



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS OF BROMINATED C-18 FATTY ACIDS AND
SURFACTANT PROPERTIES OF THEIR SODIUM SALTS**

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**SYNTHESIS OF BROMINATED C-18 FATTY ACIDS AND SURFACTANT
PROPERTIES OF THEIR SODIUM SALTS**

By

STEVEN BAPTIST

**Thesis Submitted in Fulfilment of the Requirements for
the Degree of Master of Science in the Faculty of
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LIST OF ABBREVIATIONS

A1	Oleic Acid
A2	Oleic Soap
B1	Brominated Oleic Acid
B2	Brominated Oleic Soap
C1	Stearic Acid
C2	Stearic Soap
D1	Brominated Stearic Acid
D2	Brominated Stearic Soap
μ	conductivity
γ	surface tension
μ_{cmc}	conductivity at the CMC
γ_{cmc}	surface tension at the CMC
CMC	critical micelle concentration
ppm	parts per million
IR	Infra Red
NMR	Nuclear Magnetic Resonance
$CDCl_3$	deuterated chloroform
o/w	oil-in-water
w/o	water-in-oil



Abstract of the thesis presented to the Senate of Universiti Pertanian Malaysia in fulfilment of requirements for the degree of Master of Science.

SYNTHESIS OF BROMINATED C-18 FATTY ACIDS AND SURFACTANT PROPERTIES OF THEIR SODIUM SALT

By

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Chairman: Associate Professor Dr. Karen Badri
Faculty : Science and Environmental Studies

The physicochemical properties of sodium salts fatty acid have not been thoroughly investigated and are, therefore, not well understood. In line with this, brominated and non-brominated sodium salts of C-18 chain fatty acids were prepared and their physicochemical properties and performance in aqueous solution have been investigated by means of surface tension, conductivity, NMR(^1H and ^{13}C) and emulsion stability.

The experimental results indicate that when bromine atom/s were present in the alkyl chain of the fatty acid sodium salts, the surface activity increases. It was also found that closely packed micelles were formed with the introduction of the bromine atom/s onto the hydrophobic region of the surfactant, thus a lower critical micelle concentration was registered. However, the presence of bromine did not affect the formation of stable w/o emulsions.



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**SYNTHESIS PEMBROMINAN ASID LEMAK DAN CIRI-CIRI
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Fakulti : Sains dan Pengajian Alam Sekitar

Ciri-ciri fizikal mengenai garam asid lemak tidak dikaji dengan begitu mendalam maka pemahaman mengenainya adalah amat kurang. Oleh yang demikian, garam asid lemak yang mengandungi dan yang tidak mengandungi atom bromin telah disediakan dan ciri-ciri fizikalnya dikaji. Kajian dijalankan menggunakan teknik ketegangan permukaan, konduktiviti, NMR (^1H dan ^{13}C) dan kestabilan emulsi.

Hasil kajian menunjukkan bahawa apabila atom bromin dimasukkan pada rantai carbon garam asid lemak, aktiviti permukaannya meningkat. Disamping itu, adalah didapati bahawa misel yang lebih rapat susunannya berjaya dihasilkan dengan kehadiran atom bromin pada kawasan hidrofobic surfaktan tersebut, maka dengan itu konsentrasi kritikal misel (CMC) yang lebih rendah didapati. Walau bagaimanapun, kehadiran atom bromin tidak mengganggu pembentukan emulsi air dalam minyak (w/o) yang stabil.



CHAPTER I

INTRODUCTION

World Trends for Oleochemicals

World interest in oleochemistry appears to be increasing, particularly as a means to develop new uses for what seem to be an ever-increasing supply of vegetable oils. Among the more publicized ventures in recent years are printing inks, diesel fuel, lubricating oils and surfactants.

In many cases, oleochemicals often are described as being more “environmentally friendly” than alternate raw materials as they are non-toxic and rapidly biodegradable (Wilhelm, 1993).

According to Appalasami (1995), world oleochemical demand estimated at 4.4 million tonnes in 1990 is expected to reach 6.0 million tonnes in 2000. Fatty acids and glycerine which are building blocks for the production of oleochemical derivatives comprises about fifty percent of this demand. World production of natural fatty acids increased from 1.64 million tonnes in 1980 to 2.13 million in 1990 at an average annual growth rate of 3.0% (Kaufman and Ruebush, 1990). This growth rate is expected to decline to 2% by the year 2000 because of an overall slowdown in the economies of the developed countries, closure of obsolete plants and shift of production to the developing nations, particularly the Far East. Malaysia which contributes almost 30% of the world demand for fatty acids, and with



economies shrinking in the western countries, the industry must brace itself to face the challenges in terms of overcapacity, applications, technology, quality aspects and environmental issues.

It is estimated that there is approximately 40% overcapacity worldwide due to plants operating at 60-70% of their plant capacity (Wilhelm, 1993). This “overcapacity” situation has caused an imbalance in the supply and demand for fatty acids globally in the short and medium term. This coupled with the depressed market conditions due to the continued economic slowdown in major industrialized countries has created additional burden on fatty acid operations arising from insufficient demand.

The options available by the fatty acid producers in order to overcome the problems of overcapacity are, firstly, to increase the downstream utilization of fatty acids by producing oleochemical derivatives such as soap, metallic stearates, fatty esters, fatty amines and surfactants. Secondly, to find new applications for their fatty acids, which is the development of new markets based on current products (Weiss, 1979).

The Basis and Objectives of This Research

It has been reported that fatty acids and anionic surfactants derived from these acids possess an inhibitory influence against micro-organisms (Sokoloff *et al.*, 1959). Oleic, linoleic and linolenic acids shows activity against bacteria such as *Lactobacillus helveticus*. Sokoloff *et al.* (1959) also demonstrated that unsaturation is an important factor in determining the activity of fatty acids against bacteria.



Subsequently, the length of the carbon chain was shown to be even more important than unsaturation as far as antibacterial activity was concerned and is also an essential factor in the antifungal activity of fatty acids (Linfield *et al.*, 1960a,b). Meanwhile, bromide although toxic at high concentration, has been widely used as a topical antiseptic and deodorant (Bennington, 1984 and Rahway, 1976). Hence, the prime concern of the present work was to synthesize fatty acids with bromide incorporated and to prepare carboxylate salts from these compounds. Subsequently, they were to be tested for their surfactant properties such as its micelle formation through the surface tension and conductivity methods together with their emulsion stability.

Of the points above, the rationale for undertaking a study on its physical aspects as this work intends to do has the following two interrelated points:

- (a) Fundamental scientific understanding of such a chemically useful compound should be broadened to include an understanding of its physical behaviour.
- (b) The results of a physical study may unravel potential industrial applications of the compound.

Hence, we can conclude that the objectives of the work are as follows:

- i) To synthesize brominated fatty acids from saturated and unsaturated carbon-18 fatty acids.
- ii) To prepare carboxylate salts from the brominated and unbrominated carbon-18 fatty acids.

- iii) To determine the critical micelle concentration (CMC) of the soaps by various physical methods, and
- iv) To investigate the ability of the emulsifier to form stable emulsion preparations

When one dispassionately considers the above objectives in relation to the physical properties of the surfactants, one can foresee experimental and theoretical interpretation difficulties that lie ahead. Indeed, a survey of the relevant literature will indicate that very seldom do surface properties of surfactants lead to entirely unarguable conclusions. More often than not, one's explanation can be perfectly plausible without being accepted as unarguably correct.

This work does not aim at creating unassailable theoretical models or unarguable explanations. Rather, existing accepted theories will be appropriately utilised, with modifications if necessary, to explain the acquired data. The originality of the work will lie in its being the first to study the brominated anionic surfactants prepared from fatty acids.

It is hoped that the report in this thesis will not only contribute new knowledge concerning surfactant properties of brominated anionics, but will also serve as a guiding reference to those contemplating further research on physical properties of the compounds.

CHAPTER II

LITERATURE REVIEW

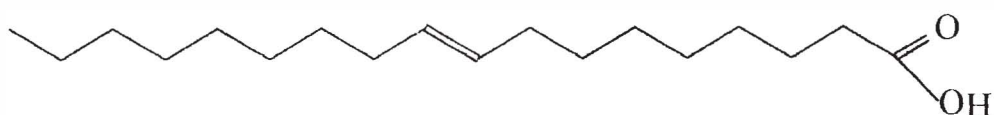
Oleochemicals

Natural Fatty Acids

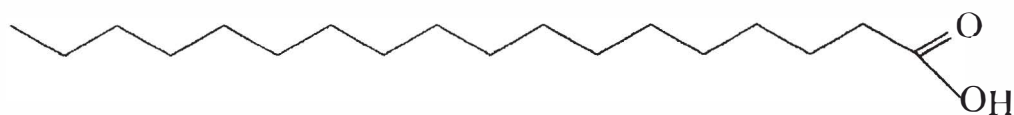
The main sources of natural fatty acids for oleochemicals have been animal fats and tall oils with supplementation of lower quality raw materials available from the major edible oils (Ooi *et al.*, 1994 and Gunstone *et al.*, 1986). This means that most straight chain, even-carbon number carboxylic acids occurring in the triglycerides of common oils and fats are readily available. The fatty acids embrace a large pool of chemical structures containing features such as homologues of C₂-C₂₄, *cis*-monoenoic acids, and double or multiple (non-conjugated) double bond (normally *cis*) systems.

Oleic acid (*cis*-octadecenoic acid), C₁₈:1, is one of the most widely distributed monounsaturated fatty acid found in most vegetable oils and is one of the main fatty acid components in palm oil, which amounts to 37.5% (by weight). It is a C-18 fatty acid with an unsaturated double bond at the C₉. Besides being useful for human consumption, oleic acid may be regarded as an important raw material for the production of oleochemicals and in the preparation of high-technology lubricants or cosmetics. Stearic acid (octadecanoic acid), C₁₈:0, is the saturated C-18 fatty acid which is commonly used in the production of surfactants,

cosmetics, detergents, soaps, pharmaceuticals and lubricants. However, palm oil's stearic acid content is considerably lower than the oleic acid content with an amount of only 4.0% (by weight). Figure 1 shows the chemical structures of oleic and stearic acid.



(a) Oleic Acid (cis-octadecenoic acid) C18:1



(b) Stearic Acid (octadecanoic acid) C18:0

Figure 1. Structures of Fatty Acids (a) Oleic Acid and (b) Stearic Acid

Halogenation of Fatty Acid

Fatty acids in today's markets find their way into thousand of uses such as cosmetics, soap, metallic soaps, rubber applications, candles and water repellents where probably most of their uses are via halogenated derivatives (Soontag, 1963 and Ong, 1992). The diversity of end use application is partially explained by the

relatively low cost of fatty acids, their physiological compatibility with humans and animals, availability of raw materials and the highly functional surface activity of the derivatives.

Synthetic Aspects of Fat Halogenation

Halogenated fats or fatty derivatives are generally prepared by the addition of halogen to carbon-carbon unsaturated functional groups or by substitution of the hydrogen atoms of methylene groups with halogen or substitution of hydroxyl component of carboxyl groups with halogen. The common free halogens such as bromine or chlorine, add to unsaturated double or triple bonds (Lyness and Quackenbush, 1955); hydrogen halide may also be added (Jungermann and Spoerri, 1958). Substitution of the hydrogen atom of a methylene group of an aliphatic chain occurs with the common free halogens, and may be directed specifically to the 2-position, or may be “random” in the sense that monohalogenation of other positions more remote from the carboxyl group may be carried out. Polychlorination, where no more than one chlorine atom may be attached to the site of a single carbon atom, may also be achieved; however, rarely do two halogen atoms enter fatty molecules by substitution at the site of a single carbon atom of the chain, except in the case of acetic acid (Soontag, 1963).

The “free-radical” substitution of hydrogen by halogen in aliphatic chains are classified with respects to the source of the halogen free radicals, thus from free halogens by irradiation (Kohen and Stevenson, 1965), from sulfuryl chloride with

peroxides, from N-halosuccinimides (Hoi and Demerseman, 1953) and from carbon tetrachloride by irradiation.

As halogenation takes place either by substitution or addition, the reaction of both types are frequently employed for analytical purposes with the fatty acids or their derivatives. The reactivity of the halogens for both substitution and addition reactions is in inverse relationship to their molecular weight, which is in the opposite of that encountered with the hydrogen halides (Soontag, 1968). Chlorine and bromine are capable of both substitution and addition reactions, whereas iodine must be added slowly and does not generally yield substitution products (Soontag, 1968).

The contention that halogen additions to ethylenes constitute chain reactions involving radicals has received substantial support. It occurs through a transition state for halogen additions, one of the halogen atoms accepting a pair of electrons from the ethylene, the other atom thus assuming a negative charge. The negative halogen then migrates to the positive carbon atom of the ethylene, thereby completing the addition. The action of bromine on the ethylene bond may be presented as follows :



The ethylenic bond thus function as a pseudo base, the intermediate assuming a linear configuration the resonating forms of which are $\text{CH}_2::\text{CH}_2\text{Br}:\text{Br}$ and $\text{CH}_2:\text{CH}_2:\text{Br}:\text{Br}$ (Ralston, 1963). The effect of alkyl substitution upon orientation,



the marked catalytic effect of water upon halogenation, and other considerations lend considerable support to this mechanism (Ralston, 1963).

The halogenation of monoethylenic acid presents the simplest case of halogenation of unsaturated fatty acids. The addition of bromine or chlorine to a monoethylenic acid yields the corresponding dihalo saturated acids; for example bromine adds to oleic acid to form 9,10-dibromostearic acid which melts at 28.5-29°C and is isomeric with the 9,10-dibromostearic acid melting at 29-30°C obtained from elaidic acid (Nevenzel and Howton, 1957 and Demetrious and Kummerow, 1963).

All the polyethylenic acids add halogens with the ultimate formation of the corresponding saturated halo acids. It is well known, however, that the rate of addition of halogens varies widely, depending upon the relative position of the double bonds. Conjugated acids, for instance, have a markedly different rate of addition than those containing unconjugated systems. The rate of addition to oleic, linoleic and linolenic acids increases with increasing unsaturation; however, a longer time is required for the complete bromination of the more highly unsaturated acids (Ralston, 1963).

The substitution of chlorine or bromine for hydrogen in the alkyl chain of the fatty acids, with the formation of either mono- or polyhalo acids, can be accomplished. It is generally assumed that a hydrogen upon the α -carbon atom is first replaced so that monohalogenation yields essentially an α -halo acid. This preference for α -halogenation has been ascribed to enolization. If the halogenation is continued, any of the hydrogens attached to methylene groups may be involved.



Halogen substitution in the saturated acids can be accomplished through the “Hell-Volhard-Zelinsky” reaction using phosphorus as a catalyst or through “free-radical” substitution by employing N-halosuccinimides. These reactions are generally employed for the preparation of their α -bromo derivatives.

Free radical bromination with N-bromosuccinimide have been shown to be an elegant way to introduce a bromine atom at the allyl position of a double bond (Vogel, 1957) and at an α -carbon of the saturated fatty acid. Naudet and Ucciani (1960,1961,1963a,c) determined the extent of mono and dibromination which occurred in the reaction of methyl oleate and N-bromosuccinimide. It was concluded that substitution of bromine for hydrogen took place on both sides of the double bond, possibly by a route other than a free radical mechanism. The products which were formed through the reaction were characterized by their behaviour towards alcoholic silver nitrate. Infrared spectroscopy can be employed to show that N-bromosuccinimide reacted with oleic and elaidic acids with geometrical isomerization at the double bond (Naudet *et al.*, 1963b). The isomerization occurred in reactions yielding brominated and nonbrominated products. Nanavati *et al.* (1959) reported that the reaction proceeds by free radical removal of allylic hydrogen, which favors subsequent free rotation at the double bond.

Surfactant Classification

Surfactants can generally be classified into four types, namely, anionic, cationic, nonionic and amphoteric. Their definitions are given as follows :

