

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Chemicals

1. Cashew nut shell liquid : Obtained locally
2. Sodium sulfate (anhydrous) : Merck
3. Diethylenetriamine : Merck
4. Formaldehyde solution : Lab Scan
5. Methanol : Merck
6. Hexane : Lab Scan
7. Petroleum ether (40 - 60 °C) : Lab Scan
8. Ethyl acetate : Merck
9. 20 % Oleum : Merck
10. Sodium hydroxide : Merck
11. Ethanol : Merck
12. Acetone : Merck
13. Dodecylbenzene sulfonate : Kao Commercial (Thailand) Co. Ltd.

### 3.2 Glasswares and Equipments

1. Stirrer hot-plate
2. Water bath
3. Thermometer and thermometer adapter
4. Other general laboratory glasswares

### 3.3 General experimental detail

IR Spectra were recorded on Omnic-Impact 410. NMR spectra were measured in  $\text{CDCl}_3$  using a Bruker ACF-200 spectrometer for  $^1\text{H}$  (200MHz) and  $^{13}\text{C}$  (50MHz). TLC was carried out on Merck aluminium plate coated with silica gel ( $^{60}\text{F}_{254}$ ) and chromatograms were initially examined under UV light.

The stability of detergent in hard water was carried out according to ISO 1063. Surface tension was determined using Kruss Tensiometer Model K 6, which was carried out according to ISO 304. The % detergency was determined by ICS 578 using Tergometer model Ueshima No. 890342 and Spectro-color-meter SE 2000 Nippon Denshoku [15-18].

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### 3.4 Experimental procedure

#### 3.4.1 Preparation of cardanol from CNSL [4, 12]

CNSL (100 g) was placed in a 800 ml beaker equipped with a magnetic stirring bar and placed on a stirrer hot-plate. The CNSL was stirred at 135-140°C for 2-3 hours using TLC (silica gel) to monitor the progress of reaction.  $R_f$  values of cardanol, anacardic acid and cardol were found to be 0.88, 0.76 and 0.43, respectively, using ethyl acetate:hexane (25:75) as solvent. The decarboxylated CNSL (100 g) was analyzed by IR and NMR. The result clearly showed that the carboxylic acid group was completely removed.

The decarboxylated CNSL (60 g), 40% formaldehyde solution (19.4 g) and diethylenetriamine (2.57 g) were mixed in methanol (200 ml). An exothermic reaction took place after mixing the reactants. After thirty minutes, a phase separation occurred into an upper, slightly reddish solution and a lower phase which solidified and was dark in colour. The upper phase was decanted and treated with water (40 ml) followed by petroleum ether. The petroleum ether extract was distilled to recover the hydrocarbon solvent. A reddish residue of cardanol (48 g, 80 % w/w) was obtained.

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### 3.4.2 Sulfonation [13,14]

Cardanol (10 g, 0.03 mole) was dissolved in methanol (100 ml) in a 250 mL erlenmeyer flask, which was equipped with a magnetic stirring bar and placed on a stirrer hot-plate and dropping funnel. The solution was stirred at about 10 °C and then the oleum (10.5 g) was added slowly into the solution. After stirring for 2 hours, the reaction mixture was allowed to cool to room temperature over a period of 3 hours. Then the mixture was neutralized with 5M aqueous sodium hydroxide solution 60 ml at room temperature. After stirring for 1 hour, the mixture was extracted with hexane in a separatory funnel. The solid residue was separated from the aqueous phase and then treated with acetone. This solid was partially soluble in acetone: the acetone-insoluble portion was filtered off and this solid was dried to give the sodium cardanol sulfonate. (11.5 g, 86.47 % by mole)



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### 3.5 Physical testing

#### 3.5.1 Determination of stability in hard water [15]

(International standard (ISO) 1063, first edition, April 1969)

Mixing solutions of the surface-active agent at different concentrations with hard water solutions of different known calcium hardness carried out the principle of this method. After leaving the solutions to stand in specified conditions, the observation of their appearance, i.e. clearness, opalescence, cloudiness or precipitation was carried out.

#### Procedure

##### 1. Preparation of hard water solutions

Prepare a solution S by dissolving  $44.1 \text{ g} \pm 0.1 \text{ g}$  of analytical reagent grade calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) in distilled water and diluted to a volume of 1000 ml.

The total hardness of this solution is 600 milliequivalents (meq) per litre.

From the solution S prepare three solutions,  $S_1$ ,  $S_2$  and  $S_3$ , by diluting to 1000 ml, with distilled water, portions of solution S according to Table 3.1 below :

**Table 3.1 Hard water solutions**

	Solution $S_1$	Solution $S_2$	Solution $S_3$
Volume of portion of solution S diluted to 1000 ml	10 ml	15 ml	20 ml
Hardness of solution obtained	6 meq per litre	9 meq per litre	12 meq per litre



## 2. Preparation of test solution

A stock solution of 50 g/l of surface-active agent in distilled water was prepared at 20 °C.

## 3. Determination

The test solution (5.0 ml) was pipetted into a test tube, and the hard water solution  $S_1$  was added to give a volume of 50 ml. Then the test tube was left to stand for more than 1 hour but less than 2 hours at  $20 \pm 2$  °C ; at this temperature, look for precipitates, cloudiness or opalescence. If it appears that the solubility of calcium salts increases with temperature, carry out the test at  $50 \pm 3$  °C and make the observation at this temperature. The similar determination was carried out with 2.5 ml, 1.2 ml, 0.6 ml and 0.3 ml of the test solutions. Identical volumes of test solution and with  $S_2$  and  $S_3$  hard water solutions were proceeded similarly.

### 3.5.2 Determination of surface tension by drawing up liquid films

(International Standard (ISO) 304, first edition, 1963) [6, 16]

#### Determination using a ring as the measuring unit

The circumference of the ring was checked in horizontal. The surface of liquid was used as a mirror and then observing the image of the ring almost in contact with the surface of the liquid.

With the apparatus calibrated, the arm of the ring is checked in horizontal. The measuring cup contained the surfactant solution was placed on the platform under the ring. The platform was raised until the arm was horizontal. The platform was raising until the tensiometer was in equilibrium once more. The platform was lowered gently until the tensiometer was slightly out of equilibrium. Then, the force was adjusting to apply to the tensiometer as well as the position of the platform, the equilibrium of the tensiometer with the horizontal arm of the ring located at the height of the free surface of the liquid.

The aim of this operation was to ensure the complete wetting of the arm of the ring. As the contact between the platinum of the ring and the surface of the liquid disturbed the arrangement of the surface layer, waited a few minutes before beginning the determination.

### **3.5.3 Determination of Critical micellization concentration.**

#### **Method by measuring surface tension with a plate, stirrup or ring (International Standard (ISO) 3411, first edition, 1979) [17]**

Curves showing the variation in the physical properties of aqueous solutions of surface-active agents are specifically to individual products. In a certain region of concentration, usually very narrow, these curves show a sharp change of slope. The phenomenon attributes to the formation of aggregated molecules, and the concentration at which this change occurs is termed the "critical micellization concentration" (C.M.C.). This International Standard specifies a method for the determination of the critical micellization concentration of anionic and non-ionic surface-active agents in solution in distilled water or other aqueous systems, by measurement of the surface tension with a plate, stirrup or ring. The principle of this method is for the determination of the surface tension of a series of solutions whose concentrations bracket the critical concentration. In plotting the graph of surface tension as a function of the logarithm of the concentration: The C.M.C. corresponds to a singular point on the curve.

#### **3.5.4 Determination of the detergency.**

**(Thai Industrial Standard (ICS), 578-2540) [18]**

This method evaluated the ability of a detergent or formulation to remove a carbon containing artificial soil from cotton cloth or clay soil from cotton cloth.

##### **Preparation of sample solution and determination of detergency**

The percentages of detergent in the finished products are 30 to 35 percent. The concentration of the solution needed to be used in the test was 0.08% w/w, therefore, 22.85 g of dedecylbenzene sulfonated, cardanol sulfonate were weighed. Then water was added into each sample to make total weight of 1000 g. The mixture was stirred for 10 minutes. About 100 ml of each sample solution was filled to the terg-o-meter and dilutes it with water to total volume of 1000 ml. The reaction was carried out at temperature of about 30 °C, spinning rate of 100 rpm and reaction time of about 10 minutes. Before washing, the cottons with the clay soil of about 5 pieces per sample were test to detect the reflectance by a spectro-color-meter SE 2000. After washing, the cottons were dried and tested for reflectance once again.

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