

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1. Cashew nut shell liquid	: Obtained locally
2. Chlorosulfonic acid	: Fluka
3. Methylene chloride	: Merck
4. Hexane	: Merck
5. Calcium hydroxide	: Merck
6. Diethylenetriamine	: Merck
7. Formaldehyde solution	: Lab Scan
8. Petroleum ether (40 – 60 °C)	: Fluka
9. Ethyl acetate	: Fluka
10. 10% palladium on activated charcoal	: Merck
11. Sodium bicarbonate	: Merck
12. Methanol	: Fluka
13. Isopropanol	: Merck
14. Silica gel	: Fluka
15. Dodecylbenzene sulfonate	: Merck

3.2 Glasswares

1. 3-necked round bottom flask size 250 cm³
2. 2-necked round bottom flask size 500 cm³ and 1000 cm³
3. Thermometer and thermometer adapter
4. Condenser and drying tube
5. Other general laboratory glasswares

3.3 General experimental detail

IR Spectra were recorded on Omnic-Impact 410. NMR spectra were measured using a Bruker ACF-200 spectrometer for ¹H and ¹³C. TLC was carried out on Merck aluminium plate coated with silica gel (⁶⁰F₂₅₄) and chromatograms were initially examined under UV light.

The solubility 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 Terg-o-meter model Ueshima No. 890342 and Spectro-color-meter ES 2000 [16-19].

3.4 Experimental procedure

3.4.1 Preparation of cardanol from CNSL [7,20]

CNSL (20 g) in toluene (100 cm^3) and CaHCO_3 (0.4 g) were placed in a two-necked round bottom flask and then heated at $120 \text{ }^\circ\text{C}$. After stirring for about 2 hours, the solvent was evaporated and the residue was heated at $120\text{-}130 \text{ }^\circ\text{C}$ for 2-3 hours using TLC (silica gel) to monitor the progress of reaction. R_f value of cardanol, anacardic acid and cardol were 0.88, 0.76 and 0.43, respectively, using ethyl acetate: hexane (25:75) as solvent. The hot residue was allowed to cool at room temperature and then filtered through the filter paper No.1. Evaporation of the solvent gave a residue of decarboxylated CNSL (20 g) and IR and NMR spectrometers analyzed the residue. The results (Figures 1-19) clearly showed that the carboxylic acid group was completely removed.

Into a solution of the decarboxylated CNSL (60 g) in methanol (200 cm^3) in a round bottom flask, was added 40% formaldehyde solution (19.4 g) and diethylenetriamine (2.57 g). An exothermic reaction took place after mixing the reactants and after thirty minutes a phase separation occurred. The upper phase was a reddish solution which was decanted and then the lower phase was extracted with water (40 cm^3) followed by petroleum ether. The petroleum ether layer was evaporated to leave a reddish residue of cardanol (48 g, 80% w/w).

3.4.2 Hydrogenation of cardanol [21,22]

A solution of the cardanol (15 g) from Exp. 3.4.1 in ethyl acetate (75 cm³) was added into the pressure reactor and then treated with hydrogen (250 psi.) in the presence of 10% palladium on activated charcoal (1 g) using agitation of 600 rpm. at 200 °C for 8 hours. After the mixture was cooled down to room temperature, it was filtered through Whatman filter paper No.1. The filtrate was evaporated to give the hydrogenated cardanol. (15 g, 100% w/w.)

3.4.3 Sulfonation [23]

3.4.3.1 Sulfonation of cardanol

The cardanol (3.75 g, 0.0125 mole) was dissolved in methylene chloride (30 cm³) in 3-necked round bottom flask, which was connected with a condenser, thermometer with thermometer adapter and a dropping funnel. The top of the condenser was connected with the drying tube containing silica. The mixture was stirred at about 0 °C for 2 hours. Then the chlorosulfonic acid (0.85 cm³, 0.0125 mole) was added slowly into the mixture. After stirring for 2 hours, the reaction was allowed to cool to room temperature over a period of 3 hours. Then ice water (50 cm³) was added into the mixture. The mixture was stirred for 10 minutes and then sodium bicarbonate (1.07 g, 0.0125 mole) was slowly added. After stirring for 1 hour, the mixture was partitioned with iso-propanol and petroleum ether in a separated funnel. The aqueous layer was separated and then evaporated to give the solids of cardanol sulfonate. (3.09 g, 61.34 % by mole.)

3.4.3.2 Sulfonation of hydrogenated cardanol

A solution of hydrogenated cardanol from Exp.3.4.3 (3.75 g, 0.0125 mole) in methylene chloride (30 cm³) was placed in a 3-necked round bottom flask, which was connected with a condenser, thermometer with a thermometer adapter and a dropping funnel. The top of the condenser was connected with the drying tube. The mixture was stirred at about 0 °C for 2 hours. Then, chlorosulfonic acid (0.85 cm³, 0.0125 mole) was added slowly into the mixture. After stirring for 2 hours, the reaction was allowed to cool to room temperature over a period of 3 hours. Then ice water (50 cm³) was added into the mixture. The mixture was stirred for 10 minutes and then sodium bicarbonate (1.07 g, 0.0125 mole) was slowly added. After stirring for 1 hour, the mixture was partitioned with iso-propanol and petroleum ether in a separated funnel. The aqueous layer was separated and then evaporated to give hydrogenated cardanol sulfonate as brown solid. (3.62 g, 71.86 % by mole.)

3.5 Physical testing

3.5.1 Determination of solubility in hard water [16]

(International standard (ISO) 1063, first edition, 1974-12-15)

Mixing solutions of the surface-active agent at difference concentrations with hard water solutions of difference 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. Hard water solution

- Solution S1, of calcium hardness 6 meq of calcium (II) ions per litre.
- Solution S2, of calcium hardness 9 meq of calcium (II) ions per litre.
- Solution S3, of calcium hardness 12 meq of calcium (II) ions per litre.

2. Preparation of test solution

Prepare a stock solution of 50 g of the surface-active agent in 1000 ml of water at 20°C. If the products are not readily soluble at 20°C, prepare at 50°C.

3. Determination

The test solution (5.0 ml) was pipetted into a test tube, and the hard water solution S1 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 °C and examine at this temperature for precipitates, cloudiness or opalescence. If it appears that the solution of the calcium salts increases with temperature, carry out the test at 50 °C and take the observation at this temperature. Carry out the similar determination with 2.5 ml, 1.2 ml, 0.6 ml and 0.3 ml of the hard water solution. Proceed similarly with identical volumes of the test solution and with S2 and S3 hard water solutions.

3.5.2 Determination of surface tension by drawing up liquid films [17]

(International Standard (ISO) 304, second edition, 1985-12-15)

3.5.2.1 Determination using a ring as the measuring unit

Check that the circumference of the ring is horizontal. Use the surface of liquid as a mirror, observing the image of the ring almost in contact with the surface of the liquid.

With the apparatus calibrated, check that the arm of the ring is horizontal. Place the measuring cup, containing the liquid to be examined, on the platform and bring it under the ring. Raise the platform until the arm is horizontal. Continue raising the platform until the dynamometer is in equilibrium once more. Lower the platform gently until the dynamometer is slightly out of equilibrium. Then, adjusting the force applied to the dynamometer as well as the position of the platform, restore equilibrium of the dynamometer with the horizontal arm of the ring located at the height of the free surface of the liquid. The aim of this operation is 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 disturbs the arrangement of the surface layer, wait a few minutes before beginning the determination.

3.5.3 Determination of the critical micellization concentration. [18]

**- Method by measuring surface tension with a plate, stirrup or ring
(International Standard (ISO) 3411, first edition, 1979-06-01)**

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 has been attributed to the formation of aggregated molecules, and the concentration at which this change occurs has been 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. [19]

(Thai Industrial Standard (ICS), 578-2540)

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 percent of detergent in the finished products are 30 to 35 percent. The concentration of the solution needed to be use in the test was 0.08 % w/w, therefore, 2.91g of dodecylbenzene sulfonate, cardanol sulfonate and hydrogenated 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 ES 2000. After washing, The cottons were dried and tested for reflectance once again.