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PROPERTIES OF SODIUM SOAP DERIVED FROM PALM-BASED DIHYDROXYSTEARIC ACID

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ABSTRACT

Sodium soap of dihydroxystearic acid (DHSA) was prepared by reacting DHSA and sodium hydroxide (NaOH). The properties of the soap, such as foamability, detergency, biodegradability and wetting power were evaluated. DHSA soap had higher foamability and detergency than stearic acid soap, comparable to palm stearin sulphonated methyl ester (SME) at room temperature. DHSA soap degraded more than 60% in 28 days, but stearic acid soap only 30%. The wetting time for DHSA soap was 2 min, comparable to SME but faster than stearic acid soap. DHSA soap also exhibited good corrosion inhibition with a corrosion rate of 0.002 mm yr^{-1} at 100 ppm.

Keywords: soap, dihydroxystearic acid, foam, detergency, biodegradability.

INTRODUCTION

In its continuing efforts to promote the oil palm industry, the Malaysian Palm Oil Board (MPOB, formerly PORIM) has produced DHSA from palm oil. DHSA is expected to have a great commercial potential as its hydroxyl group and ester linkage provide reaction sites for the preparation of many useful industrial products. Further, the functionality may be modified at the carboxyl position by a host of reactions which, *inter alia*, is saponification with alkali or alkali plus metallic salts to form soluble and insoluble soaps, respectively.

Soap (sodium salt of fatty acid) is the oldest known surfactant and has been used since the Egyptian era (Kaoru, 1998). It is now used mostly as toiletry soap bars for body cleansers and sometimes for fabric detergents. In detergents, soap is sometimes formulated as a foam control agent (Kaoru, 1998; Fujimoto, 1985). Direct saponification from fats was used initially to make soap but, today, soap is obtained by neutralizing fatty acids with NaOH. As the salt of a weak acid (fatty acid) and strong base (NaOH), soap is alkaline (pH~10) in aqueous solution. The alkalinity favours detergency but can cause skin irritation and hair damage (Kaoru, 1998). In addition, soap is not tolerant of hard water and forms scum with calcium and magnesium ions (Jungermann, 1985; 1988; Zahariah, 1999).

In this study, the properties of sodium soap made from DHSA were evaluated. This work was part of a programme to prepare new derivatives of domestically available fatty acids for various applications, such as detergents, cosmetic/personal care products and lubricants.

MATERIALS AND METHOD

Materials

DHSA was prepared in the laboratory (Roila *et al*., 1998). SME was purchased from Chemithon, USA while stearic acid soap and C18-sulphonated methyl ester (C18-SME) were obtained from the Cosmetics and Detergent Group of MPOB. Calcium chloride ($CaCl_2.2H_2O$, 99%), barium chloride ($BaCl_2$ 99%) and NaOH (98%) were purchased from Merck, Germany,

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and magnesium sulphate ($MgSO_4.7H_2O$, 99%) from BDH Chemicals, England. All the other reagents - petroleum spirit, ethanol, sulphuric acid, hydrocholic acid - were of analytical grade and used as received.

Preparation of DHSA and 12-hydroxystearic Acid Soap

DHSA (50 g) was placed in a reaction flask. Depending on the mole ratio, a sufficient amount of 50% NaOH solution was added in 5 ml portions with continuous stirring. When the addition of NaOH was complete, the mixture was stirred for a further 45 min at 70°C - 75°C. The product obtained was dried to constant weight in an oven at 80°C. The preparation of 12-hydroxystearic acid soap followed the same procedure.

Determination of Free Caustic Alkalinity

Five grammes of soap were dissolved in 100 ml hot neutralized ethanol and 20 ml 10% barium chloride solution added. A pink colour of the solution indicated the presence of free caustic alkali. The solution was titrated immediately with 0.1N hydrochloric acid (HCl) until the colour disappeared (Milwidsky and Gabriel, 1994). The free caustic alkalinity was calculated by:

% free caustic alkalinity = (0.4V)/W

where

V = volume of 0.1N HCl (ml).
W = weight of sample (g).

Total Fatty Matter (TFM)

The TFM was determined by petroleum spirit extraction. Soap (50 g) was dissolved in 500 ml warm water and transferred to a separating funnel. Three to four drops of methyl orange indicator were added, followed by 4N sulphuric acid until the indicator colour changed from orange to pink. Petroleum spirit (100 ml) was added and the separating funnel shaken vigorously for 30 s. The solution was then allowed to stand for a few minutes until the fatty acid liberated soap formed a clear layer on top. The soap was skimmed off, washed with distilled water and dried to constant weight in an oven at 60°C.

Foaming Power and Foam Stability

Soap solution (200 ml 0.1% DHSA) was poured into a 500 ml measuring cylinder. A foam was whipped up with 30 vigorous strokes of a perforated plunger. The foam volume was noted after 30 s and 5.5 min. The foam stability was expressed as a ratio of the foam volume at 5.5 min to that at 30 s (V_5/V_0).

Detergency

Preparation of hard water. A stock solution of hard water (equivalent to 5000 ppm $CaCO_3$) was prepared by dissolving 4.41 g $CaCl_2.2H_2O$ and 4.93 g $MgSO_4.7H_2O$ in 1000 ml deionized water. To prepare water of other hardness (50, 150 and 350 ppm), appropriate aliquots of the stock solution were diluted with deionized water.

Detergency test. The detergency of soap solutions containing 50 ppm, 150 ppm and 350 ppm $CaCO_3$ at room temperature on soil cloth, AS9, was determined by a Terg-o-tometer. Before washing, the reflectance of the AS9 was measured using a Macbeth Colour-Eye 3000 spectrophotometer. The washing procedure described by Salmiah *et al*. (1998) was followed. The detergency, or % soil removal, was calculated using the formula:

% soil removal = [(AW-BW)/(OC-BW)] x 100

where

AW = reflectance of the soil cloth after washing.
BW = reflectance of the soil cloth before washing.
OC = reflectance of original cloth.

Surface Tension

DHSA soap (1.08 g, equivalent to 1% TFM) was weighed and dissolved in 100 ml deionized water. The original solution was diluted to concentrations from 0.001% to 0.1% TFM. The surface tensions of the aqueous solutions were measured with a KRUSS K-10 surface tensiometer using the Du Nouy ring technique. The measurements were carried out at 25°C with the instrument calibrated against deionized water.

Corrosion Inhibition Test

Various concentrations (20, 40, 60, 80, 100, 120 and 150 ppm) of DHSA soap solution were prepared by dissolving the soap in deionized water. Glass cells were filled with the solutions and a mild steel electrode immersed in each. The mild steel used contained (%) C, Si $\leq$ 0.1; Mn 0.2 - 0.45; P $\leq$ 0.03; S $\leq$ 0.035 and Al $\leq$ 0.02. Distilled water was used as the reference to compare the corrosion on the metal surface.

RESULTS AND DISCUSSION

Properties of Soap

Table 1 shows the pH, free caustic alkalinity and TFM for DHSA soap prepared from 1.0 to 8.0 mole ratios of NaOH. Increasing the mole ratio of NaOH

TABLE 1. PROPERTIES OF DHSA SODIUM SOAP MADE FROM DIFFERENT MOLE RATIOS OF NaOH:DHSA

Mole ratio (NaOH:DHSA)	PH	Free caustic alkalinity, %	TFM, %
8.0:1.0	11.28	20.28	45.98 (54)
4.0:1.0	10.97	12.87	66.46 (73)
3.0:1.0	10.54	5.94	71.64 (81)
2.0:1.0	10.04	1.51	70.99 (89)
1.5:1.0	9.63	0.37	92.87 (94)
1.0:1.0	7.91	0.05	87.08 (100)

Note: (..) theoretical value of TFM.

to DHSA decreased TFM, while pH and free caustic alkalinity increased. The lower TFM at higher concentration of NaOH was due to the presence of unreacted NaOH in the mixture. Soap produced from the NaOH:DHSA ratio of 1.5 gave the highest TFM, and was used for further analysis.

Foam

Foam is an important aspect of detergent products and surfactants are mainly responsible for its generation. Two important properties are the speed of foam generation and foam stability. The factors that affect these properties are soil in the wash load and the concentration of hardness ions (Piyali *et al.*, 1999). The foam behaviour of DHSA soap, stearic acid soap and SME in the presence and absence of hardness ions was compared.

Figure 1 shows the foam formation by DHSA soap produced from various mole ratios of NaOH:DHSA. There was no great variation in the foam formation between the ratios 1.5 to 3.0, but a small decline at the higher ratios. Hardly any foam was formed at the 1.0 ratio. The foam stability of the soaps from mole ratios 1.5 to 3.0 was good.

The foam formation and stability of DHSA soap were compared with those of stearic acid soap and SME. In the absence of Ca^{2+} ions (*Figure 2a*), all the foam volumes increased gradually with the surfactant concentration. The foam volume for DHSA soap was higher than that for stearic acid soap and comparable to that for SME at the higher concentrations. In 200 ppm Ca^{2+} (*Figure 2b*), the foam volumes were lower but (for DHSA soap and SME) generally followed the same trend as in the absence of Ca^{2+} ions. The exception was stearic acid soap which did not form any foam at all.

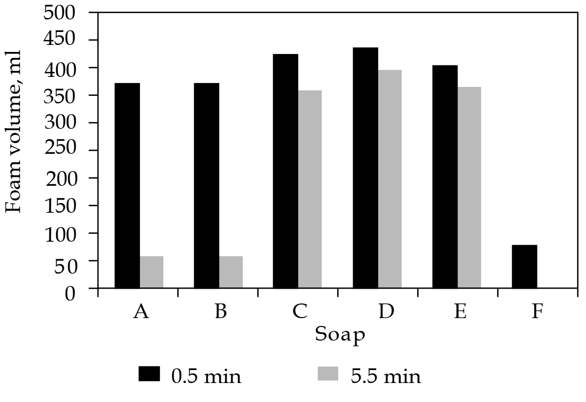

Figure 1. Foam formation of DHSA soap produced from various mole ratios of NaOH:DHSA: A (8:1), B (4:1), C (3:1), D (2:1), E (1.5:1), F (1:1).

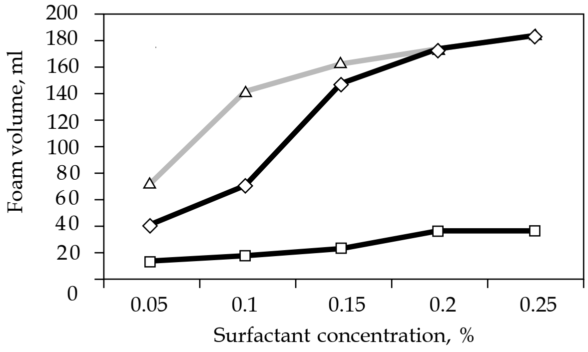

Figure 2a. Foam formation by DHSA soap, stearic acid soap and SME with concentration in the absence of Ca^{2+} ions. DHSA soap (◇), stearic acid soap (□) and SME (△).

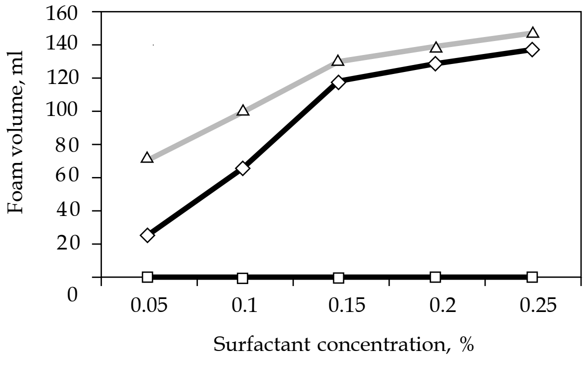

Figure 2b. Foam formation by DHSA soap, stearic acid soap and SME with concentration in 200 ppm Ca^{2+} ions. DHSA soap (◇), stearic acid soap (□) and SME (△).

Figures 3a and *b* show the foam stability of the surfactants in the presence and absence of Ca^{2+} ions.

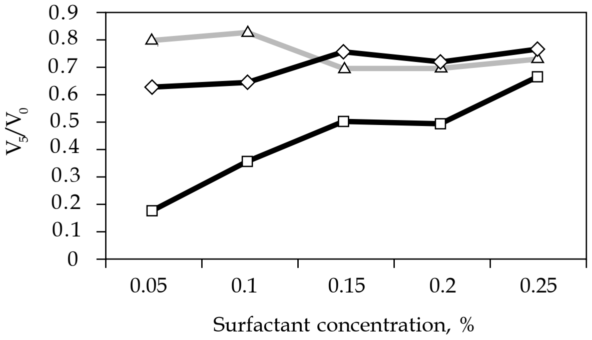

Figure 3a. Foam stability of DHSA soap, stearic acid soap and SME with concentration in the absence of Ca^{2+} ions. DHSA soap (◇), stearic acid soap (□) and SME (△).

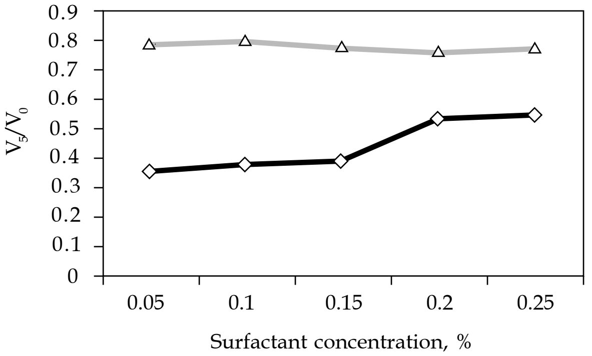

Figure 3b. Foam stability of DHSA soap and SME with concentration in 200 ppm Ca^{2+} ions. DHSA soap (◇) and SME (△).

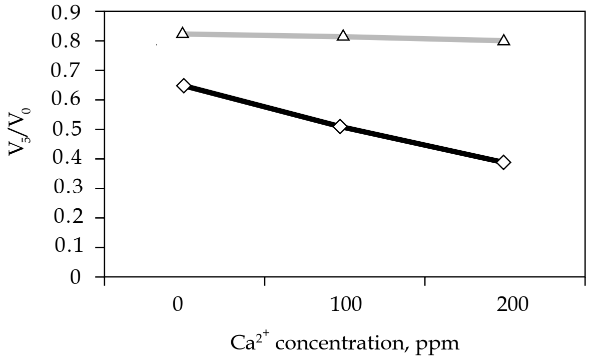

Figure 4. Foam stability of DHSA soap and SME with concentration of Ca^{2+}. DHSA soap (◇) and SME (△).

Without Ca^{2+}, DHSA soap and SME had similar foam stability, but with Ca^{2+}, SME had better foam stability as it was not affected at all by the Ca^{2+} ions (*Figure 4*).

Detergency

Detergency is defined as the removal of unwanted substances from a solid surface brought into contact with a liquid. The removal of soil from textiles depends on several factors, such as the detergent, mechanical action during washing and the substrate (Cutler and Davis, 1975; Cutler and Johnson, 1987).

Figure 5 shows the detergency of DHSA soap, stearic acid soap, SME, C18-SME and 12-hydroxystearic acid soap at room temperature as measured by the Terg-o-tometer. DHSA soap removed more soil than stearic acid soap, comparable to C18-SME and 12-hydroxystearic acid soap but less than SME (RT) *(Figure 5a)*. However, at 45°C, DHSA soap was less effective than stearic acid soap (*Figure 5b*). Detergency decreased with increasing water hardness for all the surfactants. Calcium and magnesium ions are known to interact with anionic surfactants and precipitate them as insoluble salts resulting in a loss of detergency (Kaoru, 1998; Fujimoto, 1985).

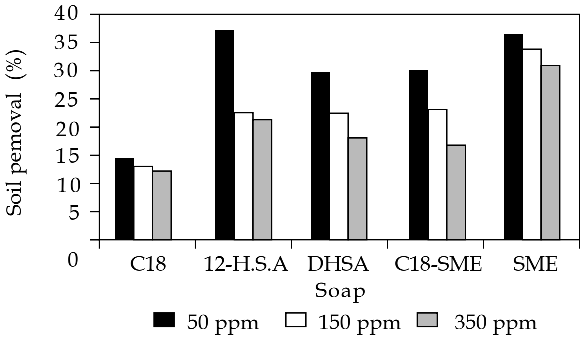

Figure 5a. Detergency of soaps and SME in various water hardness(as $CaCO_3$) at room temperature. Stearic acid soap (C18), 12-hydroxystearic acid soap (12-H.S.A), DHSA soap (DHSA), C18-SME, palm stearin SME (SME).

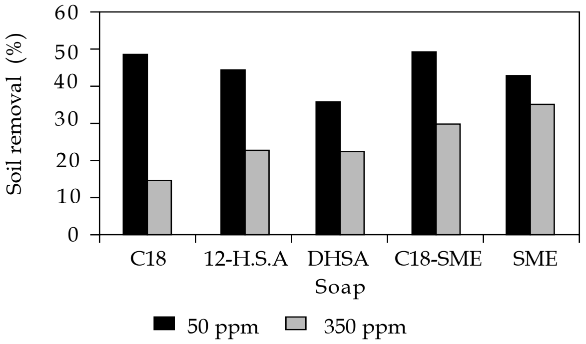

Figure 5b. Detergency of soaps and SME at 45°C in various water hardness (as $CaCO_3$). Stearic acid soap (C18), 12-hydroxystearic acid soap (12-H.S.A), DHSA soap (DHSA), C18-SME, palm stearin SME (SME).

Surface Tension

The surface tension of a surfactant solution is probably the most common physical property used to characterize the surfactant. Since the surface tension of a liquid is determined by the energy of the molecules in the interfacial region, displacement of the surface liquid molecules by an adsorbed solute will directly affect its value. It is the relationship between the chemical structure of an adsorbing molecule and the rate and extent of adsorption under given circumstances that differentiates the various surfactant types and determines their utility in applications where lowering the surface tension is of importance (Myers, 1988).

The surface tensions for DHSA soap, stearic acid soap and SME as a function of their concentrations were determined. *Figure 6* shows a typical curve of surface tension *vs.* concentration. From the graph, the critical micelle concentration (CMC) for DHSA soap and SME can be easily determined - they were at about 0.01% concentration with surface tensions of about 42 and 40 mN m^{-1}, respectively. However, the CMC for stearic acid soap was difficult to identify. *Figure 7* shows the general correlation between surface tension and detergency or soil removal. A higher detergency resulted from a lower surface tension, similar to the finding by Zahariah *et al.* (1999).

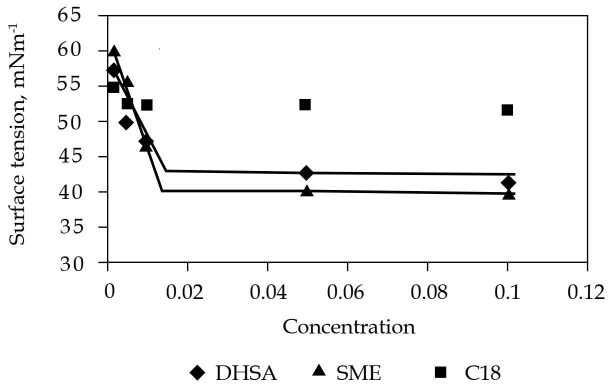

Figure 6. Surface tension of DHSA soap, stearic acid soap and SME with concentration. DHSA soap (◆), stearic acid soap (■) and SME (▲).

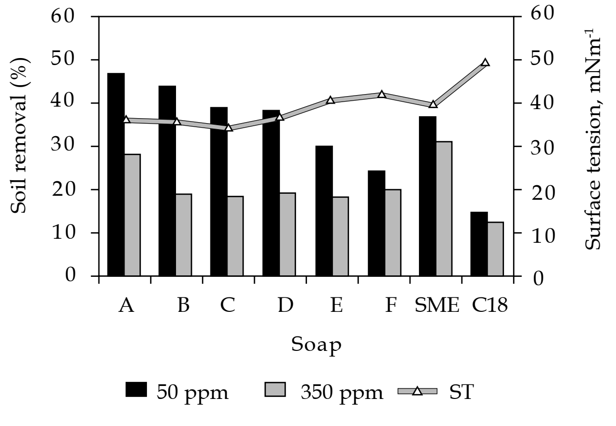

Figure 7. Correlation between surface tension and detergency of soap with various mole ratios of NaOH:DHSA in 50 ppm and 350 ppm $CaCO_3$ water hardness. A (8:1), B (4:1), C (3:1), D (2:1), E (1.5:1), F (1:1), SME (palm stearin sulphonated methyl ester), C18 (stearic acid soap).

Biodegradation

The biodegradability of DHSA soap was compared to that of stearic acid soap. The samples were subject to the OECD 301D closed bottle test method over 28 days with sodium acetate as the reference. The DHSA soap degraded more than 60% (*Figure 8a*) but the stearic acid soap only 30% (*Figure 8b*). Thus, the latter was not readily biodegradable. The low biodegradability of stearic acid soap was not caused by any inhibitory effect as more than 25% of its degradation occurred within 14 days, but probably by the insolubility of the soap at the temperature of the test.

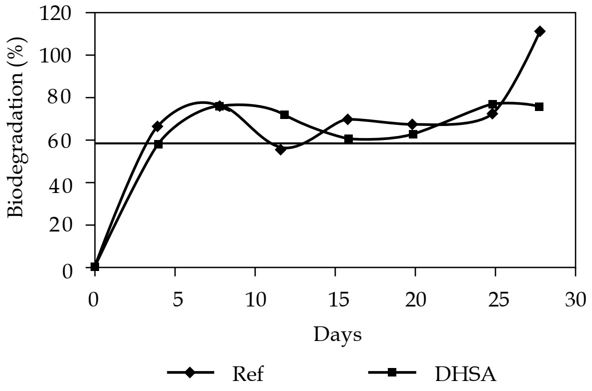

Figure 8a. Biodegradation profile of DHSA soap.

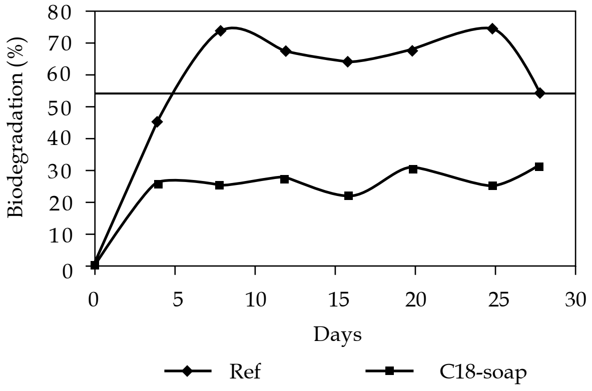

Figure 8b. Biodegradation profile of stearic acid soap.

Wetting Properties

The wetting power of DHSA soap, stearic acid soap, 12-hydroxystearic acid soap and SME was examined. Solutions of 200 ml (0.1% TFM) of each sample were prepared in different containers. Patches (1 x 1 cm) of unsoiled cloth were cut and dropped into each solution. The wetting power was the times taken by the patches to fully sink to the bottom of their containers.

DHSA soap had a higher wetting power than

Figure 9. Wetting power of DHSA soap, SME, stearic acid soap and 12-hydroxystearic acid soap.

stearic acid soap, comparable to that of SME (*Figure 9*). This was attributed to the hydroxyl group in the middle of its hydrophobic chain as such surfactants have a stronger wetting power than those with the hydrophilic groups attached to the ends of their hydrophobic groups (Fujimoto, 1985).

Corrosion Inhibitor Properties

The corrosion inhibition of DHSA soap was measured using the electrochemical method described in Materials and Methods. DHSA soap exhibited considerable corrosion inhibition with a greatly reduced corrosion rate of 0.002 mm yr^{-1} at 100 ppm concentration compared to 0.1 mm yr^{-1} in distilled water (*Figure 10*).

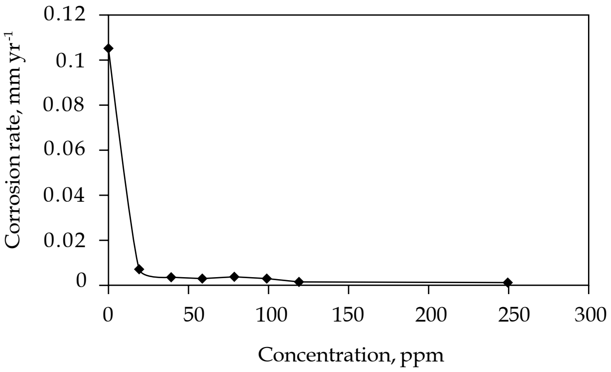

Figure 10. Corrosion rate by DHSA soap with concentration.

CONCLUSION

The sodium soap of DHSA was synthesized. It showed better detergency than stearic acid soap at room temperature and was more biodegradable. It also exhibited corrosion inhibition with a corrosion rate of only 0.002 mm yr^{-1} at 100 ppm concentration. Thus, DHSA soap can be a satisfactory surface-active agent in many applications, such as detergents, corrosion inhibitors and cosmetics/personal care products. The results were sufficiently promising to warrant further investigation.

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