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ALKANOLAMIDES FROM 9,10-DIHYDROXYSTEARIC ACID

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ABSTRACT

Alkanolamides of dihydroxystearic acid (DHSA-alkanolamides) have been synthesized. The factors that may affect their esterification, such as reaction time and temperature, were studied. Given the same time course, ethanolamine gave higher yield due to its shorter carbon chain compared to that of propanolamine. The products were identified by Fourier transform infrared spectroscopy, gas chromatography as well as nuclear magnetic resonance spectroscopy. From the gas chromatography, DHSA-ethanolamide and DHSA-propanolamide were detected at retention times of 15.62 min and 16.61 min, respectively. These compounds were found to be non-irritants to the skin and biodegraded more than 60% in 20 days.

Keywords: amidation, alkanolamines, dihydroxystearic acid, fatty alkanolamides.

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INTRODUCTION

Fatty alkanolamides are compounds that exhibit low reactivity and high thermal stability. Their chemical properties vary, depending on the lengths of their hydrocarbon chains and the nature of the substituent on the nitrogen atom (Bilyk *et al.*, 1992). Alkanolamides are of great interest for applications requiring relatively stable emulsifiers because their amide linkages are very stable chemically and not easily degraded in alkaline media (Muargard *et al.*, 1997). They have a broad spectrum of uses such as in shampoos, detergents, cosmetics, lubricants, foam control agents and water repellents (Hakan, 2004).

The most familiar monoalkanolamides are those based on ethanolamine and propanolamine. These are produced from fatty acids or fatty methyl esters and alkanolamines, by heating at 140°C-160°C for 6 hr -12 hr (Feairheller *et al.*, 1994). However, there is no complete data on the characterization of amide derived from dihydroxystearic acid (DHSA). Therefore, this work focuses on the synthesis and characterization of monoalkanolamides from DHSA (*Figure 1*).

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MATERIALS AND METHODS

Materials

DHSA was prepared in the laboratory (Roila *et al.*, 1998). Ethanolamine and propanolamine were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. All the other reagents were of analytical grade and used as received.

General Procedure for the Synthesis of DHSA-Alkanolamide

The experiments were carried out in a 250 ml three-necked round bottom flask equipped with magnetic stirrer, a thermometer and a condenser. DHSA and alkanolamine were placed in the flask and heated to the desired temperature. An oil bath was used to maintain a constant temperature. The reaction mixture was stirred continuously for a pre-determined reaction period. The progress of reaction was monitored by analysing the amount of unreacted DHSA in the reaction mixture by a titrimetric method. For purification, the product was dissolved in a mixture of methanol and chloroform

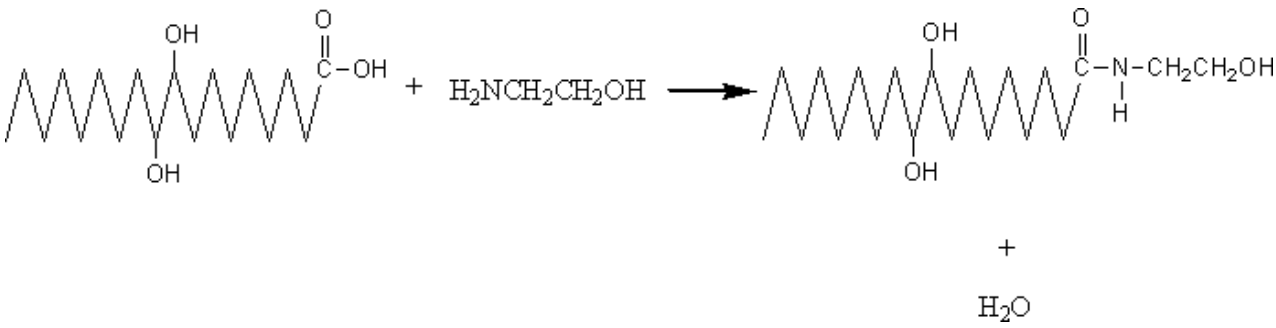

Figure 1. Reaction scheme of DHSA and ethanolamide.

(50:50, vol/vol). The solvent was then eliminated by evaporation in a rotovap. Acetonitrile was added to the resultant solid. The solution was cooled in an ice-bath. The acid remained soluble at this low temperature but the amide precipitated and was subsequently recovered by filtration through a filter paper.

Product Identification

The isolated product was identified by spectra studies (Fourier transform infrared - FTIR), nuclear magnetic resonance (NMR) and gas chromatography (GC). FTIR was recorded on a Nicolet Magna-IR550 (Nicolet, Madison, WI) spectrophotometer. The NMR spectra were recorded on a JOEL ECA-400 spectrometer at 400 MHz. The chemical shifts were expressed in ppm with tetramethylsilane as internal standard. Deuterated chloroform ($CDCl_3$) was used as a solvent.

GC analysis was carried out using a Shimadzu GC-17A GC. The trimethylsilyl (TMS) derivatives of DHSA-alkanolamides were separated on a non-polar column, BPX-5 (30 m x 0.53 mm x 1.0 µm), with helium as the carrier gas at a flow rate of 16 ml min^{-1}. The oven was programmed to hold at 150°C for 1 min, followed by ramping from 150°C to 290°C at 10°C min^{-1}. The final temperature (290°C) was held for 30 min. The injector and flame-ionization detector were set at 300°C.

Surface tension measurements (ring method) were conducted with a Krüss (Charlotte, NC) Digital Tensiometer K10T. The required sample was weighed and then dissolved in deionized water; the original solution was then diluted to various concentrations, and the surface tensions of these solutions were determined. All the data points were determined from triplicate measurements.

Irritancy Test of DHSA-Alkanolamides

Dermal irritancy of DHSA-alkanolamide was assessed using the Irritection Assay System, which consists of a test kit, instrumentation and computer (In Vitro International, Irvine, CA). Samples were weighed for four concentrations 50, 75, 100, 125 mg and placed into the membrane discs. The reagent and blanking buffer (1250 µl) were added to a 24-well assay plate. The membrane discs that contained the samples of various concentrations were inserted into the corresponding blank and test sample wells of the plate. The assay plate was then incubated at 25°C for 24 hr. After this time, the membrane discs were removed from the assay plate and 250 µl of reagent plus blanking buffer transferred into a 96-well reading plate. This plate was inserted into the MRX Microplate Reader (Dynex Technologies, Inc. Chantilly, VA).

RESULTS AND DISCUSSION

Acylation of Alkanolamines and Dihydroxystearic Acid

Figure 2 shows the percentage conversion of alkanolamides versus time. Both the reactions progressed rapidly in the first 15 min but thereafter slowed down. The conversion was as high as 95% for the reaction between DHSA and propanolamine and, 98% for DHSA and ethanolamine after 2 hr reaction time. The reaction between DHSA and ethanolamine gave higher yield than that of DHSA with propanolamine. This was due to ethanolamine having a shorter chain and being easier to form an amide bond with DHSA.

The results suggested that a reaction time of half an hour sufficed for conversion, since product yields of 77% and 87% of DHSA-propanolamide and DHSA-ethanolamide, respectively, were already obtained. However, the products may consist of amine soap, alkanolamide, aminoester and esteramide. Fortunately, the amine soap and esteramide can be minimized by a longer reaction time and curing the reaction mixture at elevated temperature can minimize aminoester (Cross, 1997).

Increasing the reaction temperature increased the conversion (data not shown). The reaction at < 150°C was not carried out because even the conversion at 150°C was very much lower than that from 180°C.

Another reason was that, there was a possibility of producing a mixture of amine soap, esteramide, alkanolamide and aminoester at the lower temperature.

Structural Elucidation

The results obtained from the FTIR spectra in the KBr pellets were as follows:
DHSA-ethanolamide, (OH) = 3300 cm^{-1}, (CH) = 2850 cm^{-1}-2920 cm^{-1}, (CO-N) =1646 cm^{-1}, (N-H) =1560 cm^{-1}, (C-N) = 1138 cm^{-1}. DHSA-propanolamide, (OH) = 3300 cm^{-1}, (C-H) = 2852 cm^{-1} – 2922 cm^{-1}, (CO-N) = 1644 cm^{-1}, (N-H) = 1556 cm^{-1}, (C-N) = 1136 cm^{-1}. GC chromatograms for the purified products, DHSA-ethanolamide and DHSA-propanolamide, appeared at the retention times (RT) 15.62 min and 16.61 min, respectively (*Figures 3* and *4*).

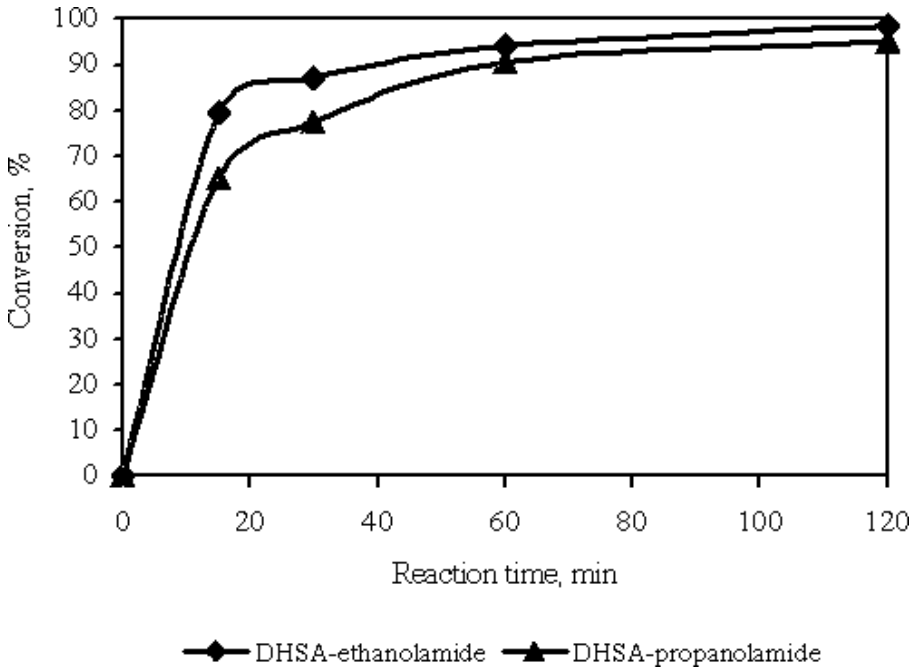

Figure 2. Effect of reaction time on amidation between DHSA and alkanolamines.

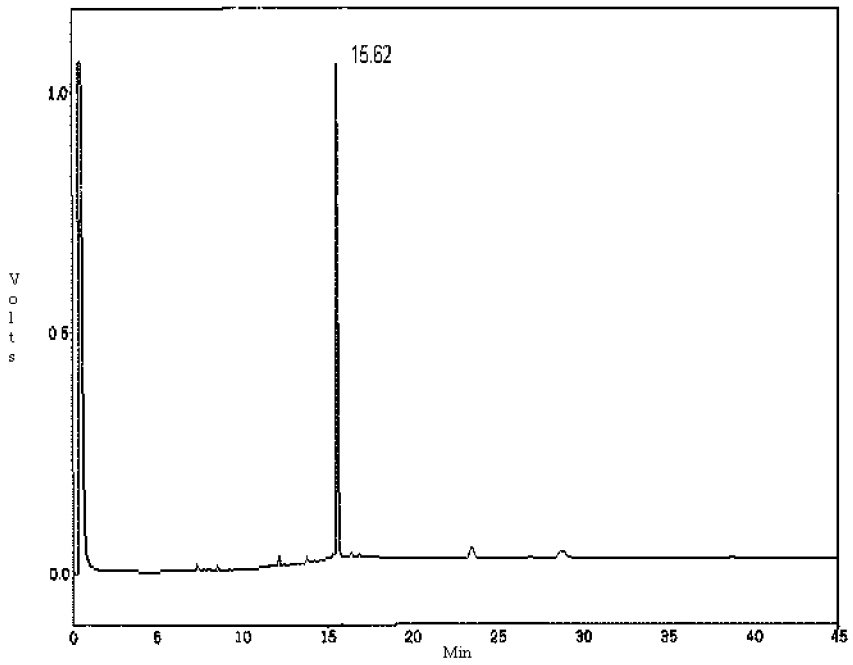

Figure 3. GC chromatogram of purified DHSA-ethanolamide.

The NMR spectra for both DHSA-alkanolamides were very similar. The presence of CH_3 saturated protons were observed at 0.89 ppm while CH_2 saturated protons covered the range from 1.30-1.80 ppm. The hydrogen attached to the amide functional group H-NC=O was found at 5.90 ppm. As for ^{13}C-NMR (*Figure 5*), the existence of the C-N bond was detected at 59.18 ppm. The signal resonating at 76.67 ppm showed the presence of hydroxyl groups. C=O for the product was slightly shifted to 174.58 ppm compared to 177.3 ppm for the C=O of DHSA.

Properties of DHSA-Alkanolamides

The properties of DHSA-alkanolamides, such as their hydroxyl value, acid value and melting point, are shown in *Table 1*. The acid value decreased as the reactants converted to the product. This indicates the formation of amide compounds. The hydroxyl value also decreased with the increasing molecular weight of the product.

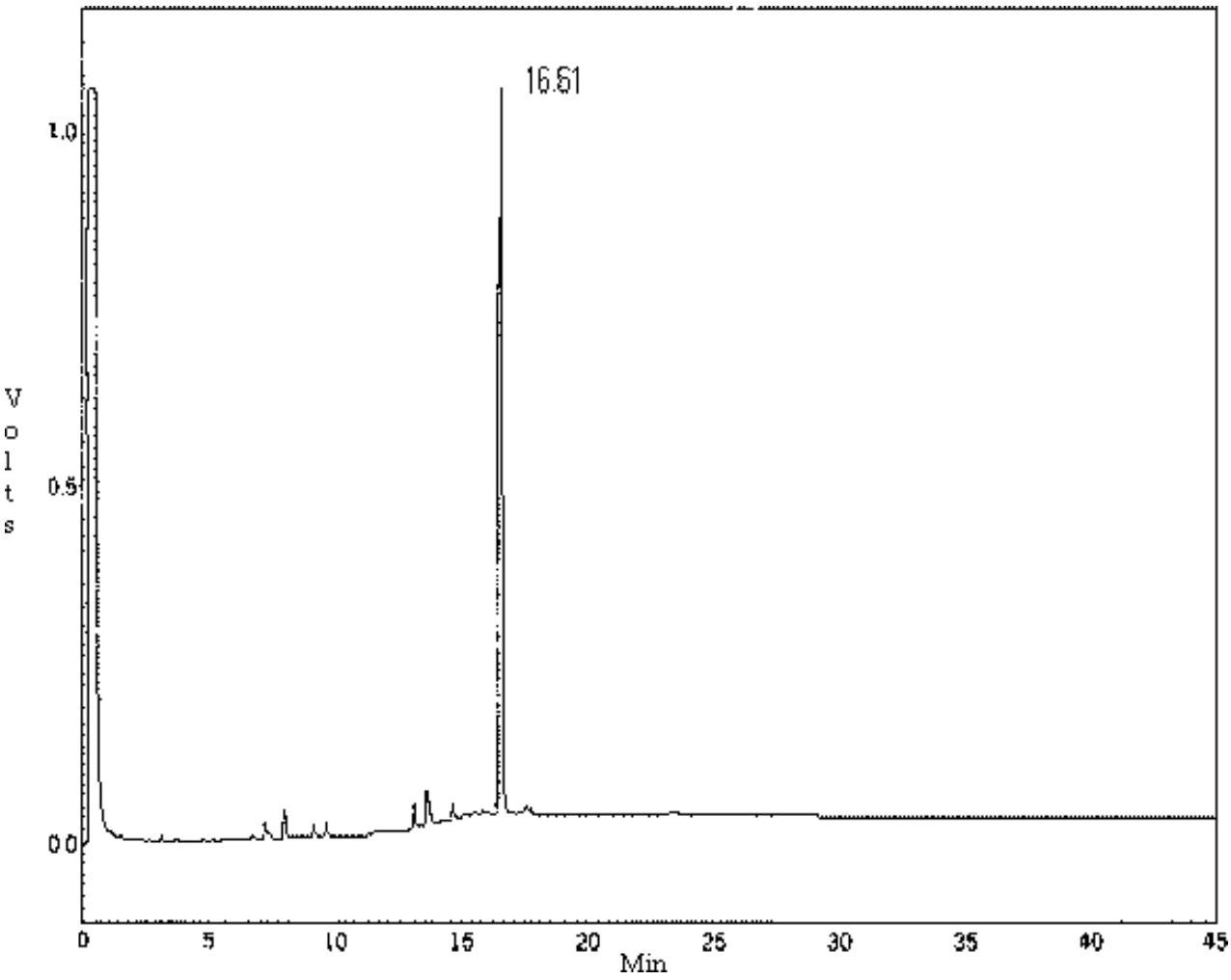

Figure 4. GC chromatogram of purified DHSA-propanolamide.

TABLE 1. PROPERTIES OF DHSA-ALKANOLAMIDES

Parameter	Alkanolamide of DHSA	
	Monoethanolamide	**Monopropanolamide**
Colour	yellowish	yellowish
Acid value, mgKOH g^{-1}	1.05	2.18
Hydroxyl value, mgKOH g^{-1}	281.25	267.71
Melting point, °C	83-85	84-86
Ecotoxicity, LC_{50}, mg $litre^{-1}$	22.63	22.63
Solubility	Soluble in water	Soluble in water

Surface Tension and Foaming Properties

The surface tension for deionized water (70.19 mN m^{-1}) was used as reference for the initial surface tension before adding the product. The critical micelle concentrations (CMC) were determined graphically by plotting the surface tension against concentration of the DHSA-alkanolamide solutions. The CMC of the product was about 0.005% (wt/vol) with a surface tension of about 35 mN m^{-1} for DHSA-ethanolamide and 39 mNm^{-1} for DHSA-propanolamide (*Figure 6*).

The foaming properties were examined by pouring the surfactant solution (0.1% DHSA-alkanolamides) into a 500 ml measuring cylinder and foam whipped up with 30 vigorous strokes of a perforated plunger. DHSA-ethanolamide had better foaming power and stability (*Figures 7* and *8*). The foaming power and stability increased with the concentration of surfactant. DHSA-alkanolamides could be used as foam improver when added to the solution containing sodium dodecyl sulphate (1%, wt/vol), *Figure 9*. Raymond and Prislinger (1989) reported a similar observation on the foaming properties of blended alkanolamides and various fatty alcohol sulfates.

Irritancy Property

The irritancy property of DHSA-alkanolamides was determined according to the Dermal Irritection Assay Method as described in the Materials and Methods section. This test is a useful screening tool in all stages of raw material selection, product formulation development, and final product selection. The DHSA-alkanolamides were predicted to be non-irritants with Human Irritancy Equivalent (HIE) scores < 0.90 at all the concentrations tested (*Table 2*). This result showed the skin compatibility of the DHSA-alkanolamides. Therefore, they have potential for use in cosmetics and personal care products.

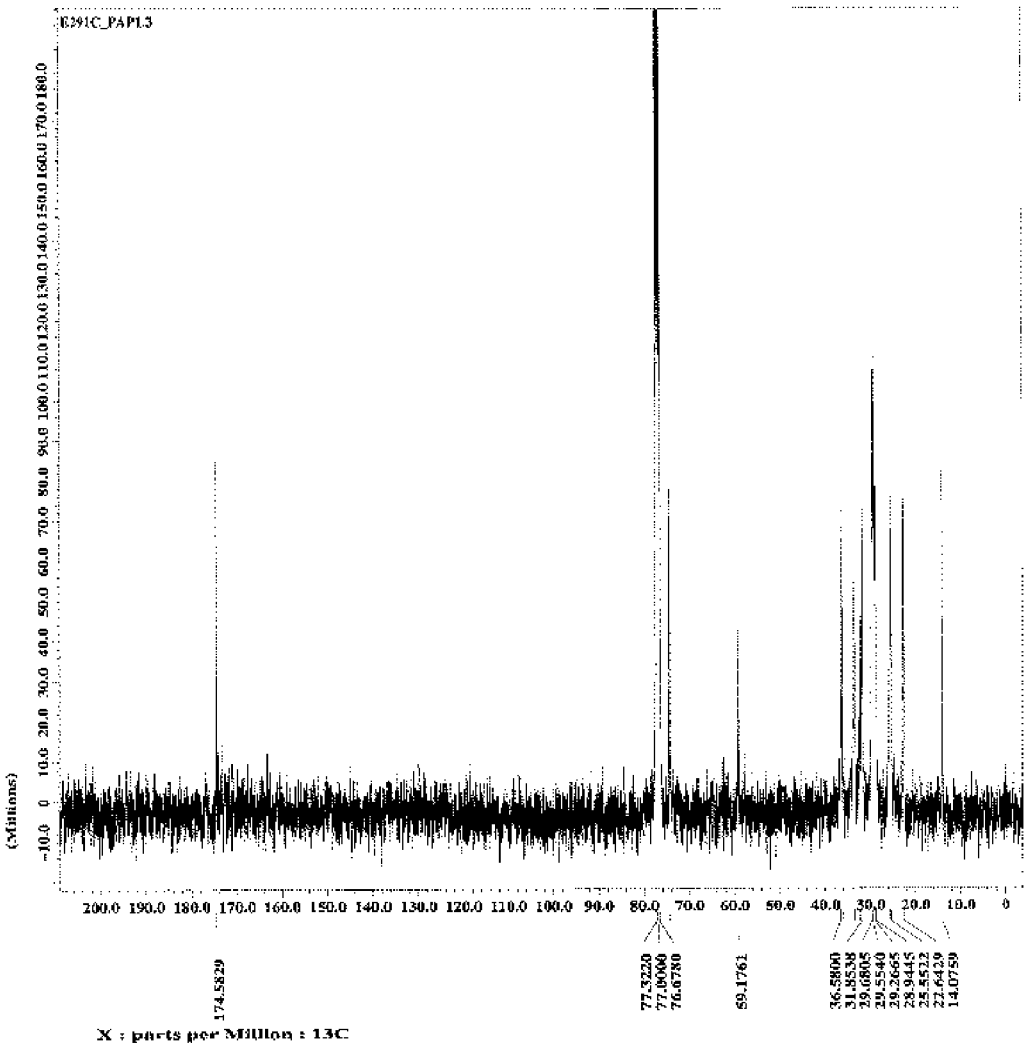

Figure 5. ^{13}C-NMR spectrum of purified DHSA-ethanolamide.

TABLE 2. IRRITANCY TEST OF DHSA-ALKANOLAMIDES[a,b]

Sample	Dose,mg	Irritancy score	Irritancy classification
DHSA-ethanolamide	50	0.76	Non-irritant
	75	0.78	Non-irritant
	100	0.70	Non-irritant
	125	0.68	Non-irritant
DHSA-propanolamide	50	0.50	Non-irritant
	75	0.68	Non-irritant
	100	0.79	Non-irritant
	125	0.77	Non-irritant

Notes: [a]Data from single analyses.
[b]Data obtained using the Irritection Assay System (In Vitro International, Irvine, CA) as described in the Materials and Methods section.

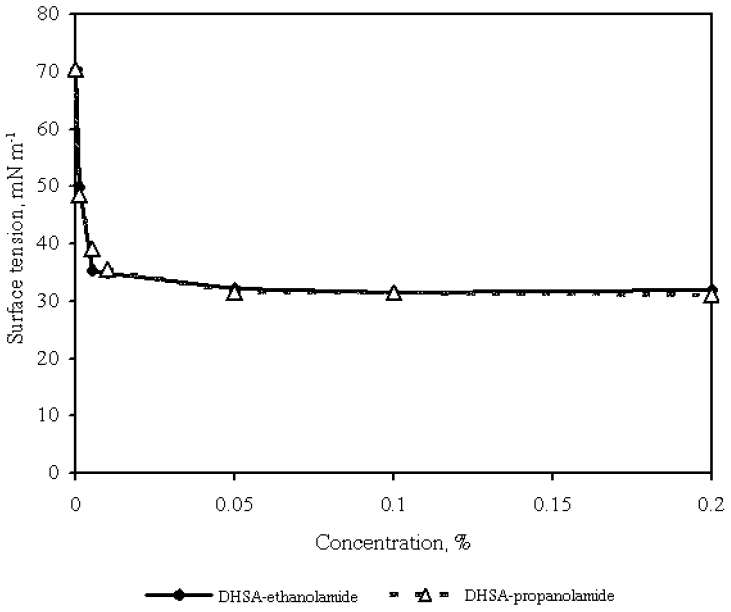

Figure 6. Surface tension vs. concentration of DHSA-alkanolamides.

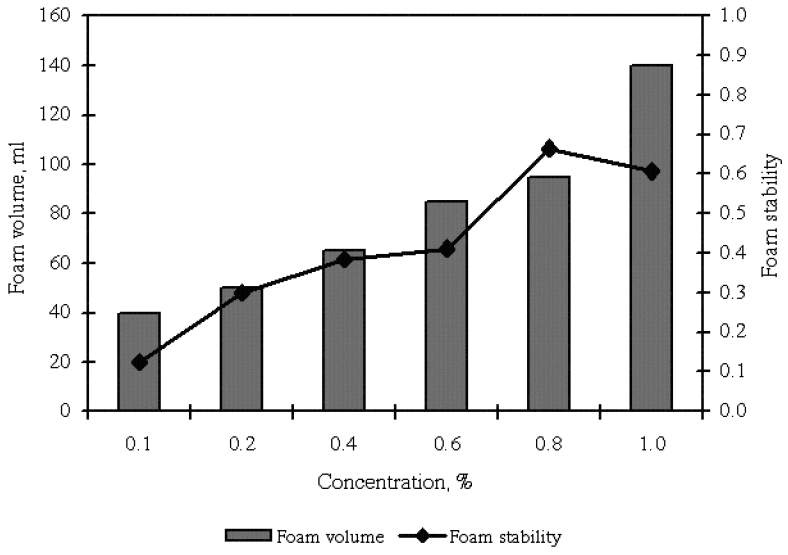

Figure 7. Foaming power and stability of DHSA-ethanolamide at various concentrations.

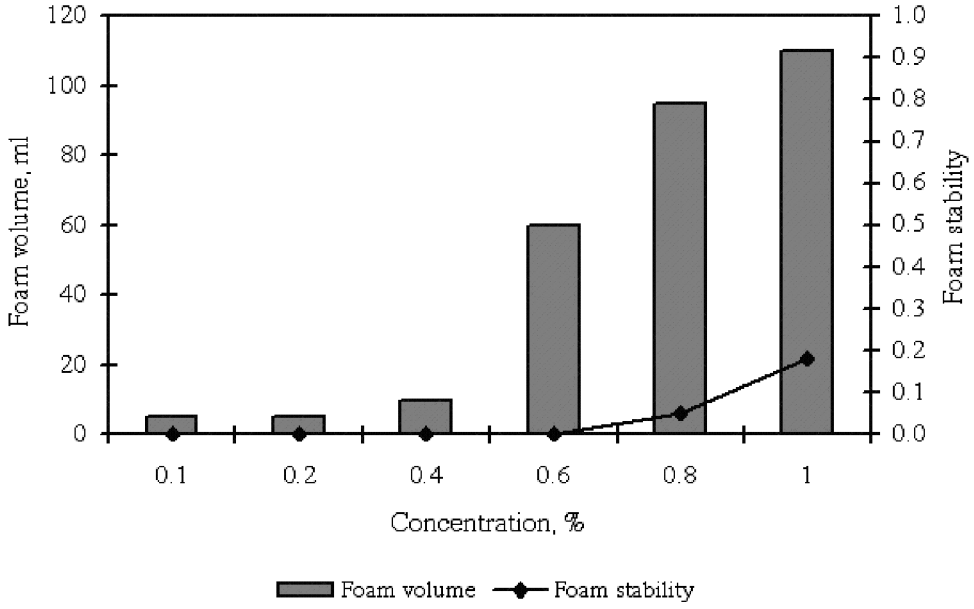

Figure 8. Foaming power and stability of DHSA-propanolamide at various concentrations.

Biodegradation

A quick and complete biodegradation after use is one of the indispensable factors for the next generation surfactants, because they are generally difficult to recover or recycle. The biodegradability of DHSA-alkanolamides was evaluated using the OECD 301D Closed Bottle Test method. *Figure 10* shows the time course of the biodegradation of the DHSA-alkanolamides based on their biochemical oxygen demand (BOD) and theoretical oxygen demand (ThOD). All the samples were more than 60% degraded in 20 days, which is considered readily biodegradable.

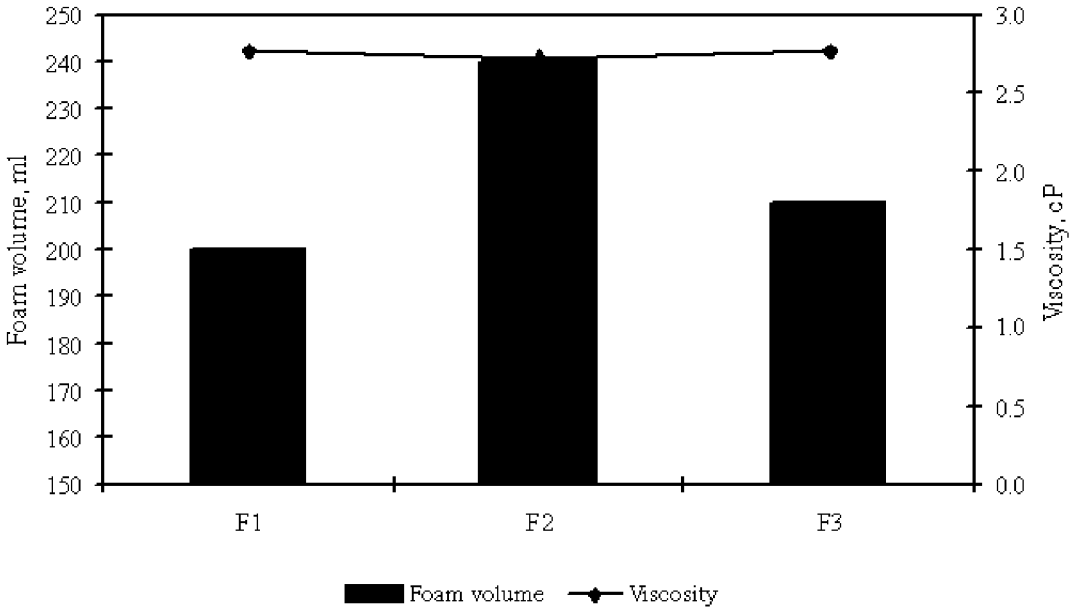

Figure 9. Foaming properties of simple formulations using DHSA-alkanolamides as additives. F1: sodium dodecyl sulphate 1%, water 99%; F2: sodium dodecyl sulphate 1%, DHSA-ethanolamide 0.5%, water 98.5%; F3: sodium dodecyl sulphate 1%, DHSA-propanolamide 0.5%, water 98.5%.

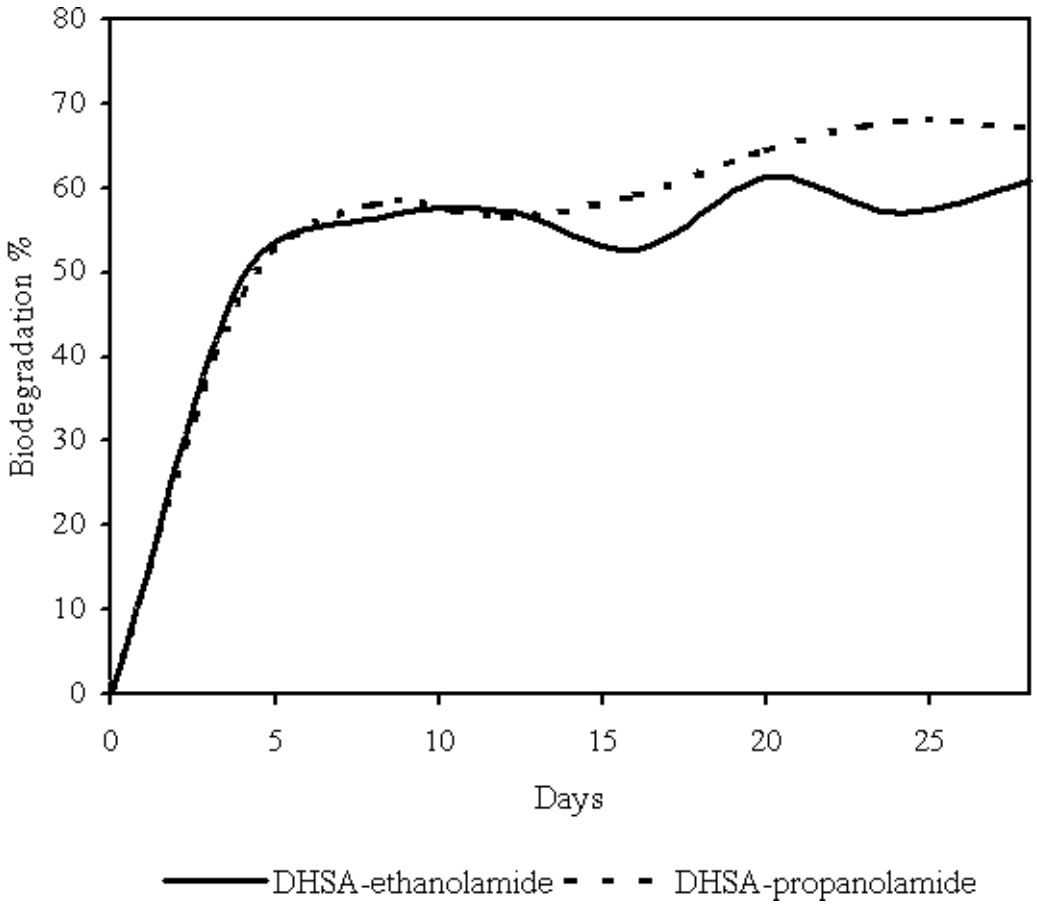

Figure 10. Biodegradation profile of DHSA-alkanolamides.

CONCLUSION

DHSA-alkanolamides were synthesized at moderate condition with high percentage of conversion. These compounds were found to be non-irritants to the skin and degraded more than 60% in 20 days

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