CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural rubber latex

Natural rubber latex is the from in which rubber is extruded from the *Hevea brasiliensis* tree as an aqueous emulsion, as rubber and non rubber particles dispersed in an aqueous serum phase, as a milk-like liquid.

Latex is harvested from the tree by a process called tapping. Freshly tapped latex (field latex) has a pH of 6.5-7.0, a density of 0.98 g/cm^3, and a surface energy of 4.0-4.5 $\mu J/cm^2$ (0.96-1.10 $\mu cal/cm^2$) [2-4]. The proportions of composition in natural rubber latex varied between wide limits are given in Table 2.1. The following composition is typical:

Table 2.1 Typical proportions of composition in natural rubber latex [4].

Composition	%
Water	55
Rubber hydrocarbon	35
Proteins	4.5
Acetone extract	3.9
Lipids, aminoacids, etc.	0.2
Quebrachitol	1.0
Inorganic salts	0.4

The total solid of fresh latex varies typically from 30 to 40%. The latex has a rubber content varied between the limits of 25 and 30%, depending on factors such as type of tree, tapping method, soil conditions, and season. The difference between the total solids and dry rubber contents of fresh latex is of the order of 3%.

Both rubber and non rubber, in freshly tapped latex are distributed between three principal phases, which can be separated by ultracentrifugation. They are the top or rubber phases, which account for some 35% of the latex by weight; the middle or serum phases, which is approximately 55% by weight of the whole; and the bottom or lutoid phases, which accounts for most of the remaining 10%.

(i) The Rubber Phase

The rubber particles are usually spherical in shape with a diameter ranging from about 0.01 μm to 5 μm. The particle in latex comprising a sphere of mainly rubber hydrocarbon, surrounded by concentric spherical shells, phospholipid and then of protein.

A typical composition for the rubber phase of natural rubber latex is shown in Table 2.2.

Table 2.2 Typical composition of the rubber phase [2].

Composition	%
Rubber hydrocarbon	86
Water (dispersed in the rubber hydrocarbon)	10
Proteinous substance	1
Lipid substance	3

Trace amounts of metals, notably magnesium, potassium, and copper are also associated with the rubber particles to an aggregate extent of approximately 0.05%.

(ii) The serum phase

The serum phase, sometimes referred as the C-serum or aqueous phase, is a dilute aqueous of density slightly over 1.0 $g.ml^{-1}$. The serum contains many different chemical species, including carbohydrates, proteins, amino acids, enzymes, and nitrogeneous bases.

(iii) The lutoid phase

The lutoid phase or bottom fraction consists mainly of luioid particles. Lutoid particles contain 20 wt% of water-soluble protein of which 70 wt% is have in. The yellow color of the lutoid phase is caused by Frey Wyssling particles which are spherical non rubber particle whose color is due to the presence of carotenoid pigments [5].

2.1.1 The preservative of natural rubber latex

Natural rubber latex coagulation within a few hours of leaving the tree. The actual time required for coagulation to occur depends very much upon the ambient temperature and upon the stability of the latex itself. But always the result is a separation into clots of rubber and a clear serum. At a later stage, putrefaction sets in, with the development of bad odours. It is to prevent both of these processes that preservation is necessary [2].

The preservation protect the latex against spontaneous coagulation and putrefaction by suppressing the activity and growth of microorganisms, enhancing colloid stability, and deactivating trace metals by sequestration in solution or precipitation as insoluble salts.

The most widely used preservative for natural rubber latex is ammonia. Short-term preservation (0.2% of ammonia) is sufficient to ensure that the latex remains in a liquid condition for a few hours or a few days before being processed into various forms of dry rubber. Short-term preservative is commonly known as anticoagulants. Long-term preservation (0.7% of ammonia) includes measures that will keep the intact and free of decay during transportation and storage in the country of final use [2,4,5].

2.1.2 The concentration of natural rubber latex

Natural Rubber Latex as it emerges from the tree (field latex) has a dry rubber content (d.r.c.) of about 30% to 40%, the average being about 33%. Although field latex can be preserved with ammonia or fixed alkali, its low rubber content and high non-rubber solid content severely limit its usefulness. Hence it is necessary to increase the d.r.c. in natural rubber latex to 60% or more to reduce transportation costs and enhance suitability for various latex processes [2]. Concentrated latexs are economically useful as they contain less water to be shipped from the plantations, they are also more efficient in the manufacture of finished products directly from latex. Additionally, latex concentrates tend to be more uniform in quality than do field latices. This is due in part to the partial removal of non-rubber constituents in several concentration processes [1,4].

Four methods are used for concentrating natural rubber latex; centrifugation, creaming, evaporation, and eletrodecantation. Of these processes, centrifugation is the most widely used. Centrifuged latex of 60% rubber content is by far the most widely used latex for dipping. The types of centrifuges latex specially suitable are:

(i) High ammonia latex (HA), preserved with not less than 0.61% of ammonia on latex weight.

(ii) Low ammonia-TMTD/zinc oxide or LA-TZ latex-preserved with more than 0.31% of ammonia by latex weight, plus 0.025% of 1:1 TMTD/zinc oxide mixture and 0.05% of lauric acid soap. The typical properties of concentrated natural rubber latex are given in Table 2.3.

Table 2.3 Typical properties of concentrated natural rubber latex [1].

Item	HA	LA-TZ
T.s.c (%)	61.31	61.25
D.r.c (%)	59.69	59.61
NRS[a](%)	1.64	1.64
Alkalinity, as NH_3 (%)	0.68	0.21
pH	10.65	10.28
VFA No.	0.07	0.05
KOH No.	0.63	0.58
MST(s)	1.168	1.131
ZST(s)[c]	223	352
Viscosity (MPa.s)[d]	77	70
Nitrogen (% of TS)	0.29	0.28
Potassium (% of TS)	0.19	0.18
Phosphorous (p.p.m.of TS)	394	385
Magnesium (p.p.m. of TS)	38	96

[a]Non –rubber solids (i.e. t.s.c-d.r.c)

[b]Expressed as weight NH_3 per g latex

[c]Zinc oxide-mechanical stability test

[d]Bookfield LVT viscometer, 60 r.p.m., 25°C

2.1.3 Vulcanising system

A typical vulcanisation system must have a crosslinking agent e.g., sulphur, an accelerator zinc diethyldithiocarbamate (ZDC), or zinc dibutyldithiocarbamate (ZDBC), etc. and activator-zinc oxide. The level of the additives in any compound is dependent on the processing and product requirements. Typically for gloves the range is as follows:
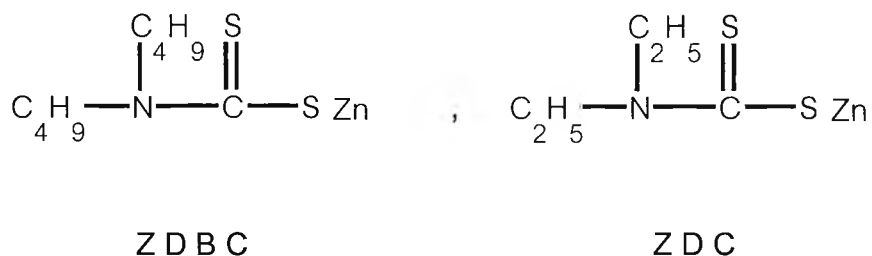
	Dry Rubber (p.p.h.)
Sulphur	0.4 - 1.2
ZDC or ZDBC	0.3 - 1.0
Zinc oxide	0.1 - 1.0

(i) Crosslinking agent

Sulphur contributes to crosslink formation in the vulcanisate and thus influences its tensile strength and modulus greatly.

(ii) Accelerator

The accelerator help in speeding up the vulcanisation process. Zinc diethyldithiocarbamate and zinc dibutyldithiocarbamate are ultra-accelerators and widely employed in rubber industries.

$$C_4H_9 \underset{C_4H_9}{N} - \overset{\overset{\displaystyle S}{\|}}{C} - S\ Zn \qquad , \qquad C_2H_5 \underset{C_2H_5}{N} - \overset{\overset{\displaystyle S}{\|}}{C} - S\ Zn$$

ZDBC   ZDC

ZDC is a cream-white power, density 1.47-1.50 g/cm^3, mp 173-180°C, soluble in carbon disulfide, benzene, chloroform, alkalis; nontoxic. Ensures a rapid low-temperature vulcanization in the presence of small amount of sulpfur. The ZDC is active in latex mixtures in the absence of zinc oxide.

ZDBC is ultra-accelerator, with an activity analogous to that of ZDC. It is a cream-white power, density 1.24-1.28 g/cm^3, mp 100-104°C. The ZDBC does not impart color to light-colored rubber.

The accelerator ZDC and ZDBC can as organic chelating agent react with copper ion rapidly and form stable colored complexes. Figure 2.1 shows the color-forming reaction between copper ion and dibutyldithiocarbamate.
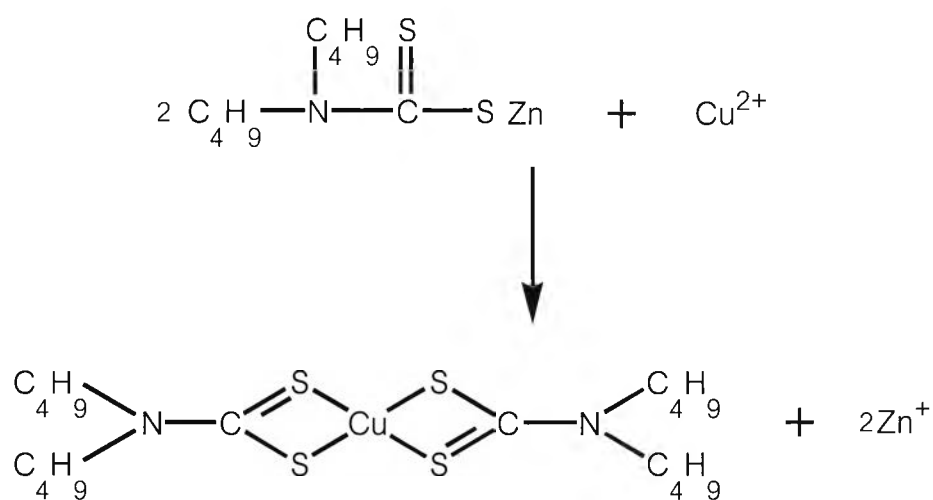
Figure 2.1 The color-forming reaction of dibutyldithiocarbamate.

2.2 Production of natural rubber examination gloves

Dipping processes

Two dipping techniques are being used, namely straight dip and coagulant dip techniques. The latter technique is the most familiar and therefore popular among the manufacturers. The coagulant dipping technique has two different systems of operation, namely an automatic continuous batch system and an automatic chain drive system. The latter system of operation is the most widely used in the industry.

A typical process line for a natural rubber (NR) examination glove plant is shown in Figure 2.2. The dipping process begins with cleaning of the formers and finishes up with stripping of the gloves from the formers. The dipping cycle is normally repeated continuously for 24 h a day, for 300 days for a year.

Former cleaning

Porcelain formers are normally used. These could either be glazed or unglazed. A partly glazed former has also been used. The formers are classified into three different sizes: small, medium and large. Former cleaning ensures good wetting. There are various ways of cleaning the formers, namely using chemicals such as strong inorganic acids or alkalis and other proprietary chemicals, ultrasonic wave, mechanical scrubbing or brushing followed by rinsing and drying.

Coagulant dip

In coagulant dip, the formers are immersed into the coagulant solution such that a thin and uniform layer of coagulant is deposited on the surface of the formers. This can be achieved by a slow immersion and withdrawal of the formers followed by mechanical manipulation and fast evaporation of the coagulant solvent.

A typical coagulant formulation consists of calcium salt, water or alcohol, a wetting agent and an anti-tack. The coagulant concentration varies in the range of 5%-10%. The coagulant tank is normally fitted with a stirrer and heater.

Latex dip

In latex dip, the formers are immersed into the latex compound for a predetermined time followed by a slow withdrawal of the formers such that a smooth and uniform thickness of deposit is obtained. This can be achieved by using a proper latex compound and correct dipping technique and conditions. The well time is normally varied between 5-20 s.

The latex tank is preferably made of stainless steel. The tank should have features for latex circulation, screening or filtration, water jacket or chiller to maintain temperature control.

Beading and leaching

Beading involves the rolling down of thin film of rubber deposit by means of small rotating brushes or rollers. It can be done before or after leaching. Leaching is normally done in hot water to remove water soluble materials or residues such as coagulant, soaps and serum. A sufficient time of leaching is required to give a good quality product.

Drying and vulcanisation

Drying is required to remove the water content in the gel to the lowest possible value as fast as possible. This may be done by direct gas heating, by the use of infrared rays, by hot air or by steam. A lower drying temperature of 70°-80°C is preferred.

Vulcanisation is necessary to give the product with desired strength after drying. For completely prevulcanised latex, the vulcanisation stage will not be necessary. In practice, drying and vulcanisation take place together. A vulcanisation temperature of 100°-120°C for 15-20 min should be adequate.

Powdering

Powdering is necessary to prevent the glove from sticking after removal from the former. A wide range of dusting powders has been used which include specially treated corn starch, magnesium carbonate and calcium carbonate. They may be applied dry or wet (as dispersion in water). Wet powdering can be done before or after drying and vulcanisation.

Stripping and inspection

Manual stripping is normally employed. Visual inspection followed by inflation test is normally done. The level of inspection will depend upon the level of defects occurring in the production. A 100% inspection is required if the level of defects is higher than the required acceptable quality level.

Packing

Gloves are normally packed in 100 pieces per box and ten or twenty boxes per case.

Former cleaning

⇩

Former drying

⇩

Coagulant dip

⇩

Coagulant drying

⇩

Latex dip

⇩

Latex drying

⇩

Beading

⇩

Leaching

⇩

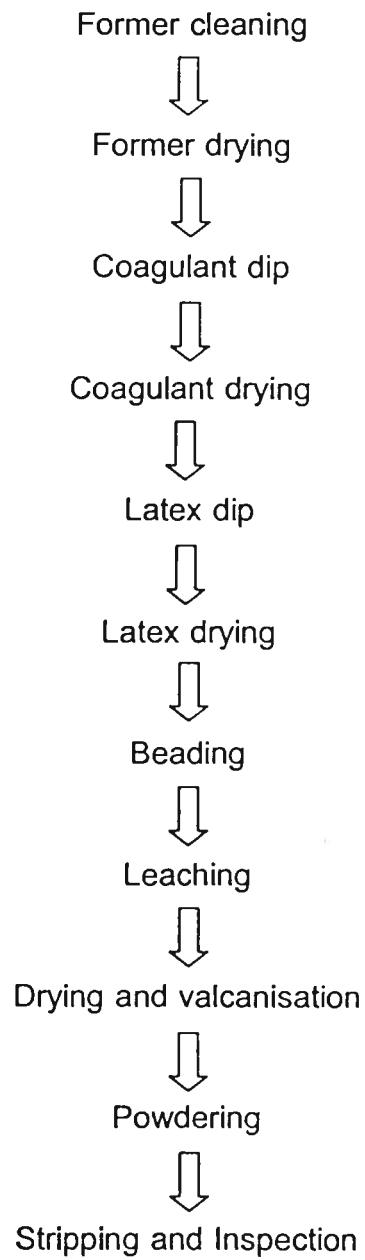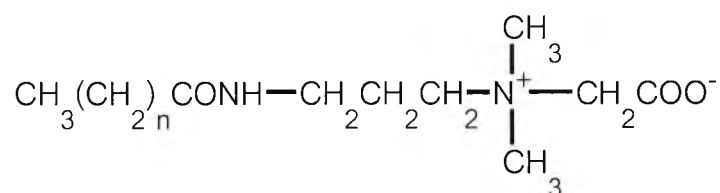Drying and valcanisation

⇩

Powdering

⇩

Stripping and Inspection

Figure 2.2 A typical process line for NR examination glove plant [1].

2.3 Theory

2.3.1 Nature of surfactants

A surfactant or surface-active agent has a characteristic molecular structure consisting of hydrophilic (water-love) which is usually polar group and hydrophobic (water-hating) which is usually hydrocarbon or non polar group. One of important properties of surfactant was to adsorb onto the surface or interface of the system resulting in decreasing the surface or interfacial tention of the medium in which it is dissolved. The interface indicates aboundary between any two immiscible phases and the surface indicates an interface where one phase is a gas, usually air.

Depending on the nature of hydrophilic group, surfactants are classified into four main groups;

1. Anionic: The surface-active portion of molecule bears a negative charge, for example, sodium dodecyl benzene sulphonate (MW=323), CMC=1.2×10^{-3}

2. Cationic: The surface-active portion of molecule bears a positive charge, for example, benzethonium chloride (MW=448), CMC= 1.1×10^{-3}

3. Nonionic: The surface-active portion of molecule bears no apparent ionic charge. For example, nonylphenol ethoxylate $[C_nH_{2n+1}(OCH_2CH_2)_mOH]$ (MW=616), CMC= 8.5×10^{-6}

$$R-\langle \bigcirc \rangle-OCH_2CH_2O\left(CH_2CH_2O\right)_x H$$

$$R = C_{15}H_{24}O \quad , \quad X = 8$$
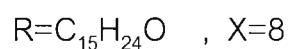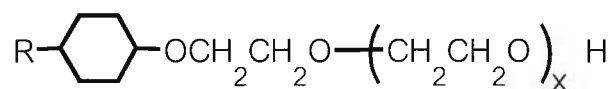
4. Zwitterionic: Both positive and negative charge are present in the surface-active portion, for example, coco amidopropylbetaines (MW= 338), CMC= 4.9×10^{-3}
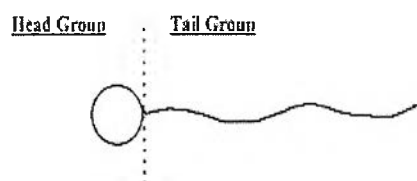
$$CH_3(CH_2)_n CONH-CH_2CH_2CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^+}}-CH_2COO^-$$

$$n = 10$$

Head Group | Tail Group

Figure 2.3 General representation of a surfactant molecule [9].

2.3.2 Micelle formation by surfactants

Micellization is the property that surface-active solute form colloidal-sized clusters in solution. Micelle formation, or micellization, is an important phenomenon not only because a number of important interfacial phenomena, such as detergency and solubilization, depending on the existence of micelled in solution, but because it affects other interfacial phenomena, such as surface or interfacial tension reduction, that do not directly involve micelles.

In an aqueous media, when surfactants are at low concentration, the hydrophobic groups distort the structure of the water and increase the free energy of the system. To minimize the free energy of the system, surfactant monomers should orient so that their hydrophobic groups directed away from the solvent. Therefore surfactant monomers concentrate at the surface by replacing molecules of solvent at the interface, leading to surface tension reduction. If the surfactant concentration increase beyond the point at which the interface is completely covered with surfactant monomers, then the free energy of the system can be reduced by the aggregation of the surfactants monomers into clusters with their hydrophobic groups directed toward the interior of the clusters (micelles) and their hydrophobic groups directed toward the solvents. These clusters containing 50 to 200 monomers are called micelles. And this phenomenon is called micellization. At a specific concentration of monomers, the micellization begins to occur, is called critical micelle concentration (CMC). Above the critical micelle concentration, the total monomer concentration still remains at the CMC. If surfactants are added in the solutions, it forms micelles instead of monomers. At the critical micelle

concentration, bulk properties are unusual. Changing in almost measurable physical property such as electrical conductivity, surface tension, light scattering and refractive index have been observed.
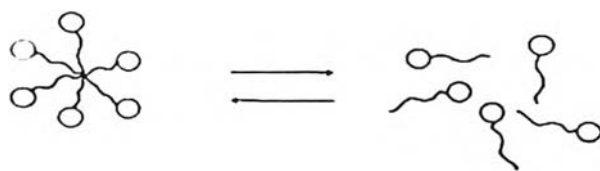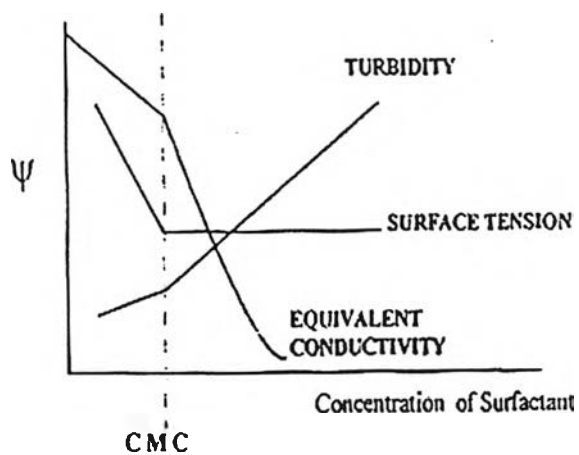

Figure 2.4 Micellization [9].

Figure 2.5 Changes in some physical properties of surfactant solution [9].

A theory of micellar structure, based upon the geometry of various micellar shapes and the space occupied by the hydrophilic and hydrophobic groups of the surfactant molecules, has been developed by Israelachvili, Mitchell and Ningam (1976,1977) and Mitchell and Ninham (1981). The volume V_H occupied by hydrophobic groups in the micellar core, the length of the hydrophobic groups in the core l_c and the cross-sectional area a_o occupied by the hydrophilic group at the micelle-solution interface are used to calculate a parameter, $V_H/l_c a_o$, which determines the shape of the micelle.

Value of $V_H/l_c a_o$	Structure of Micelle
0-1/3	Spherical in aqueous media
1/3-1/2	Cylindrical in aqueous media
1/2-1	Lamellar in aqueous media
>1	Inverse (reversed) micelles in nonpolar media

When the value of the parameter $V_H/l_c a_o$ reaches a value of approximately 1, the surfactant can form either normal lamellar micelles in aqueous media or reversed micelles in nonpolar media. As the value of the parameter gets larger and larger than 1, the reverse micelles in nonpolar media tend to become less asymmetrial and more spherical in shape.
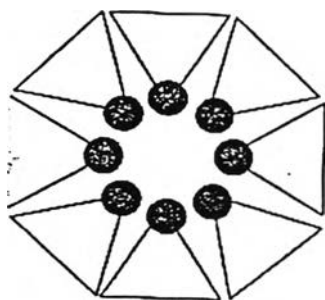
As the hydrophobic groups becomes bulkiers, $V_H/l_c a_o$ increases.
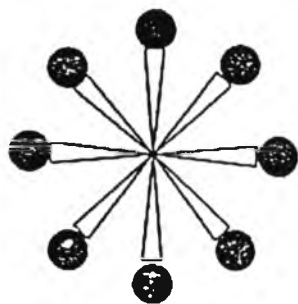
Normal Micelle
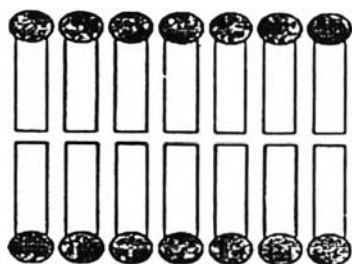
Bilayer structure

Figure 2.6 Model of micelle when $V_H / l_c a_o$ increases [10].

2.3.3 Micelle formation model

The two popular models for describing monomer-micelle equilibrium are the pseudo-phase separation model and the mass action model (Hiemenz,1986 ; Rosen 1989).

The pseudo-phase separation model is based on the assumption of a constant monomer concentration at total surfactant concentration at or above the CMC. This can be viewed as thermodynamically analogous to the vapor-liquid equilibrium. The monomer act as a vapor and micelle act as a liquid phase. The vapor pressure at the dew point is analogous to the monomer concentraion at the CMC. All the surfactant interaction is in the dense phase that is the micelle.

The mass action model describes monomer-micelle equilibrium as a chemical rection equilibrium between monomers and micelles. It considers the micelle as a reversible complex with a distribution coefficient. This treatment is exactly like a weak acid degree of dissociation calculation, except the stoichiometric coefficients are much larger.

Consider a simple nonionic surfactant monomer (A) forming a micell

$$nA \leftrightarrow A_n \dots\dots\dots\dots\dots\dots\dots(2.1)$$

The equilibrium constant of micellization (K_m) is defined as follows:

$$K_m = [A_n]/[A]^n \dots\dots\dots\dots\dots\dots(2.2)$$

Where n: the aggregation number, which is the number of surfactant monomer.

A: the surfactant monomer.

*where n is typically 50 to 100 a spherical micelle.

2.4 LITERATURE REVIEW

Scamehorn and Harwell (1989) reported that at low surfactant concentration below the CMC, the minimum Ca^{2+} concentration required to cause precipitation decreases as the surfactant concentration increased to satisfy the solubility product relationship since all the surfactant and calcium are unassociated. Above the CMC, the hardness tolerance increased with increasing sodium dodecyl sulfate (SDS) concentration. This is due to the micelles formed above the CMC binding with calcium making it unavailable for precipitation. Another reason is when more SDS is added to the system a higher concentration of unbound sodium is present. Lowering the CMC increases the fraction of surfactant which is present in micelles instead of monomeric form.

Scamehorn and Harwell (1996) used Micellar-enhanced ultrafiltration (MEUF) to remove Zn^{2+} from water. Sodium dodecyl sulfate (SDS) was added to aqueous stream at a concentration greater than its CMC and membrane pore size 1000 MWCO. Under the condition used, the rejection of Zn^{2+} was greater than 99% for all run.

Dunn, Christian and Scamehorn (1994) used Micellar-enhanced ultrafiltration (MEUF) to remove Cu^{2+} from water by added sodium dodecyl sulfate (SDS) 80 mM. At the lowest Cu^{2+} concentration (1.2 mM), the retentate is over 500 times as concentrated in copper as the permeate (rejection 99.82%). At the highest Cu^{2+} concentration (32 mM) the rejection is 93.25%.

Krieg (1980) used Neodol 25-3A for recovering Cu^{2+} from very dilute aqueous solutions by bubble fractionation process comprising countercurrent contacting of the aqueous solution containing 1.0 ppm of Cu^{2+} and bubbles 41.6 ppm of the Neodol 25-3A in an elongated vertical column. The percentage removal of the Cu^{2+} of 88% was found.

Fillipi, Brant and Scamehorn (1999) use Micellar-enhanced ultrafiltration (MEUF) to remove Zn^{2+} from water by adding nonylphenol polyethoxylate (NPE) into micelles of sodium dodecyl sulfate (SDS). The Zn^{2+} rejection is 99.2%.