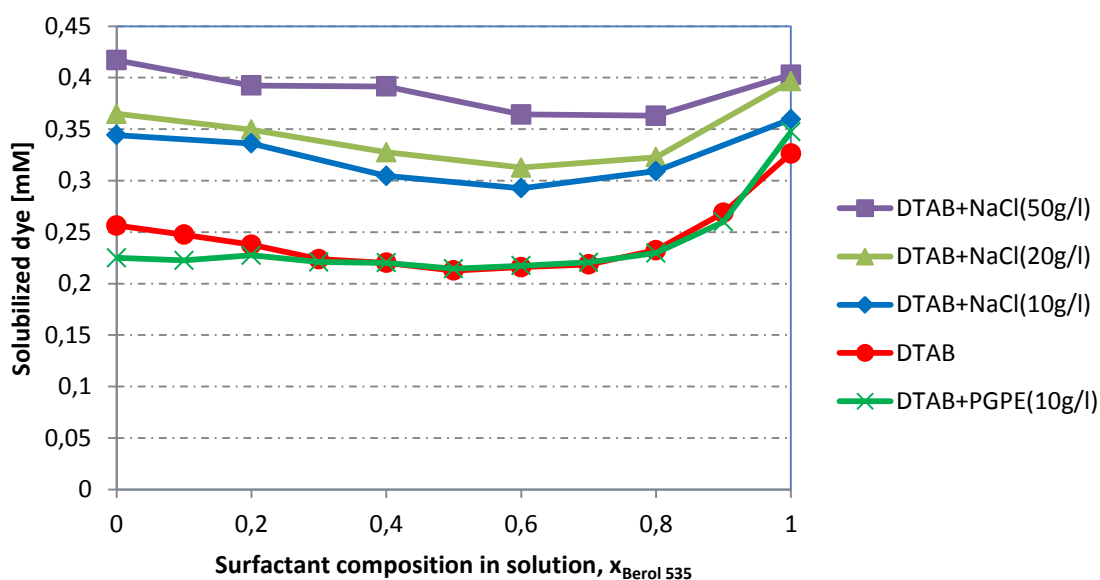


Figure 4.13 The amount of solubilized dye (Sudan I) as a function of surfactant composition

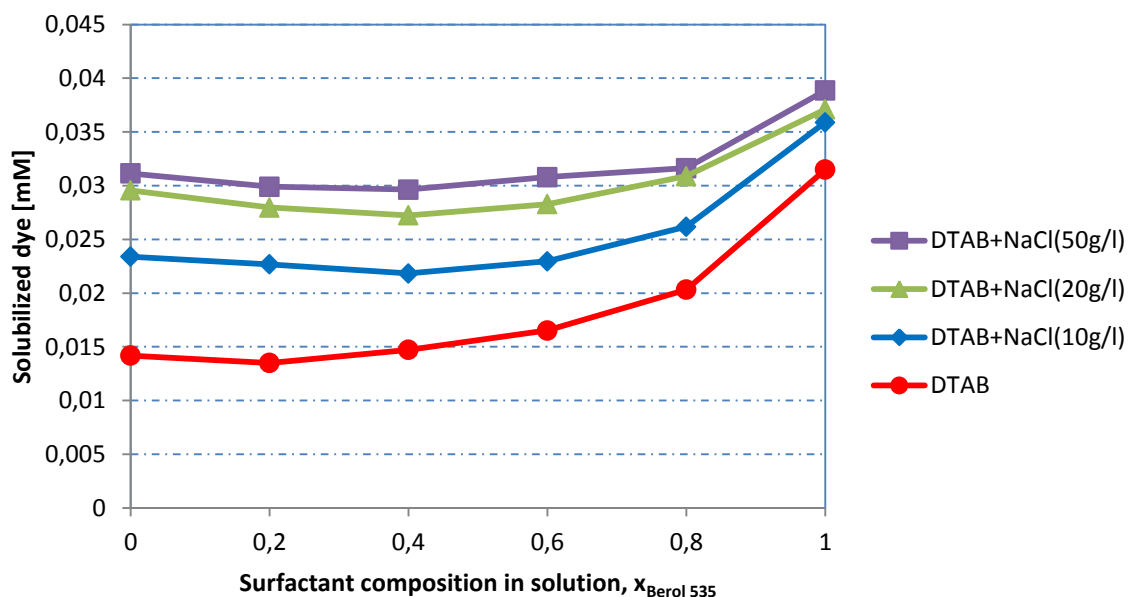


Figure 4.14 The amount of solubilized dye (Quinizarin) as a function of surfactant composition

#### 4.6.2 The binary mixture of Berol 535 and SDS

The solubilization of Sudan I and Quinizarin in the binary mixture of Berol 535 and SDS were illustrated in Figure 4.15 and Figure 4.16, respectively. The effect of addition of NaCl at different concentrations was also presented in these figures. The same trend as solubilization of these dyes in the presence of DTAB was observed. There was not any synergy effect and the solubilization increased by addition of salt. However, SDS was more sensitive to addition of salt and its Krafft temperature was also increased to above the room temperature (see Table 4). Thus, the low amount of solubilized dye for SDS at 20 and 50 g/l salt was due to the high Krafft temperature of the SDS solutions. By adding salt to SDS solution, SDS started to precipitate and the amount of solubilized dye decreased to a high extent. For the Krafft temperature of the SDS with 20 g/l salt solution was around room temperature and since precipitation is a slow process, especially at room temp, the amount of solubilized dye dropped over time. The results also show that in a binary mixture of SDS and Berol 535, even addition of low amount of a nonionic surfactant increased the solubility of anionic surfactant even in the presence of high salt content (50g/l) and no precipitation can be observed in the system. Although, there was not any synergy effect on binary mixture of surfactants, surfactants cooperatively solubilized the dye molecules in mixed micelles and the Krafft temperature of the system was lowered and solubility of both surfactants in the system was increased.

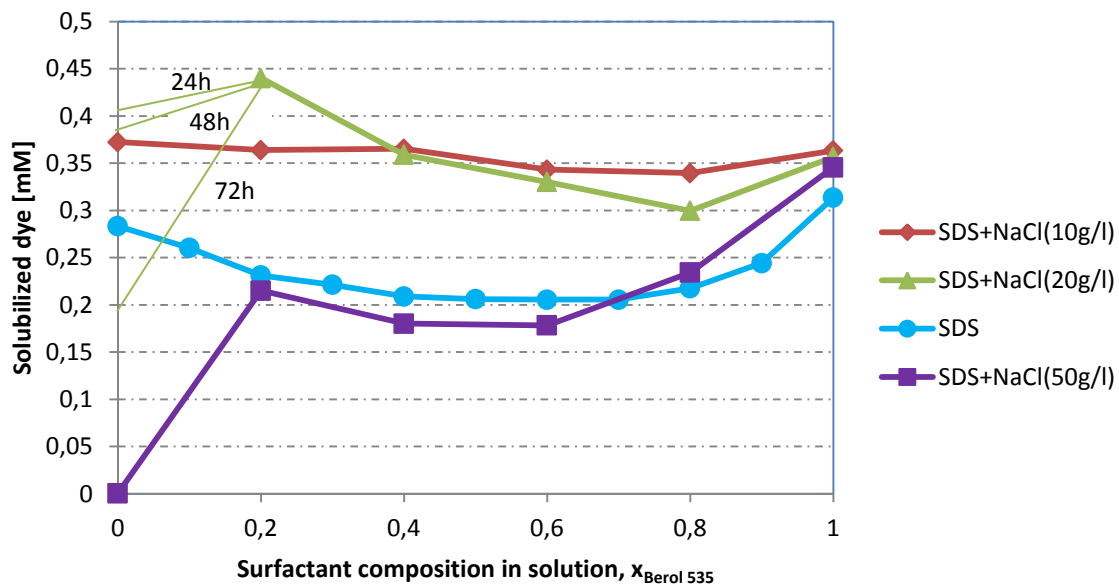


Figure 4.15 The amount of solubilized dye (Sudan I) as a function of surfactant composition

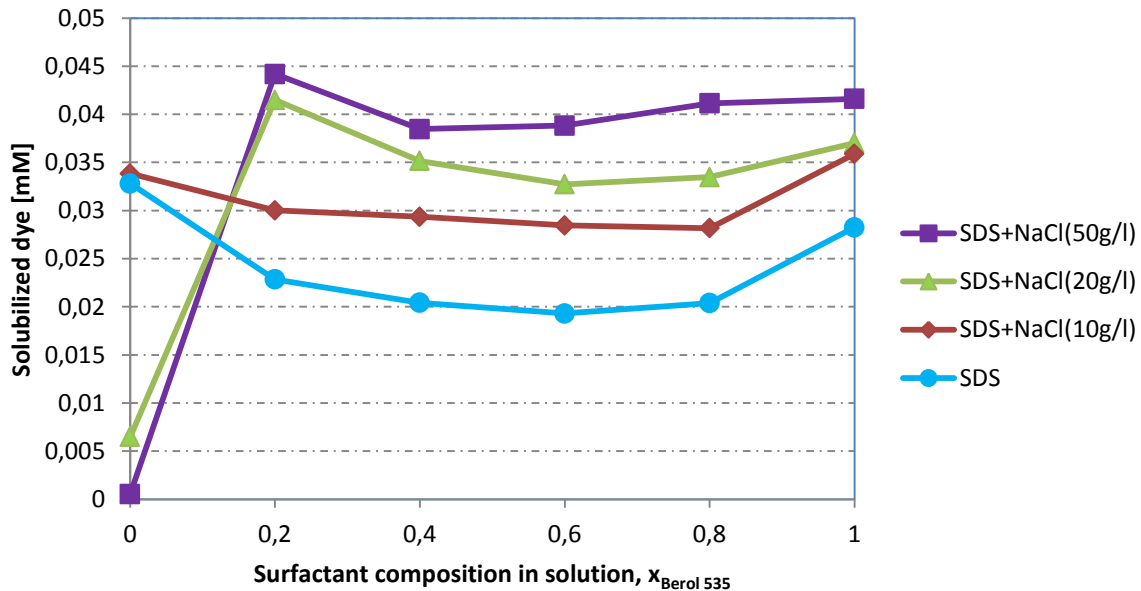


Figure 4.16 The amount of solubilized dye (Quinizarin) as a function of surfactant composition

### 4.6.3 Mixing Berol 535 with SDBS

A synergy effect for the solubilization has been reported when the anionic surfactant had a benzene ring between the ionic head group and hydrophobic tail (e.g. SDBS) and when a nonionic surfactant with a long ethylene oxide chain was used (at least 15 EO) [33,34]. Thus, SDBS was mixed with Berol 535 to see if there is any synergy effect in solubilization of Sudan I and Quinizarin. The results were illustrated in Figure 4.17 and Figure 4.18. As shown in Figure 4.17 and Figure 4.18, there was again no synergy effect for the solubilization when SDBS was used. Hence, no further experiments with SDBS were conducted and we concluded that the synergistic effect in solubilization of materials was also dependent to the structure of solubilisate (dyes).

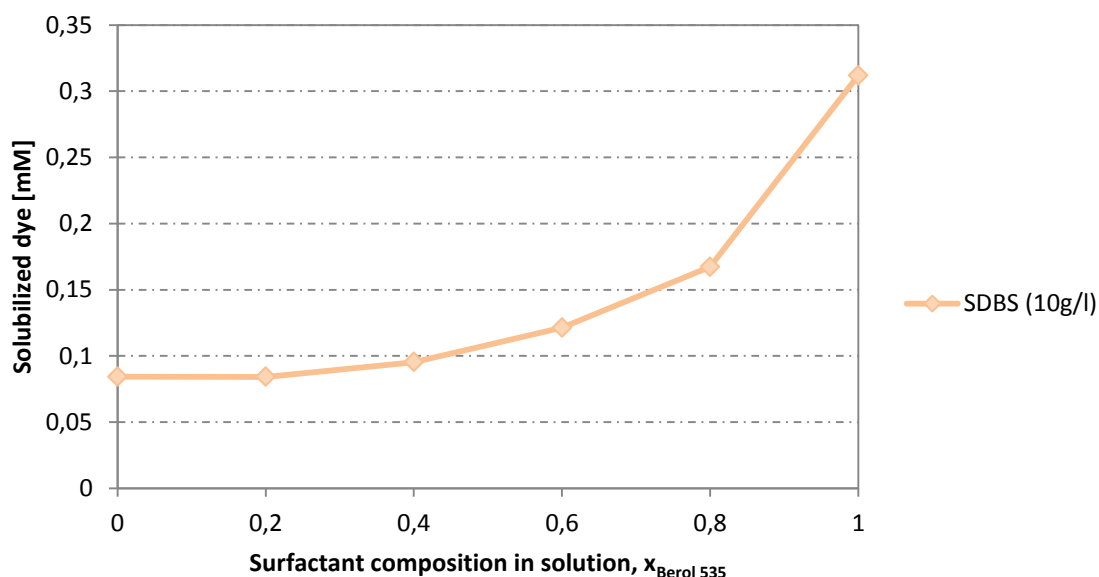


Figure 4.17 The amount of solubilized dye (Sudan I) as a function of surfactant composition

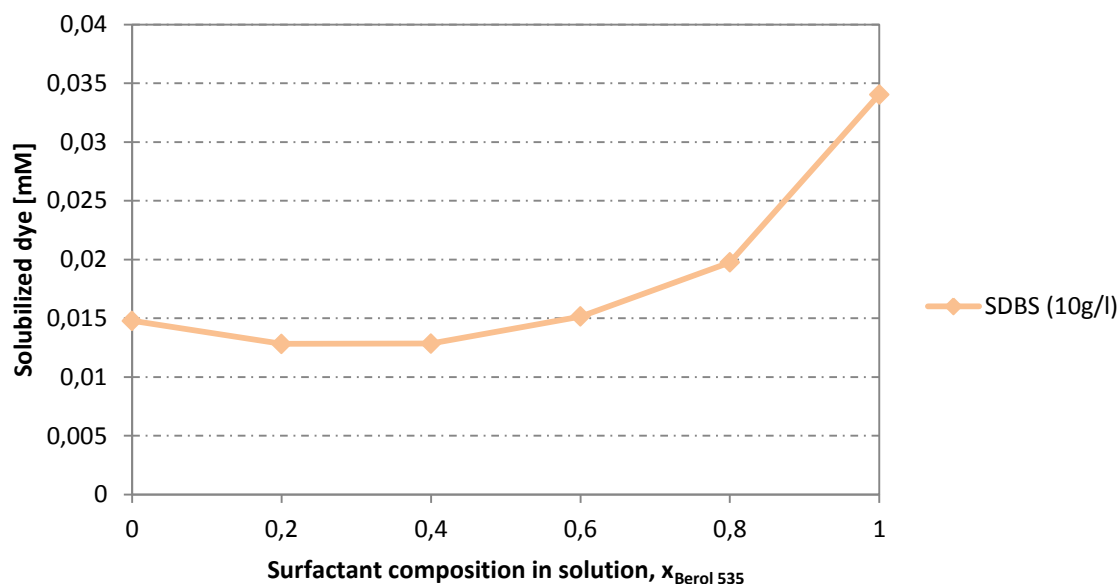


Figure 4.18 The amount of solubilized dye (Quinizarin) as a function of surfactant composition

#### 4.7 Location of dye in micelle

For understanding the location dye in the surfactant micelles, the UV-Vis absorption spectra of dyes in surfactants micelles and in solvents with different polarity were recorded and compared. The dyes have a similar surrounding as the hydrophobic inner core of the micelles when the dyes are dissolved in non-polar solvents (solvents with a low polarity index). If they are instead dissolved in more polar solvents (solvents with a higher polarity index), that simulates the surrounding of the semi-polar outer part of the micelles [14]. So by comparing the shapes of the spectra for Sudan I and Quinizarin in the different solvents with the surfactant solutions, the location is determined. The polarity indexes for the solvents are listed in Table 6. The spectra for Sudan I and Quinizarin in solvents and surfactant solutions were shown in Figure 4.19 and Figure 4.20.

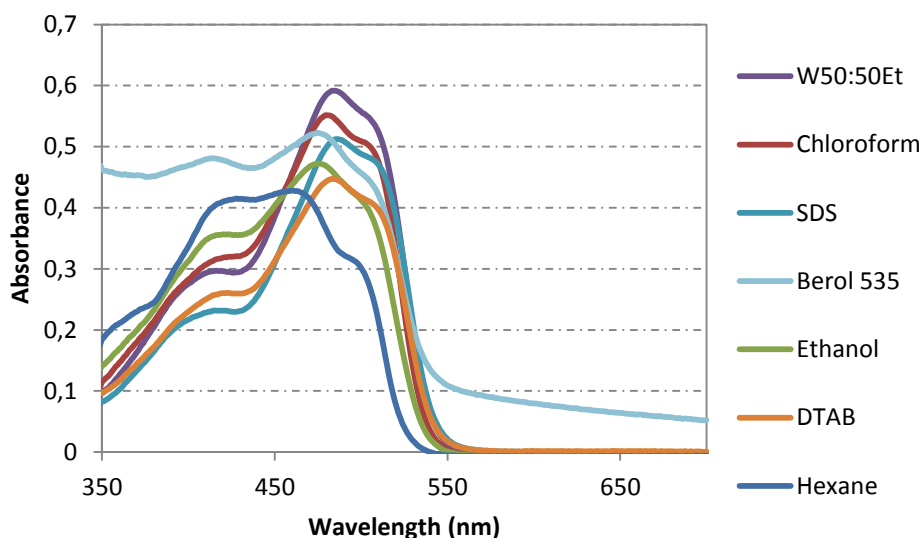


Figure 4.19 Absorption spectra for Sudan I in different solvents and surfactant solutions

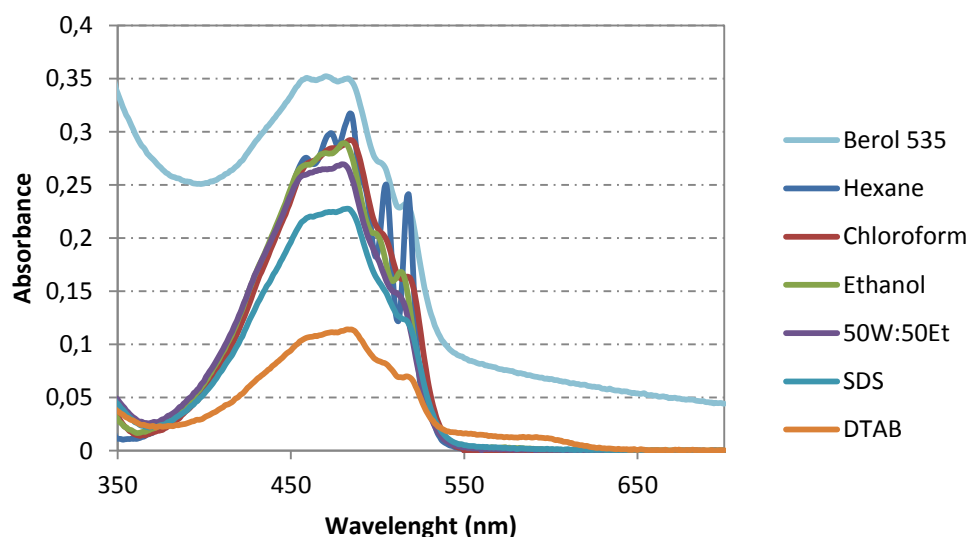


Figure 4.20 Absorption spectra for Quinizarin in different solvents and surfactant solutions

The spectrum of both dyes in DTAB and SDS was very similar to that of 50% aqueous ethanol, indicating that dyes are located in a relatively polar media. Thus, they should have been located in the outer part, near the hydrophilic head groups of the micelles. The dye spectrum in the presence of Berol 535 looked quite different from other surfactant solutions as Berol solution was turbid at room temperature and could not be used for comparison.

The wavelength of maximum absorption,  $\lambda_{\max}$ , for Sudan I and Quinizarin in the different solvents and aqueous surfactant solutions together with their polarity indexes were listed in Table 6.

Table 6. The wavelength of maximum absorption ( $\lambda_{max}$ ) for Sudan I and Quinizarin in different solvents and aqueous surfactant solutions

	$\lambda_{max}$ for Sudan I (nm)	$\lambda_{max}$ for Quinizarin (nm)	Polarity index [35]
Hexane	460-462	483-484	0
Cyclohexane		484	0.2
Toluene	476	483	2.4
Diethyl ether	466-468	479	2.8
Dichloromethane	477-478	481	3.1
Chloroform	480-483	483-484	4.1
Acetone	470-472	475	5.1
Methanol		477	5.1
Ethanol	476-478	479-481	5.2
Ethanol50:50Water	484-486	478-480	
Berol 535	475-478	470	
DTAB	484-486	483	
SDS	486-488	483	

#### 4.8 pH-effect

The effect of pH on solubilization of dyes was shown in Figure 4.21 and Figure 4.22. There was not a noticeable change in the absorption of dye-surfactant solution at different pH, except for DTAB. The absorbance of the dye solutions in the presence of the cationic surfactant (DTAB) was increased to a great extent at pH greater than 8.

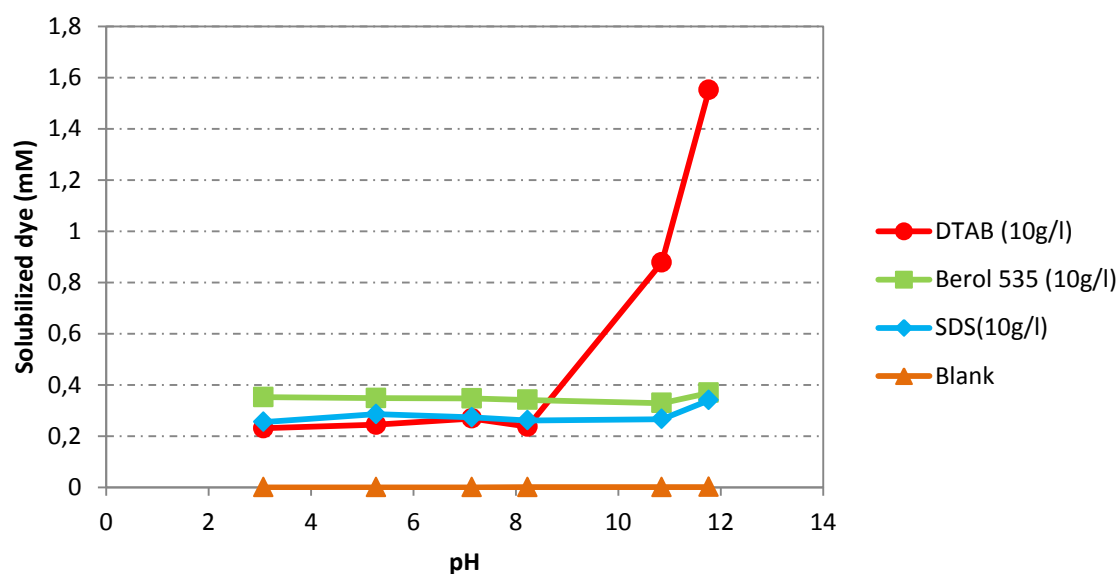


Figure 4.21 The amount of solubilized dye (Sudan I) as a function of pH

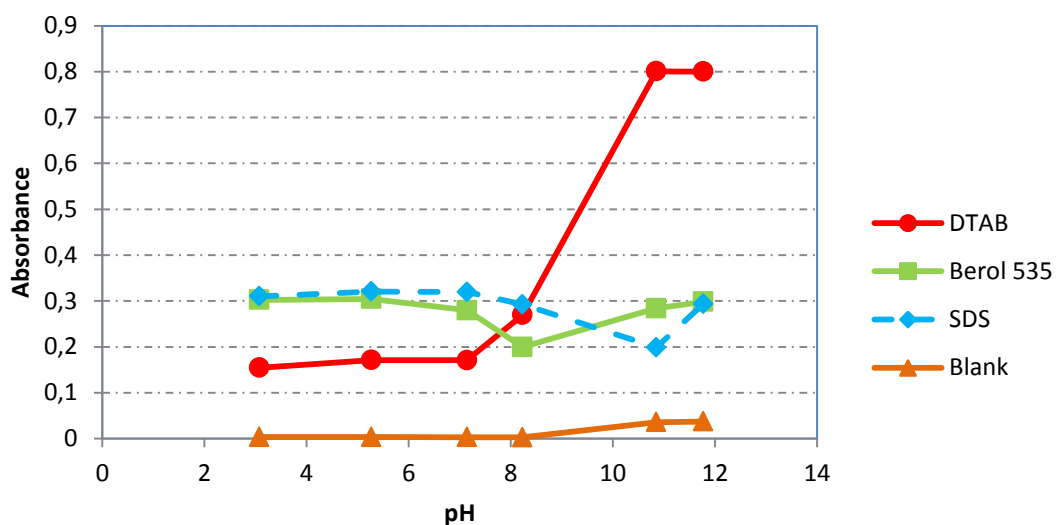


Figure 4.22 The absorbance as a function of pH (Quinizarin)

This change in absorbance of the solution was at the same  $\lambda_{\max}$  for Sudan I (Figure 4.23), while the change in both absorbance and  $\lambda_{\max}$  was observed for Quinizarin (Figure 4.24). Therefore, the calibration curve in 50 wt.% ethanol:water could not be used for determining the amount of solubilized Quinizarin at pH>8. It should be noted that the  $\lambda_{\max}$  of Quinizarin solutions had a bathochromic shift (from 480 to 550 nm) in alkaline condition.

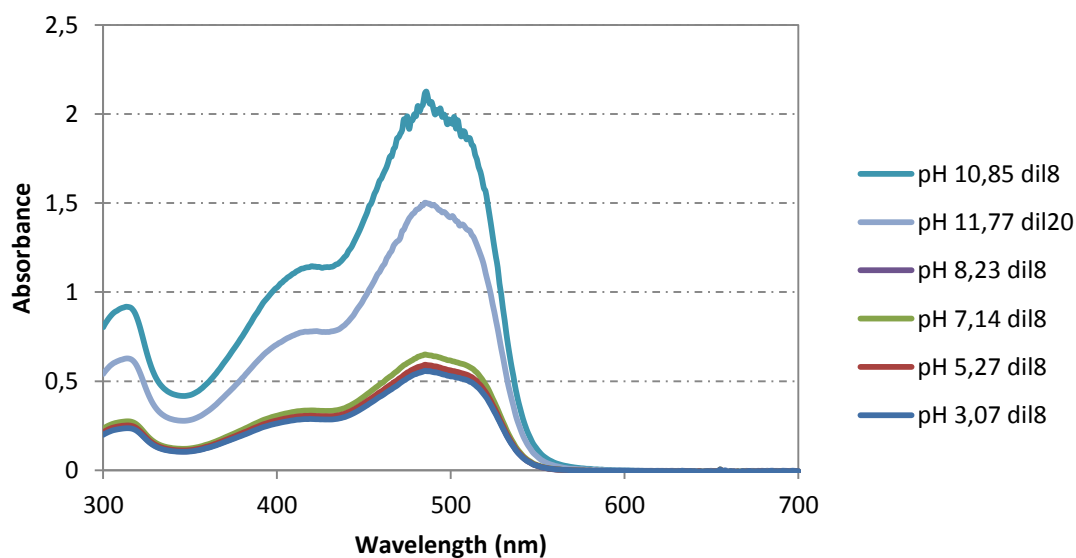


Figure 4.23 Absorption spectra of Sudan I when DTAB was used as surfactants



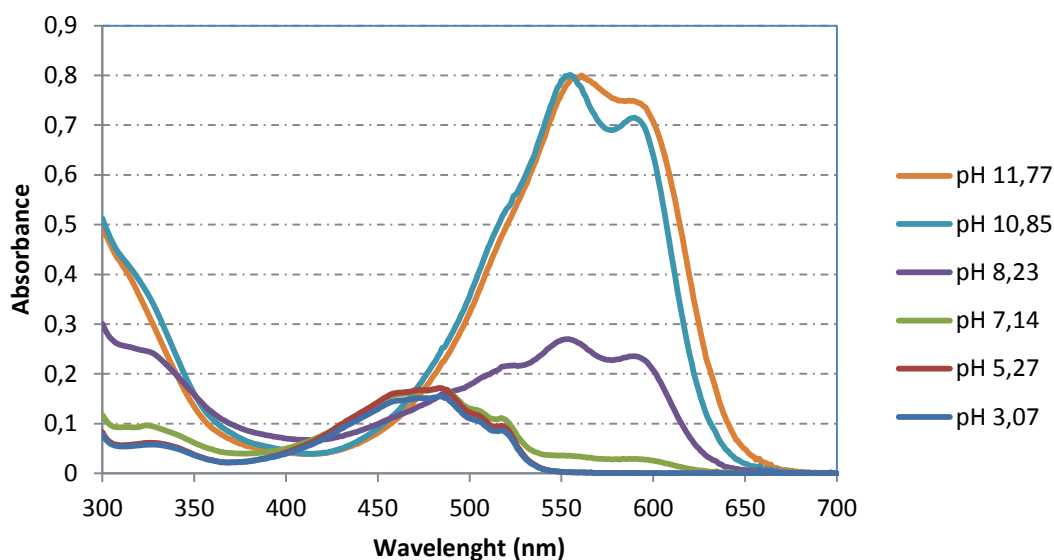


Figure 4.24 The bathochromic shift of Quinizarin when DTAB was used as surfactant

Photos from dye samples in glass vials showing the effect of pH on color change of Quinizarin (in the absence and presence of DTAB) were presented in Figure 4.25 and Figure 4.26. As can be seen here, there is a bathochromic shift for the Quinizarin solution even in the absence of any surfactant. The absorbance of light at wavelengths around 550-600 nm leads to the appearance of violet and blue to the eye, which can be seen in these figures.

The reason why such a bathochromic shift can be observed in Quinizarin solutions at  $\text{pH} > 8$  can be explained by dominating a new form of tautomers in the system. In alkaline condition, hydroxyl ions can polarize the  $-\text{OH}$  groups in Quinizarin and therefore a new form of tautomers is made which is more stable and soluble in water [36]. Quinizarin can be used as an optical pH sensor in alkaline conditions as it has been reported in another paper [12].

The fact that the change in absorbance of the Sudan I alkaline solution was at the same  $\lambda_{\text{max}}$  and it did not show any red or blue shift was another evidence that dye molecule is located inside micelles just below the surface and close to the surfactant head groups as it can sense the presence of alkaline condition. This needs further investigation.

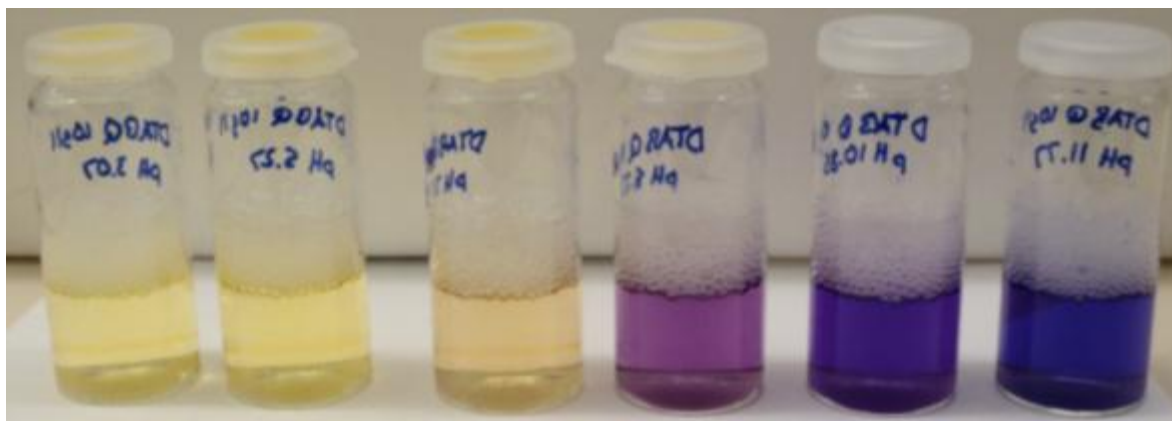


Figure 4.25 The effect of pH on color change of Quinizarin solution in the presence of DTAB. pH has been increased from left to right.

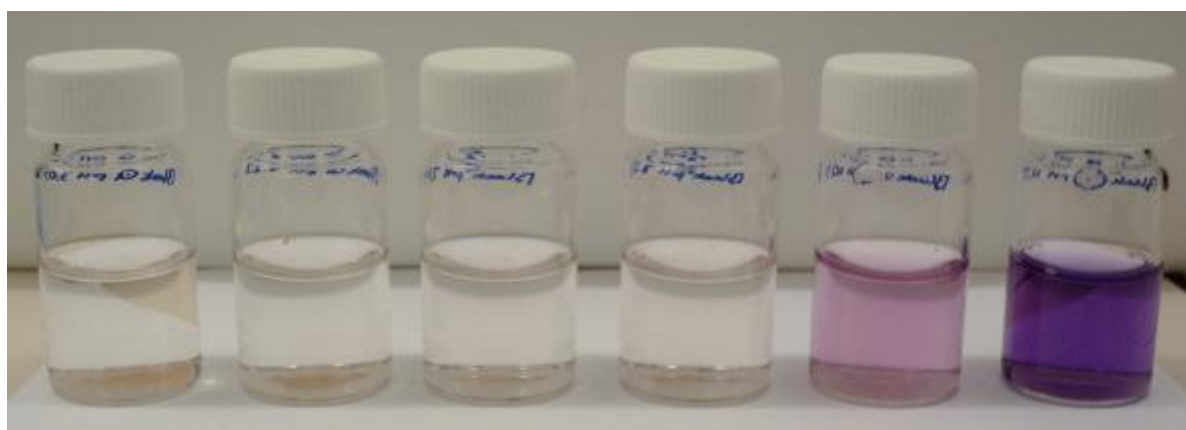


Figure 4.26 The effect of pH on color change of Quinizarin solution in the absence of any surfactant. pH has been increased from left to right.

#### 4.9 Electrolyte effect

The solubilization of dye in DTAB aqueous solution was studied by adding a small amount of different electrolytes (0.5 mM) to the solution Figure 4.27. The pH of the different solution was also listed in Table 7. The figure showed that the CMC of DTAB did not change so much by adding 0.5 mM of different electrolytes. However, the solubilization of Sudan I increased to some extent for a couple of electrolytes (NaOH and Na<sub>2</sub>CO<sub>3</sub> because of the increase in pH as previously mentioned). The addition of NaCl did not affect the solubilization, whereas the addition of NaI and NaSCN slightly decreased the solubilization of Sudan I. The addition of higher amounts of electrolytes (NaCl, NaI, NaSCN) would probably increase the solubilization as they cause micellar growth. This has been shown for NaCl in section 4.6.

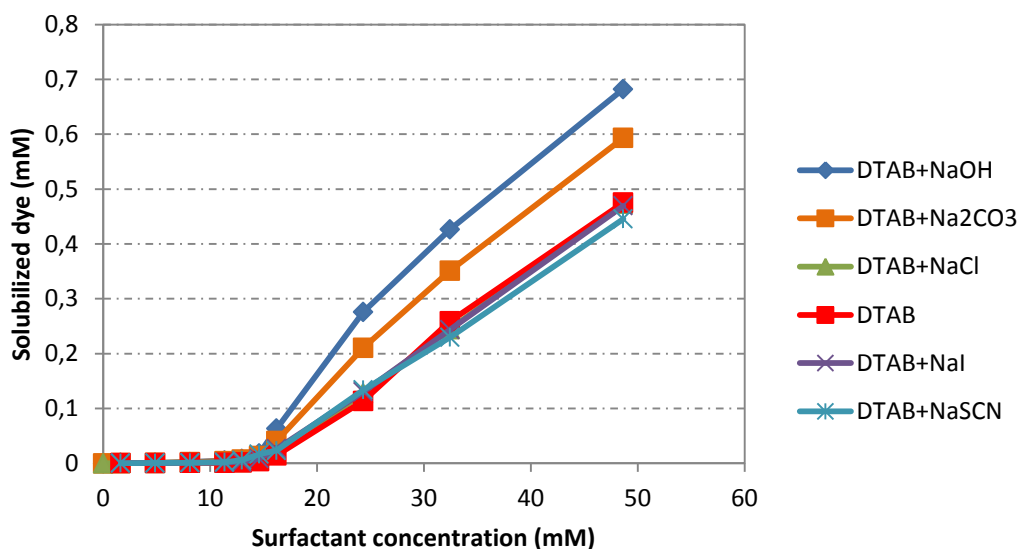


Figure 4.27 The amount of solubilized dye (Sudan I) as a function of surfactant concentration with added electrolytes (0.5 mM)

Table 7. pH of the DTAB solutions with added electrolytes (0.5 mM)

Solution	pH
DTAB+NaOH	9.69-9.91
DTAB+Na <sub>2</sub> CO <sub>3</sub>	9.57-9.86
DTAB+NaCl	7.82-7.91
DTAB+NaI	7.3-7.64
DTAB+NaSCN	7.3-7.36

The effect of addition of NaOH and Na<sub>2</sub>CO<sub>3</sub> on solubilization of Sudan I in the presence of DTAB (10g/l) was studied and the results were presented in Figure 4.28 and Figure 4.29. The amount of solubilized dye increased almost linearly by increasing the concentration of NaOH and Na<sub>2</sub>CO<sub>3</sub>. The slope of increment was much higher in case of NaOH. The only difference between Figure 4.28 and Figure 4.29 was that the later was the amount of solubilized dye vs. pH instead of electrolyte concentration. This figure showed that the higher amount of dye solubilization was related to both pH and the nature of electrolyte as there is a deviation in solubilization at the same pH between NaOH and Na<sub>2</sub>CO<sub>3</sub>.

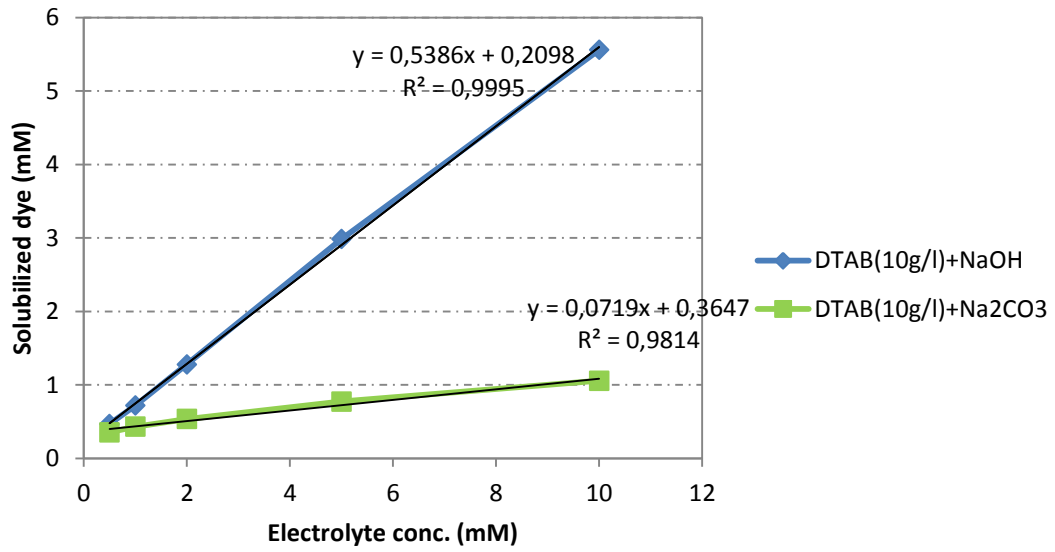


Figure 4.28 The amount of solubilized dye (Sudan I) as a function of electrolyte concentration (NaOH and Na<sub>2</sub>CO<sub>3</sub>)

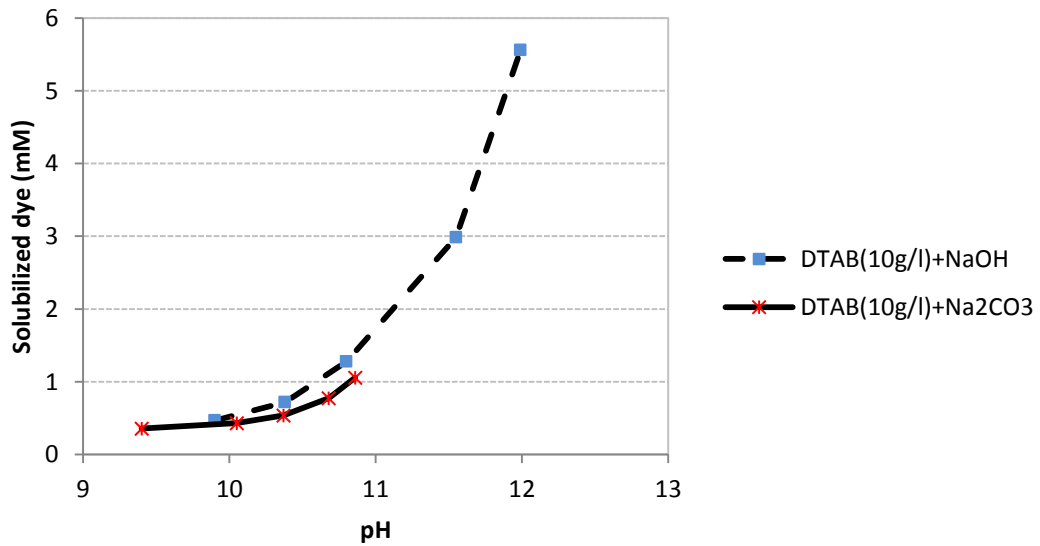


Figure 4.29 The amount of solubilized dye (Sudan I) as a function of pH

## 5. Conclusions

The conclusion remarks can be summarized as follows:

- The solubilization power,  $S_e$ , of Sudan I with azo structure in the presence of all surfactants was almost 6 times higher than that of Quinizarin. This showed the importance of the chemical structure of solubilisate in solubilization process.
- The polymeric surfactant Pluronic P123, and other conventional nonionic surfactants (IGEPAL CO-630 and Berol 535) showed the highest solubilization power (mol/mol) for both dyes (Sudan I and Quinizarin). Nonionic surfactants with low CMC values probably had larger micelle size and dye molecules were able to accommodate within their micelles better and more.
- The amount of solubilized dye in the micelles was increased by temperature. This was generally attributed to higher thermal agitation of dye molecules and easier accommodation in surfactant micelles. In case of nonionic surfactants, the hydrophobicity of surfactant molecules increases by increasing the temperature as their polyoxyethylene chains become less soluble at elevated temperatures.
- The binary mixture of surfactants (DTAB:Berol 535 and SDS:Berol 535) did not show any synergistic effect on solubilization of dyes.
- Addition of NaCl (10, 20 and 50 g/l) to the binary mixture of surfactants had generally a positive effect on the amount of solubilized dye. That was due to increasing the size of micelles (higher aggregation number) at high salt concentration. However, the addition of salt increased the Krafft temperature of ionic surfactant (SDS) and caused precipitation of surfactant at room temperature and, therefore, had a negative influence on dye solubilization which could be overcome by increasing the temperature of the system or addition of low amount of nonionic surfactants.
- The absorption spectra of both dyes in surfactant micelles were similar to that of 50% aqueous ethanol, indicating that dyes are located in a relatively polar media (palisade region of micelles).
- The solubilization of both dyes in the presence of cationic surfactant (DTAB) was increased at alkaline pH (>8). Other surfactants (anionic and nonionic) did not show any similar effect.

## 6. Future studies

For future work, it would be of interest to study the followings:

- The size and shape of surfactant micelles and mixed micelles in order to have a better understanding about the change in the shape and size of micelles by increasing the temperature and addition of electrolytes
- Further investigation of dye solubilization in cationic surfactant micelles in alkaline condition especially for Sudan I
- Study the effect of more electrolytes and hydrotropes at different concentration on solubilization of surfactants.
- Study the solubilization of dyes in surfactant vesicles, microemulsion, and etc.

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