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CRYSTALLIZATION OF DIHYDROXYSTEARIC ACID (DHSA) PRODUCED FROM COMMERCIAL GRADE PALM OIL BASED CRUDE OLEIC ACID EMPLOYING ISOPROPYL ALCOHOL AS SOLVENT

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ABSTRACT

In recent years, oleo-based chemicals have made its presence felt among the ever blooming personal care segment, slowly but gradually chipping into the industry once dominated by petrol-based chemicals. In particular, the industry has shown considerable interests in hydroxyl fatty acids due to their different behavior compared with ordinary fatty acids. Hydroxyl fatty acids and their derivatives are multipurpose intermediates in the synthesis of fine chemical products such as special cosmetics known as decorative cosmetics or make up products. One of the possible derivatives is known as dihydroxystearic acid (DHSA). The potential of DHSA (produced from palm oil based oleic acid via epoxidation with performic acid followed with hydrolysis of the epoxide) and its derivatives, e.g. octyl-dihydrostearate, sodium-dihydrostearate, zinc-dihydrostearate and magnesium-dihydrostearate, in the formulation of decorative cosmetics have been explored, mainly at laboratory scale. However, one aspect that was left out was the scaled-up production of purified DHSA to meet the demand of this multi-billion industry. This paper emphasizes on the purification of DHSA from its crude waxy form to its refined granular form, ideal for formulation, re-melting and transportation purposes, through solvent crystallization employing isopropyl alcohol (IPA). Gas chromatography (GC) analysis showed that crude DHSA had a purity of 69.0%. After crystallization, the purity of DHSA had increased to 92.2%. Particle size distribution (PSD) analysis showed that the crystals of refined DHSA had diameter ranging from 49 to 1783 microns.

Keywords: *hydroxyl fatty acids, dihydroxystearic acid, decorative cosmetics, solvent crystallization, gas chromatography, particle size distribution*

INTRODUCTION

Hydroxyl fatty acids are fatty acids (in chemistry, fatty acid is a type of carboxylic acid) that contain one or more hydroxyl (-OH) functional groups in their chemical structure. These hydroxyl functional groups may occur at various positions in the carbon chain, which in turn can be saturated or unsaturated. Hydroxyl fatty acids, due to the presence of both hydroxyl and carboxyl (-COOH) functional groups, offer alternative behaviors as compared to simple fatty acids and are much in demand within the personal care industry. Hydroxyl fatty acids and their derivatives were used commercially for the preparation of a wide variety of products, *e.g.* as additives in lubricants and cosmetics, as emulsifiers, as polyols for polyurethanes and as surfactants for detergent [1]. Their uses as auxiliaries for the textile industry [2] and as corrosion inhibitor in lubricants [3] had been investigated.

Currently, the main source of hydroxyl fatty acids supplied by nature is castor oil. However, since castor oil is not available in Malaysia, other means to produce hydroxyl fatty acids had been initiated. Oleic acid is a valuable oleochemical available from many natural sources including palm oil and is an important raw material for the preparation of hydroxyl fatty acids. In Malaysia, palm oil emerged as an alternative to castor oil, owing to its oleic acid composition [1], [4] and [5]. The Malaysian Palm Oil Board (MPOB) through its research and development (R&D) efforts had successfully prepared 9,10-dihydroxystearic acid (DHSA), one of the variations of hydroxyl fatty acids, from commercial grade crude oleic acid, a low value byproduct of the palm oil industry.

The commercial grade palm oil based crude oleic acid had purity between 70 to 78%. This palm oil based crude oleic acid contained a certain degree of unsaturation and therefore offered chemical reaction sites for further modifications to produce various useful derivatives. DHSA, one of the possible derivatives, was a specialty chemical derived from epoxidation of the unsaturation present in the palm oil based crude oleic acid with performic acid (HCOOH) in the presence of sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) followed with *in-situ* hydrolysis of the epoxide with hydrogen donor such as water [1], [4], [6] and [7]. The crude DHSA preparation process was described in detail by Siwayanan *et al.* [1] and is summarized in Figure 1:

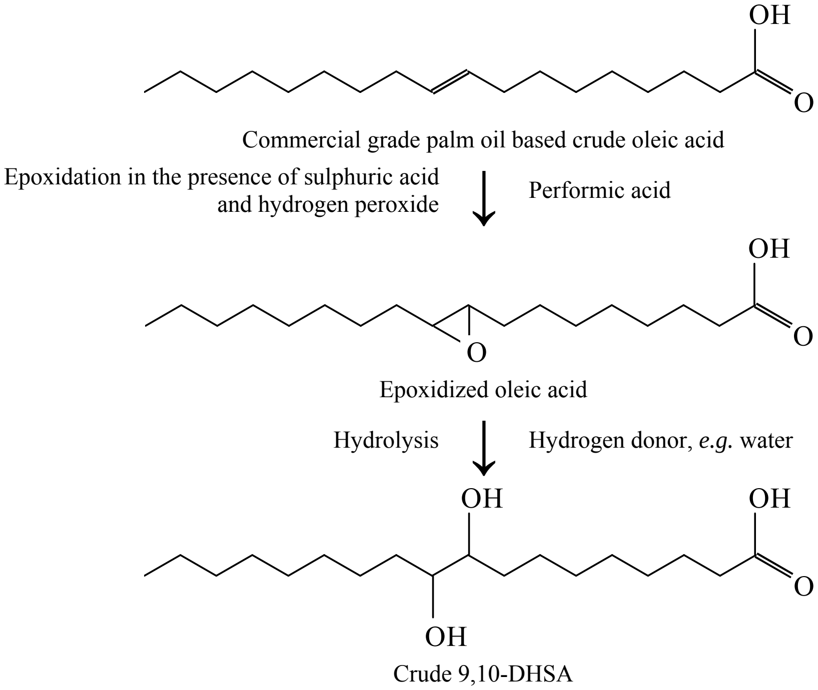

Figure 1:Crude 9,10-DHSA formation process from commercial grade palm oil based crude oleic acid [1, 4, 6, 7]

The DHSA produced bore three functional groups, *i.e.* one carboxyl and two hydroxyl functional groups. The two hydroxyl functional groups were located at position-9 and position-10 respectively on an aliphatic 18-carbon chain. The structure of the DHSA is shown in Figure 2:

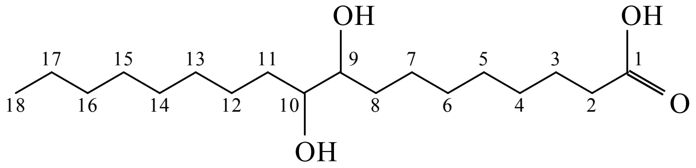

Figure 2:Structure of 9,10-threo-DHSA [4, 6, 7, 8]

Currently, DHSA is used as primary and secondary emulsifiers, coating agent for pigments and gelling agent for oils and/or fats in the colored cosmetic formulations and research. Some of the applications and/or functionalities of DHSA, with regards to personal care finish products were shown in Table 1:

However, due to the purity of the commercial grade palm oil based crude oleic acid, the crude DHSA produced had a purity range of only 55 to 70% and contained substantial amount of octanoic and decanoic acids (commonly known as caprylic and capric acids, respectively) and small amount of long chain saturated and unsaturated fatty acids. The medium chain acids, octanoic and decanoic acids, inherited from the palm oil based crude oleic acid, were irritants to the human skin. Successful usage of DHSA as additive ingredient into decorative cosmetics could be achieved if and only if the DHSA produced was non-irritant. The objective of this preliminary study was to investigate the feasibility of employing crystallization process with isopropyl alcohol (IPA) as the solvent, to produce purified DHSA.

Table 1:The applications and/or functionalities of DHSA in personal care finish products [9-11]

Personal care finish products	Applications and/or functionalities of DHSA
Lipsticks	DHSA increased the mechanical properties of lipsticks. Lipsticks with DHSA coated pigments possessed higher breaking point.
Liquid foundations	DHSA gave better color development in liquid foundations. Liquid foundations with DHSA coated pigments gave brighter color, implying that in order to achieve the same color brightness, less pigment was needed. DHSA also eased the spreading of liquid foundations onto the skin and thus enhanced the dispersion of pigments.
Mascaras	Mascaras with DHSA coated pigments had shorter drying time, gave better curling effect and increased apparent size of the eyelashes (added volume to the eyelashes).
Compact powders	DHSA, as a binding agent, increased the skin adhesion properties of compact powders. Compact powders with DHSA coated pigments gave velvety skin feel and was found to be easily distributed when applied to the skin.
Metal soaps	Sodium soaps of DHSA had better detergency than stearic soap at room temperature and were more biodegradable. The soaps also exhibited corrosion inhibition with a corrosion rate of only 0.002 mm yr^{-1} at 100 ppm concentration.

MATERIALS AND METHODS

Crystallization and Filtration Processes

Crude DHSA was melted in an oven at an elevated temperature of 80°C. Depending on the amount of crude DHSA melted, the melting process which was to destroy all crystal memories, would take two to eight hours. The crude DHSA in molten form was kept under the elevated temperature for an extra 30 minutes to ensure the destruction of all nuclei remnants. The melted crude DHSA was then mixed with IPA of different concentrations. The different concentrations of IPA were achieved by diluting it with reverse osmosis water. The concentrations of IPA used were 60%, 70%, 80%, 90% and 100%. The total amount of solvent used was also manipulated with the crude DHSA to solvent weight over weight ratios varied between 1.0:1.0 and 1.0:1.5. Assuming that the total amount of melted crude DHSA in each crystallization vessel was 600g, the amount of IPA and reverse osmosis water present would then be as shown in Table 2:

Table 2:Theoretical composition of the mixture present in the crystallization vessel

DHSA (g)	IPA : H_2O (w/w)	DHSA : Solvent (w/w)			
		1.0:1.0		1.0:1.5	
		IPA (g)	H_2O (g)	IPA (g)	H_2O (g)
600	60 : 40	360	240	540	360
600	70 : 30	420	180	630	270
600	80 : 20	480	120	720	180
600	90 : 10	540	60	810	90
600	100 : 0	600	0	900	0
Total solvent (g)		600		900	

DHSA - Melted crude DHSA
IPA - Isopropyl alcohol
H_2O - Reverse osmosis water

The crystallization time was set to 12 hours, since for most industrial applications; crystallization was carried out for 12 to 16 hours [12]. The mixture of crude DHSA and solvent was left to cool down and crystallize in a room without any mechanical induced convective air flow. The crystallization process took place under natural cooling condition without any temperature disturbances. Due to the presence of impurities in the crystallization system which would both expedite and enhance nuclei formation, cooling below room temperature was not required. After 12 hours of crystallization, the crystals were emptied onto a bush funnel which was coated with 25 µm pore size nylon fabric filter cloth and connected to a jet water aspirator to provide vacuum suction needed to perform vacuum filtration. The filtration process to segregate the DHSA crystals from the mother liquor would take 30 to 120 minutes depending on the amount of solvent used and on the tendency of caking. The semidry crystal particles were then removed from the filter cloth, scattered on metal trays and subjected to mechanically induced ventilation for 24 hours. This drying process was carried out under normal room temperature. The dried DHSA crystal particles were then stored in the presence of silica gel as drying agent. All experiments were conducted in triplicates in order to ensure reproducibility.

Gas Chromatography Analysis

The Gas Chromatography (GC) analysis was carried out using a Hewlett-Packard HP-6860A Plus gas chromatograph (Palo Alto, CA). The DHSA samples had to undergo silylation process before being injected into the GC equipment. The silylation process was carried out by preparing the trimethylsilyl (TMS) derivatives of DHSA where 0.01g of DHSA was weighted into a vial followed with the insertion of 2 ml of N, N-dimethylformamide (DMF) and 1ml of Bis(trimethylsilyl)trifluoroacetamide (BTSFA). The vial was then vortexed for 30 seconds in order for the content to achieve homogeneous mixing before being incubated at 60°C for 30 minutes. The derivatives were allowed to cool down for a few minutes. About 1.5ml of the derivatives was then transferred into a 2 ml clear wide opening crimp vial laced with a very small amount of sodium sulphate anhydrous. The vial was sealed off and injection followed. The derivatives concoction was separated on a non-polar column, HP-5 (Hewlett-Packard, 30 m × 0.25 mm × 0.25 μm) with helium as the carrier gas. The oven was programmed to hold at 150°C for one minute, followed by ramping from 150 to 290°C at a rate of 10°C per minute. The final temperature was held at 290°C for 30 minutes. The injector and flame-ionization detector were set at 300°C.

Particle Size Distribution Analysis

The Particle Size Distribution (PSD) analysis was carried out by determining the wet dispersion laser diffraction measurements using Malvern Instruments Mastersizer 2000 and Hydro 2000S particle size analyzer (United Kingdom). The equipment was set to process the particle size ranging from 0.020 to 2000.000 μm. The Mie-Scattering analysis model was chosen for the measurement of the diffraction pattern. The principal was based on simultaneous multi angle detection of scattered light where the scattering behavior was strongly dependent on the particle size. In this analysis, the reflective index (RI) of the particle, DHSA, was 1.520 while the RI of the dispersant, water, was 1.330. The Mastersizer 2000's operating procedures were set to record the background measurement for 20 seconds followed by sample measurement for 20 seconds. A small amount of DHSA crystal samples were then inserted into the designated vessel containing water, where they were introduced into the dispersion module, until an adequate obscuration level was obtained and the laser obscuration was stable (± 0.2%). The ideal obscuration level ranged from 10.0 to 20.0. A total of three measurement cycles were carried out for each sample and the average value was taken as the final result. The crystal particles' specific surface area, surface weighted and volume weighted mean diameters were determined along with the d(0.1)-, d(0.5)- and d(0.9)-cumulative undersize.

Fourier Transform – Infra Red Analysis

The Fourier Transform – Infra Red (FT-IR) analysis was carried out to determine the functional group(s) present in the DHSA compound. The spectra were recorded on a Nicolet Magna-IR550 Series II (Nicolet, Madison, WI) spectrophotometer. A potassium bromide (KBr) pellet was used to determine the background signal. Since the DHSA crystals were in powder form, they were mixed with KBr powder to form a pellet before being inserted in the sample compartment to undergo 64 scans. The spectral range (wave-numbers) for the spectrophotometer was set at 4000 to 400cm^{-1} and the final output format was in percent transmittance.

Scanning Electron Microscopy Analysis

The Scanning Electron Microscopy (SEM) analysis was carried out using Quanta 400 and EDAX (GENESIS 7000) scanning electron microscope to observe the morphology of the DHSA crystals formed under different solvent crystallization conditions. The scanning electron microscope was able to create very detailed three dimensional images using electrons and the images created had very high magnification. As SEM was supposed to illuminate the DHSA crystal samples with electrons, they had to be made to conduct electricity. This was achieved by mounting the samples on metal stub and coating them under near vacuum condition with a very thin layer of gold through a machine called a sputter coater. The coated samples were then placed inside the microscope's vacuum column through an airtight door. After the column was vacuumed, an electron gun emitted a beam of high energy electrons that traveled through a series of magnetic lenses designed to focus the electrons to a very fine spot. From the bottom, a set of scanning coils would move the focused beam back and forth across the samples. As the electron beam hit each spot on the samples, secondary electrons were knockloosed from the samples' structure. A detector counted these electrons and sent the signals to an amplifier. The final images were built up from the number of electrons emitted from each spot on the samples.

RESULTS AND DISCUSSION

Gas Chromatography Analysis

The GC chromatograms of DHSA prepared from commercial grade palm oil based crude oleic acid (Figures 3a and 3b) were compared with the GC chromatograms of standard fatty acids (caprylic acid – $C_{8:0}$; capric acid – $C_{10:0}$; lauric acid – $C_{12:0}$; myristic acid – $C_{14:0}$; palmitic acid – $C_{16:0}$, stearic acid – $C_{18:0}$ and oleic acid – $C_{18:1}$) and 9,10-*threo*-DHSA. The GC analysis showed the presence of compounds other than DHSA in the study samples. According to Awang *et al.* [13], the presence of other compounds in the crude DHSA was due to the saturated fatty acids of various chain lengths present in the commercial grade palm oil based crude oleic acid.

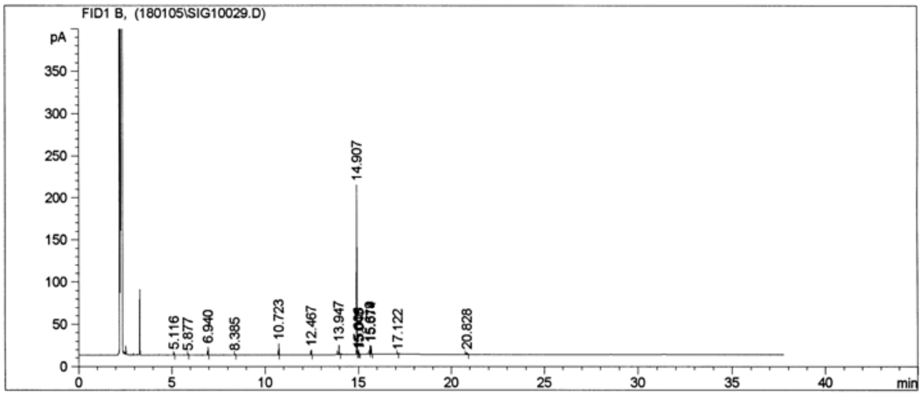

Figure 3a:GC separation of the components of DHSA prepared from commercial grade palm oil based crude oleic acid – Crude DHSA

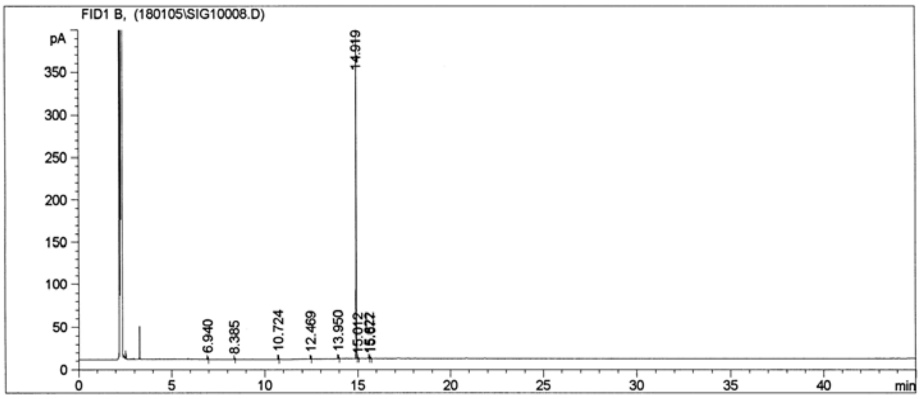

Figure 3b: GC separation of the components of DHSA prepared from commercial grade palm oil based crude oleic acid – Purified DHSA

Based on the retention time and the area percent, the chromatograms revealed that the crude DHSA had a purity of 69.0% while the purified DHSA had purity of 86.0 to 90.5% and 87.8% to 92.2% for DHSA to solvent ratios of 1.0:1.0 and 1.0:1.5, respectively. This showed that when more solvent was used during the crystallization process, the effectiveness of impurities removal became higher. A possible explanation for this phenomenon was the solvent reduced the viscosity of the DHSA mixture and thus resulted in higher diffusivity which led to better selectivity and phase separation.

The chromatograms also revealed that when the same amount of solvent was used, the solvent with higher IPA concentration yielded purer crystals. This showed that IPA was a suitable solvent to remove the organic impurities present in the crude DHSA (Figure 4). The removal efficiency of capric, lauric, palmitic and stearic acids were 51.9, 54.3, 49.1 and 26.6%, respectively (Table 3). Theoretically, crystallization should produce pure crystals. However, Table 3 clearly showed that the impurities removal was not 100% efficient. A possible explanation was that when the crystals were removed from the final magma, some mother liquor adhered to the crystal surfaces and resulted in the impurities being carried into the final product [14].

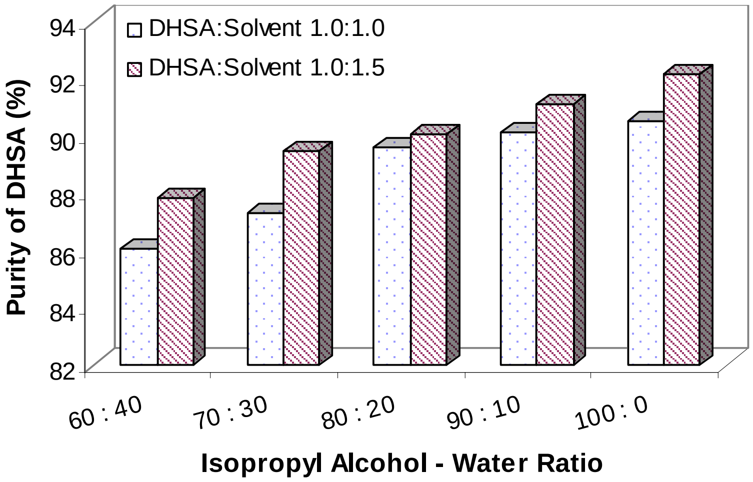

Figure 4: Effects of ratios of crude DHSA to solvent and ratios of IPA to water on the purity of the purified DHSA

Table 3: Some major fatty acids composition in crude and purified DHSA

Components	% in crude DHSA	% in purified DHSA	% removal
Capric acid	0.81	0.39	51.9
Lauric acid	3.15	1.44	54.3
Palmitic acid	4.64	2.36	49.1
Stearic acid	2.33	1.71	26.6

Particle Size Distribution Analysis

A series of experiments were carried out to determine the effects of different ratios of crude DHSA to solvent and different IPA concentrations on the PSD of purified DHSA. Figure 5a showed that increasing the concentration of IPA from 60% to 70% and 80% decreased the height of the volume percent peak. Further increment to 90% and 100% showed no consistent trend.

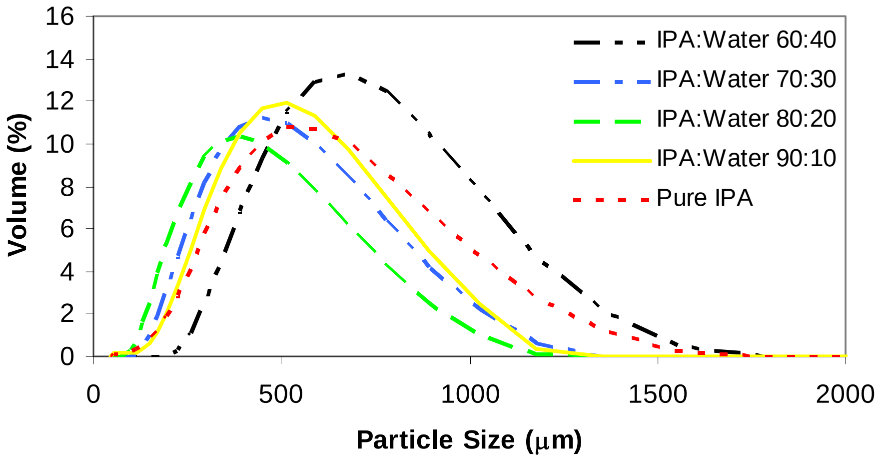

Figure 5a: Effects of IPA concentration on PSD of DHSA crystals for crude DHSA to solvent ratio of 1.0:1.0

However, by increasing the IPA concentration, the DHSA's d(0.1) cumulative undersize showed a down-warding trend. The finest crystals obtainable using solvent with higher IPA concentration was smaller than the finest crystals obtainable using solvent with lower IPA concentration. This was noticed from the stretch at the lower end of the distribution curve in Figure 5a. The finest crystals obtained using IPA of 60% concentration was 224 μm compared to 49 μm obtained using pure IPA. This suggested that water acted as a binding agent and agglomerated the fine DHSA particles.

Although IPA of 80% concentration produced the lowest volume percent peak, the spread of the curve remained the narrowest, *i.e.* the crystal particles had sizes that distributed nearest to the mean particle size. The standard deviation of DHSA crystals' PSD for crude DHSA to solvent ratio of 1.0:1.0 is shown in Table 4:

Table 4: Standard deviation of DHSA crystals' PSD for crude DHSA to solvent ratio of 1.0:1.0

IPA concentration (%)	Mean particle size (μm)	Standard deviation
60	681.03	257.90
70	475.83	211.43
80	406.66	195.50
90	499.10	211.25
100	561.84	268.55

Figures 5b – 5e showed that regardless of the amount of solvent used, the IPA concentration of 80% would produce DHSA crystals with the highest specific surface area, smallest particle size, smallest surface weighted mean diameter and smallest volume weighted mean diameter. The high specific area would render the DHSA crystals ideal for re-melting purposes should the needs arise, *e.g.* to be incorporated into decorative cosmetics while the small particle size and diameters would render them ideal for transportation purposes as compact packing could be achievable.

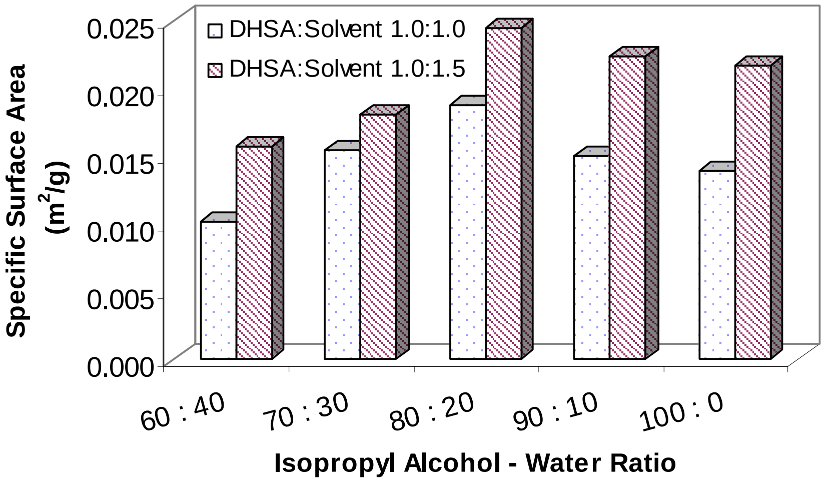

Figure 5b: Effects of crude DHSA to solvent ratios and IPA concentration on the specific surface area of DHSA crystals

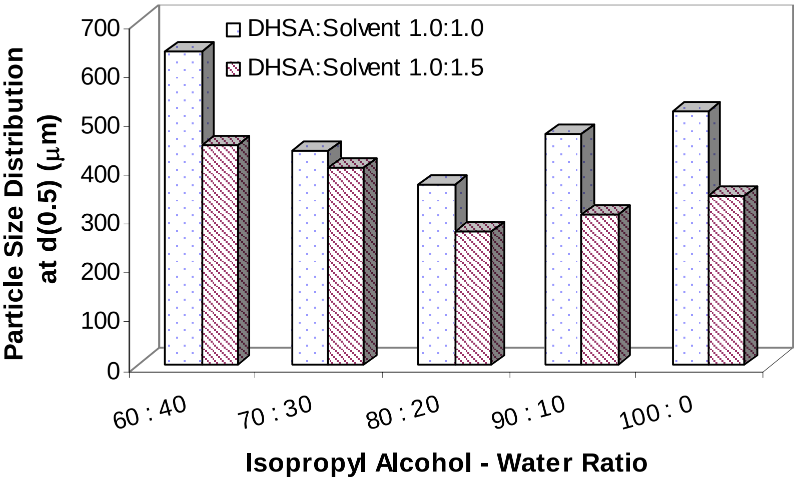

Figure 5c:Effects of crude DHSA to solvent ratios and IPA concentration on the PSD at d(0.5) cumulative undersize of DHSA crystals

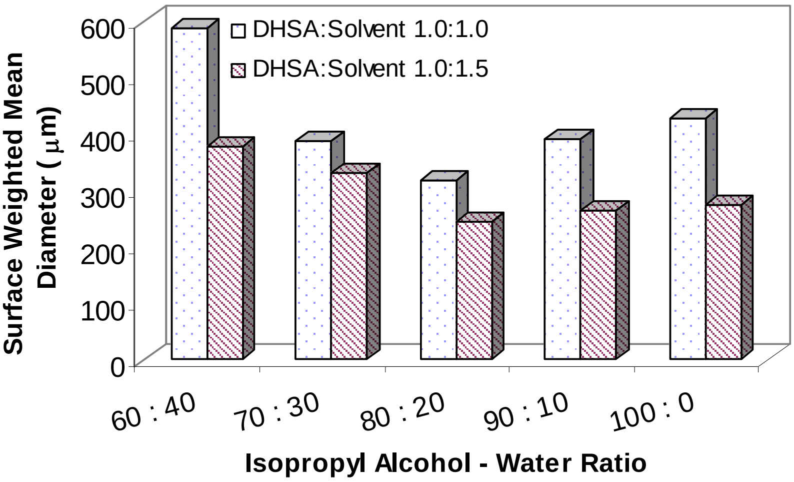

Figure 5d: Effects of crude DHSA to solvent ratios and IPA concentration on the surface weighted mean diameter of DHSA crystals

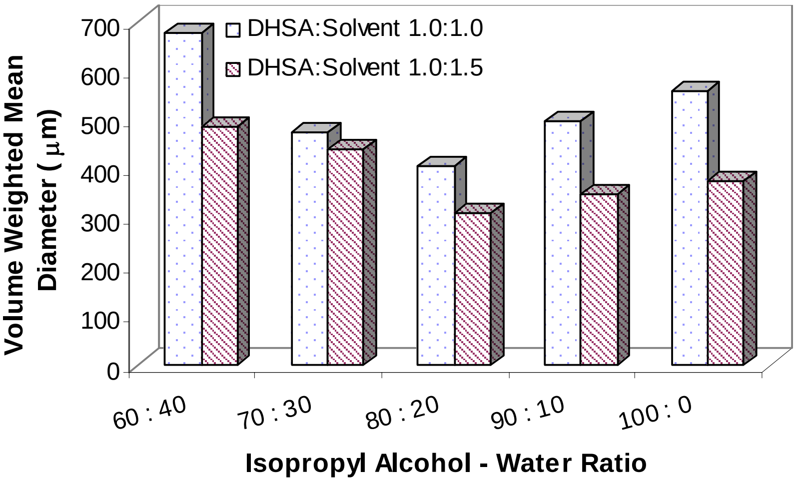

Figure 5e: Effects of crude DHSA to solvent ratios and IPA concentration on the volume weighted mean diameter of DHSA crystals

Fourier Transform – Infra Red Analysis

Figure 6 showed the typical FT-IR spectrum of the DHSA crystals produced. All ten DHSA samples (prepared using different crude DHSA to solvent ratios and different IPA concentrations) showed similar spectrum. In the FT-IR spectrum, the absorption band at 1620-1780 cm^{-1} was assigned to the carboxyl functional group while the band at 3300-3400 cm^{-1} was assigned to the hydroxyl functional group. The transmission peak for C-H bonding could be observed at 2800-3000 cm^{-1}.

Since all ten samples bore all the major adsorption bands expected in DHSA, it indicated that the different ratios and IPA concentrations used did not affect the chemical structure of the DHSA crystals at the temperature where the experiments were carried out. The DHSA produced from commercial grade palm oil based crude oleic acid bore three functional groups, *i.e.* one carboxyl functional group and two hydroxyl functional groups. The two hydroxyl groups were located at position-9 and position-10 respectively on an aliphatic 18-carbon chain.

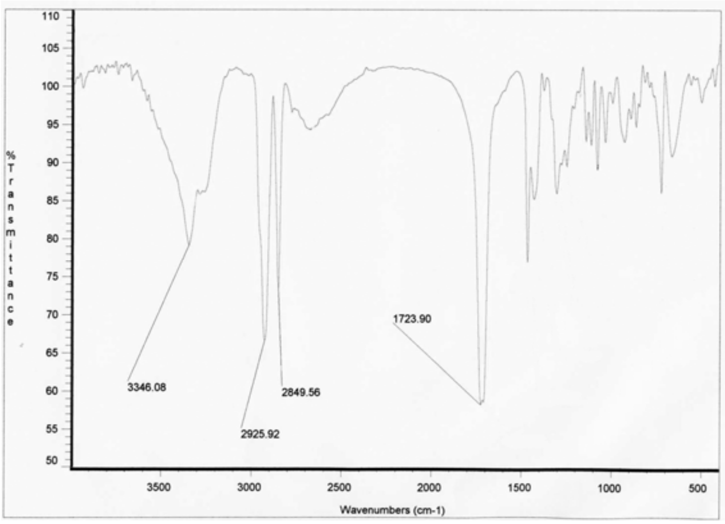

Figure 6: Typical FT-IR spectrum of the DHSA crystals

Scanning Electron Microscopy Analysis

Figure 7b and 7d showed the SEM photos of DHSA crystal particles at 2000× magnification for crude DHSA to solvent ratios of 1.0:1.0 and 1.0:1.5 respectively. Both ratios produced flake-like platelets that grew in a layer-by-layer fashion. The flowerlike structure was very similar to that of the desert rose structure which occurred among gypsum crystals in arid areas. Almost all of the flake-like platelets had the same crystallographic axes as those of the basal crystals. At high magnification, the platelets may appear to be piled up in unorganized manner but Figure 7a and 7c clearly showed that at a lesser microscopic scale, the crystal array were indeed organized, periodically repeating itself three dimensionally, as was expected in all crystals. The SEM photos also showed that the size of the crystal lump, the ‘desert rose’, produced with higher IPA concentration was smaller and more compact than the crystal lump produced with lower IPA concentration. This was in line with the PSD analysis findings as shown in Figures 5b – 5e.

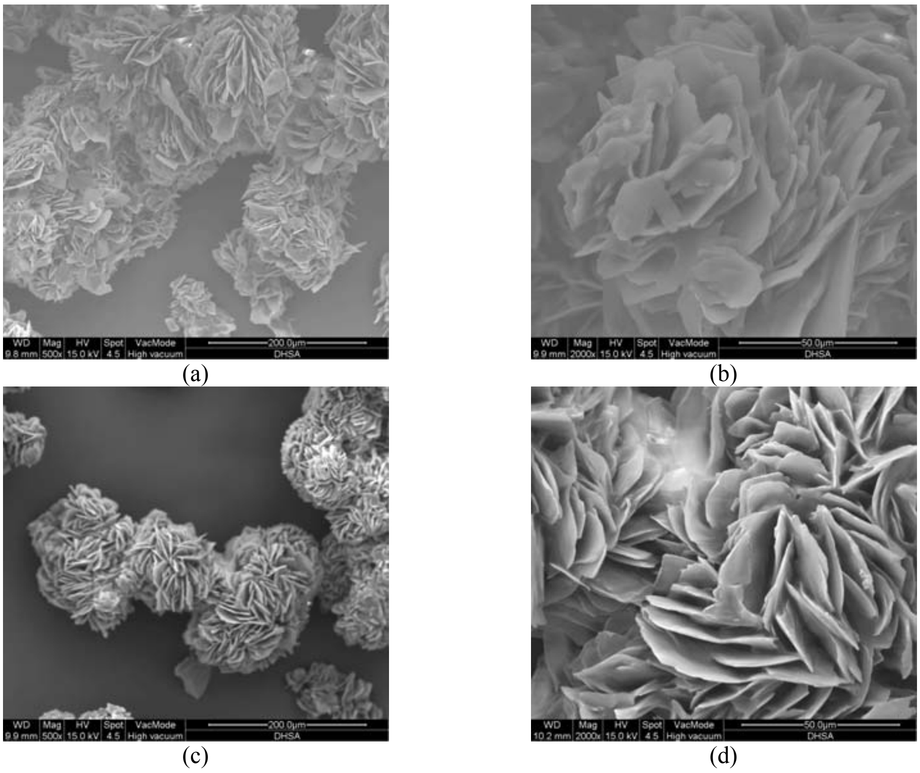

Figure 7: SEM photos of DHSA crystals: (a) DHSA to solvent ratio of 1.0:1.0, 500× magnification; (b) DHSA to solvent ratio of 1.0:1.0, 2000× magnification; (c) DHSA to solvent ratio of 1.0:1.5, 500× magnification, and (d) DHSA to solvent ratio of 1.0:1.5, 2000× magnification

CONCLUSIONS

Purification of crude DHSA produced from commercial grade palm oil based crude oleic acid through solvent crystallization employing IPA as solvent had been successfully carried out. The DHSA crystals obtained had been subjected to GC, PSD, FT-IR and SEM analysis. The results showed that the purity of the crystals increased with concentration of IPA used. Water acted as a binding agent that agglomerated the fine crystal particles. The results also showed that the IPA concentration of 80% produced the most desirable PSD quality while all concentrations of solvent used in the experiments did not affect the chemical structure of DHSA as the operating temperature was not high enough to trigger chemical reactions. From the SEM results, both solvent ratios used produced similar 'desert rose'-like crystals.

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