UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND SURFACTANT PROPERTIES OF ALPHA· SULFONATED POLYHYDRIC ALCOHOL ESTER (ASPA)

ADAM IBRAHIM AHMED NUR

FSAS 1999 37

SYNTHESIS AND SURFACTANT PROPERTIES OF ALPHA-SULFONATED POLYHYDRIC ALCOHOL ESTER (ASPA)

BY

ADAM IBRAHIM AHMED NUR

Thesis Submitted in Fulfilment of the Requirements for the
Degree of Master of Science in the Faculty of
Science and Environmental Studies
Universiti Putra Malaysia

November 1999

ACKNOWLEDGEMENT

I would like to express my gratitude to PORIM board for providing financial assistance to pursue my graduate studies at Universiti Putra Malaysia (UPM). A special thanks is extended to Professor Jalani for facilitating the research project during the preparation period.

I wish also to express my deepest appreciation to my supervising committee Associate Professor Dr. Mohd Zaizi Desa, Associate Professor Dr. Dzulkefly Kuang and Dr. Salmiah Ahmad for their kind advice, encouragement, assistance, and constructive criticism. I also thank Mr. Azman and Mr. Zuhairi for their technical assistance. My deepest appreciation to the staffs in Chemistry Department and AOTC, especially Dr. Mohtar, Mr. Tang, Miss. Rolia, Mr. Lim, Dr. Hazimah, Mrs Zainab, and Mrs Zahariah for their kind help. Last but not least, I thank my parents and brothers for their encouragement and moral support during my studies in Malaysia.

Statement of Originality

Except where specific acknowledgement is given, the research work reported in this thesis is entirely that of the author.

(A. I. Ahmed Nur)

Date:

I certify that an Examination Committee has met on 23 November, 1999 to conduct the final examination of Adam Ibrahim Ahmed Nur on his Master of Science thesis entitled "Synthesis and Surfactant Properties of Alpha-Sulfonated Polyhydric Alcohol Ester (ASPA)" in accordance with Universiti Pertanian Malaysia (higher Degree) Act 1980 and Universiti pertanian Malaysia (higher Degree) Regulations 1981. The committee recommended that the candidate be awarded the relevant degree. Members of the examination Committee are as follows:

MAWARDI RAHMANI, Ph.D.
Associate Professor/Head
Department of Chemistry
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

MOHD ZAIZI DESA, Ph.D.
Faculty of Science
Universiti Putra Malaysia
(Member)

DZULKEFLY KUANG, Ph.D.
Faculty of Science
Universiti Putra Malaysia
(Member)

SALMIAH AHMAD, Ph.D.
Advance Oleochemical Technology centre (AOTC)
Palm Oil Research institute of Malaysia (PORIM)
(Member)

MOHD. GHAZALI MOHAYIDIN, Ph.D.
Professor/Deputy Dean of Graduate School
Universiti Putra Malaysia

Date: 28 DEC 1999

This thesis was submitted to the Senate of Universiti Putra Malaysia and was accepted as fulfillent of requirements for the degree of Master of Science.

KAMIS AWANG, Ph.D
Associate Professor/Dean of Graduate School
Universiti Putra Malaysia

Date: 4 JAN 2000

TABLE OF CONTENT

CHAPTER

LIST OF TABLES

LIST OF FIGURES

List of Abbreviations

Abbreviation	**Full name**
ASPA	Alpha-Sulfonated Polyhydric Alcohol Ester
DMF	Dimethyl Formamide
EtOH	Ethanol
FA	Fatty Acid
FAME	Fatty Acid Methyl Ester
H-AC	Acetic Acid
Hex	Hexane
IPA	Iso-Propyl Alcohol
MeOH	Methanol
SFA	Sulfonated Fatty Acid
SME	Alpha-Sulfonated Methyl Ester
Eth	Diethyl Ether
Pen	Pentane
Rpm	Rotation Per Minute
WAS	Washing Active Substance
MMT	Million metric Ton

Abstract of thesis presented to the senate of Universiti Putra Malaysia
in fulfilment of the requirements for the Degree of Master of Science.

SYNTHESIS AND SURFACTANT PROPERTIES OF ALPHA-SULFONATED POLYHYDRIC ALCOHOL ESTER (ASPA)

by

ADAM IBRAHIM AHMED NUR

November 1999

Chairman: **Associate Professor Dr. Mohd Zaizi Desa**

Faculty: **Science and Environmental Studies**

A new anionic surfactant, alpha-sulfonated polyhydric alcohol ester (ASPA) was prepared by transesterification of palm-based alpha-sulfonated methyl ester (SME) or by esterification of palm-based alpha-sulfonated fatty acid (SFA) with glycerol in non-solvent media. The product was isolated as sodium salt by crystallization using methanol as solvent. The purity of the product was confirmed by TLC, yielding a single spot while the melting point was found to be sharp at 35°C.

The structure of the ASPA was identified by Fourier Transform Infrared (FTIR) and confirmed by ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR). FTIR analysis of ASPA from SME indicated the presence of broad OH group at wavenumber 3402 cm^{-1}, while the presence of OH group in ASPA from SFA was detected at 3397 cm^{-1}. The presences of CH_2OH and CHOH groups of ASPA molecule via SME were indicated by peak δ at 3.6 and 3.7 ppm respectively in ^{1}H-NMR spectrum. The two OH groups also appeared at 4.25 and 4.27 ppm corresponding to primary and secondary alcohols respectively. The ^{1}H-NMR of ASPA via SFA showed the overlapping of CH_2OH/CHOH at 3.6 ppm and the two OH groups also overlapped at 4.11 ppm. The ^{13}C-NMR of ASPA via SME showed the presence of carbon primary alcohol at 70 ppm and carbon secondary alcohol at 72 ppm, while the carbon primary alcohol and carbon secondary of ASPA via SFA were overlapped at 72 ppm.

The effects of reaction temperatures, reaction times and catalyst on the synthesis were also evaluated. The maximum yield of ASPA via SME was 48%, at the reaction temperature of 70°C and the reaction time of 50 minutes, while the optimum yield of ASPA via SFA was 95%, at reaction temperature of 40°C and the reaction time of 60 minutes.

These new products gave low surface tension (26 dyne/cm). Other properties, such as foaming power/stability, wetting ability and anti-rust power were evaluated. The washing active substance (WAS) as a function of aging time was also studied.

Abstrak tesis yang dikemukakan kepada senat Universiti Putra Malaysia
bagi memenuhi keperluan Ijazah Master Sains

PENYEDIAAN DAN SIFAT SURFAKTAN ESTER ALKOHOL POLIHIDRIK ALFA-TERSULFONAT (ASPA)

Oleh

ADAM IBRAHIM AHMED NUR

November 1999

Pengerusi: Prof. Madya Dr. Mohd Zaizi Desa

Fakulti: Sains dan Pengajian Alam Sekitar

Surfaktan anionik baru, ester alkohol polihidrik alfa-tersulfonat (ASPA) telah disediakan melalui tindak balas pengesteran diantara ester metil tersulfonat (SME) atau asid lemak tersulfonat (SFA) dengan gliserol dalam keadaan tanpa pelarut. Hasil tindak balas diasingkan dalam bentuk garam natrium. Proses penghabluran dilakukan dalam pelarut metanol. Ketulenan hasil tindak balas disahkan dengan kehadiran satu spot pada ujian kromatografi lapisan nipis (TLC) dan dengan julat takat lebur bahan, yang kecil pada 35°C.

Struktur ASPA dikenalpastikan dengan kaedah spektroskopi inframerah transformasi fourier (FTIR) dan resonans magnet nukleus (^{1}H

Struktur ASPA dikenalpastikan dengan kaedah spektroskopi inframerah transformasi fourier (FTIR) dan resonans magnet nukleus (^{1}H dan ^{13}C-NMR). Analisis FTIR menunjukkan serapan bagi kumpulan OH pada panjang gelombang 3402 cm^{-1} untuk ASPA yang disediakan dari SME dan 3397 cm^{-1} untuk ASPA dari SFA. Kajian ^{1}H-NMR bagi ASPA yang dihasilkan dari SME menunjukkan puncak-puncak pada δ 3.6 dan 3.7 ppm membuktikan kehadiran masing-masing kumpulan CH_2OH dan CHOH. Kehadiran kumpulan hidroksi primer dan sekunder juga dipastikan dengan kewujudan puncak pada 4.25 dan 4.27ppm masing-masing. Walau bagaimanapun, spektrum ^{1}H-NMR bagi ASPA yang dihasilkan dari SFA menunjukkan pertindihan puncak pada 3.6 ppm bagi CH_2OH/CHOH dan juga bagi dua kumpulan hidroksi pada 4.11 ppm. Spektrum ^{13}C-NMR mengesahkan kehadiran OH primer (1°) dan sekunder (2°) bagi ASPA yang disediakan dari SME dengan kewujudan puncak-puncak 70 ppm dan 72 ppm, manakala pertindihan puncak-puncak berlaku pada 72 ppm bagi ASPA dari SFA.

Kesan beberapa parameter tindak balas seperti suhu tindak balas, masa tindak balas dan mangkin juga dikaji. ASPA yang disediakan dari SME memberikan hasil maksimum 48% apabila tindak balas dilakukan pada suhu 70°C selama 50 minit, manakala ASPA dari SFA memberikan hasil maksimum 95% pada suhu 40°C dengan masa tindak balas 60 minit.

Produk baru yang dihasilkan mempunyai tegangan permukaan yang rendah. Sifat-sifat lain seperti kuasa/kestabilan busa, keupayaan basahan dan kuasa anti karat telah diselidiki. Sebagai bahan aktif basuhan (WAS) juga dikaji terhadap masa.

CHAPTER 1

INTRODUCTION

Palm Oil

Palm oil is extensively (80%) used for edible purposes. The rest of it goes into nonedible applications. Currently, ASEAN region is the world's largest producer of palm oil and palm kernel oil. ASEAN accounts for 83.2% of the world's palm oil production, and 80.1% of palm kernel oil. The two leaders in the region are Malaysia and Indonesia. They are able to produce this commodity in abundance, and at competitive price compared to other vegetable oils. Malaysia produced 9.1 MMT of palm oil and 1.2 MMT of palm kernel oil, in 1997, while Indonesia produced 5.1 and 0.53 MMT of palm and palm kernel oils respectively (Yusof and Thiagarajan, 1998).

The production of 4 major oils increased from 1986 to 1996. Palm oil increased by 76%, soybean by 34%, rapeseed by 59% and sunflower by 30%. In export market palm oil plays significant role in supplying the world's demand for oils and fats. In 1996, about 28 MMT of oils and fats was traded, the contribution of palm oil was 38% of the total while the soybean oil was merely 17% (Yusof, 1999).

Palm oil is in the unique position to dominate world's production in the coming decades because of its high yield per hectare than any seed oil and low production costs in terms of US Dollar (due to devaluation of ASEAN currencies). This means that all producers in ASEAN countries are gaining high profit particularly Malaysia and Indonesia. Currently soybean oil leads global production at 20 MMT compared to 17 MMT for palm oil but in the year 2010 palm may exceed soy by at least 5 MMT annually and will become major supplier of edible oils for the world population. Soybean utilizes 35.7% of land used for growing oil-bearing crops and produce 28.2% of total oil produced in the world while oil palm utilizes 2.7% of the land and produce 25.6% of the world's production (Jalani, 1997).

Crude palm oil (CPO) is extracted from the fleshy portion (mesocarp) of the oil palm fruit while the kernel (endosperm) yields palm kernel oil (PKO). CPO is refined into refined, bleached and deodorized oil (RBDPO) and may be fractionated to olein and stearin. Refining waste, palm fatty acid distillate (PFAD) is a rich source of free fatty acids, which are good substrates for soap, esters and other derivatives. Palm stearin and olein are normally used to produce edible and nonedible products. Stearin contain a higher proportion of saturated acid (palmitic) than unsaturated (oleic). The saturated acid content makes the stearin solid at room temperature. Olein on the other hand is liquid and is normally used as cooking oil.

Development of Oleochemical Industry in Malaysia

Oleochemicals are chemicals derived from oils or fats, by hydrolysis (fat splitting), distillation, hydrogenation and methylation of oils and fats. These chemicals inclusive fatty acids, fatty alcohol, glycerin, fatty methyl esters and fatty amines are known as basic oleochemical.

The oleochemical industry in Malaysia was started in 1980, when a local company was set out to produce 100,000 tons of fatty acids and glycerol. This sector developed very rapidly due to joint venture between the multi-national companies and local companies. The main factors leading the multi-national company to joint venture are:

- The availability of raw materials (palm oil and palm oil products, especially lauric oil).
- The incentive given by Malaysian government (Salmiah et al, 1998a).

Malaysian Industrial Master Plan 1 (IMP-1) was set to promote the production of oleochemical as one of the potential growth sectors of the oil palm Industry. The oleochemicals to be produced are fatty acids, methyl esters, fatty alcohols, glycerine and their total capacity is forecasted to reach 1.2 million tons by the year 2000 (Table 1). Today in addition to basic oleochemicals, their derivatives such as food esters, soap noodles, metallic soap, ethylene bisstearamide, alkanolamides are also produced (Salmiah et al., 1998a).

Table 1: Oleochemical Capacity in Malaysia

Product	1992	2000
Fatty Acids	590,000	560,000
Methyl Esters	150,000	70,000
Fatty Alcohols	150,000	350,000
Fatty Esters	10,000	40,000
Fatty Amines	-	60,000
Glycerine	78,000	120,000
TOTAL	978,000	1,200,000

Source: (Ibrahim and Jaafar, 1993)

In 1995, the Malaysian oleochemical industry consumed about 4% of the total Malaysian production of palm oil and 57% of the palm kernel oil production, overall average was 10% of the total palm oil and palm oil products. About 550,000 metric tons of oleochemical products, including fatty acids, glycerine, fatty esters, and fatty alcohols produced in 1997 are exported (Salmiah et al, 1998b).

Glycerol

Glycerol is obtained as a co-product during the production of soaps, fatty acids, fatty methyl esters, and other processes. In other words, glycerol is obtained when oils and fats are split, transesterified, or saponified. The most important sources of glycerol are oils and fats but it can also be obtained from petrochemical sources. An abundance of glycerol can be anticipated if methyl ester were to be extensively use as biodiesel (Kaufman, 1998).

The term glycerine, glycerin, and glycerol, often is used interchangeably, some differences do exist between them. The Soap and Detergent Association uses these definitions:

- Glycerine is the commonly used commercial name in the United States for products whose principal component is glycerol.
- Glycerin refers to purified commercial products containing 95% or more of glycerol.
- Glycerol is the chemical compound 1,2,3 propanetriol (Croy and Dotson, 1995).

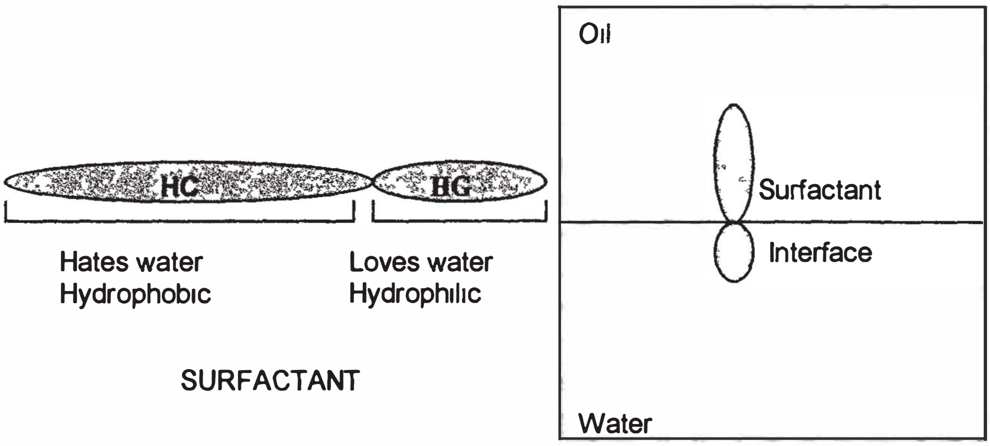
Glycerol has diverse applications. It is extensively used as a solvent or drugs carrier in pharmaceutical and medicinal products, in cosmetics, explosives and in making of paper.

Surfactants

The word surfactant is derived from the phrase “surface-active agent” and maybe defined as any substance, which is strongly adsorb at a surface or interface. The term interface implies a boundary between any two immiscible phases. The phases can be between a solid and a liquid, between air and liquid or between a liquid and a different immiscible liquid. The term surface indicates that one of the phases is gas, usually air. The definition for surfactant encompasses the majority of substances which function as wetting, cleansing and emulsifying agents. Surfactants comprise large molecules containing both polar and nonpolar groups, which are referred as “hydrophilic” and “hydrophobic” respectively (Figure 1).

Surfactant’s Raw Materials

The main raw materials for surfactants are oleochemicals and petrochemicals (Figure 2). Oleochemical-based surfactants are widely used in various fields of applications. This is mainly because of their environmental-friendly and derived from renewable resources. These products are important and major efforts are devoted to synthesize and produce them for diverse purposes. They are known to be active ingredients in detergents, cosmetics, foods, drugs, etc and they provide the capability to solubilize water and oil like substances into homogeneous system.



SURFACTANT

Surfactant at oil/water interface

Figure 1: Surfactant and Surface Activity

Source (Salmiah et al, 1997)

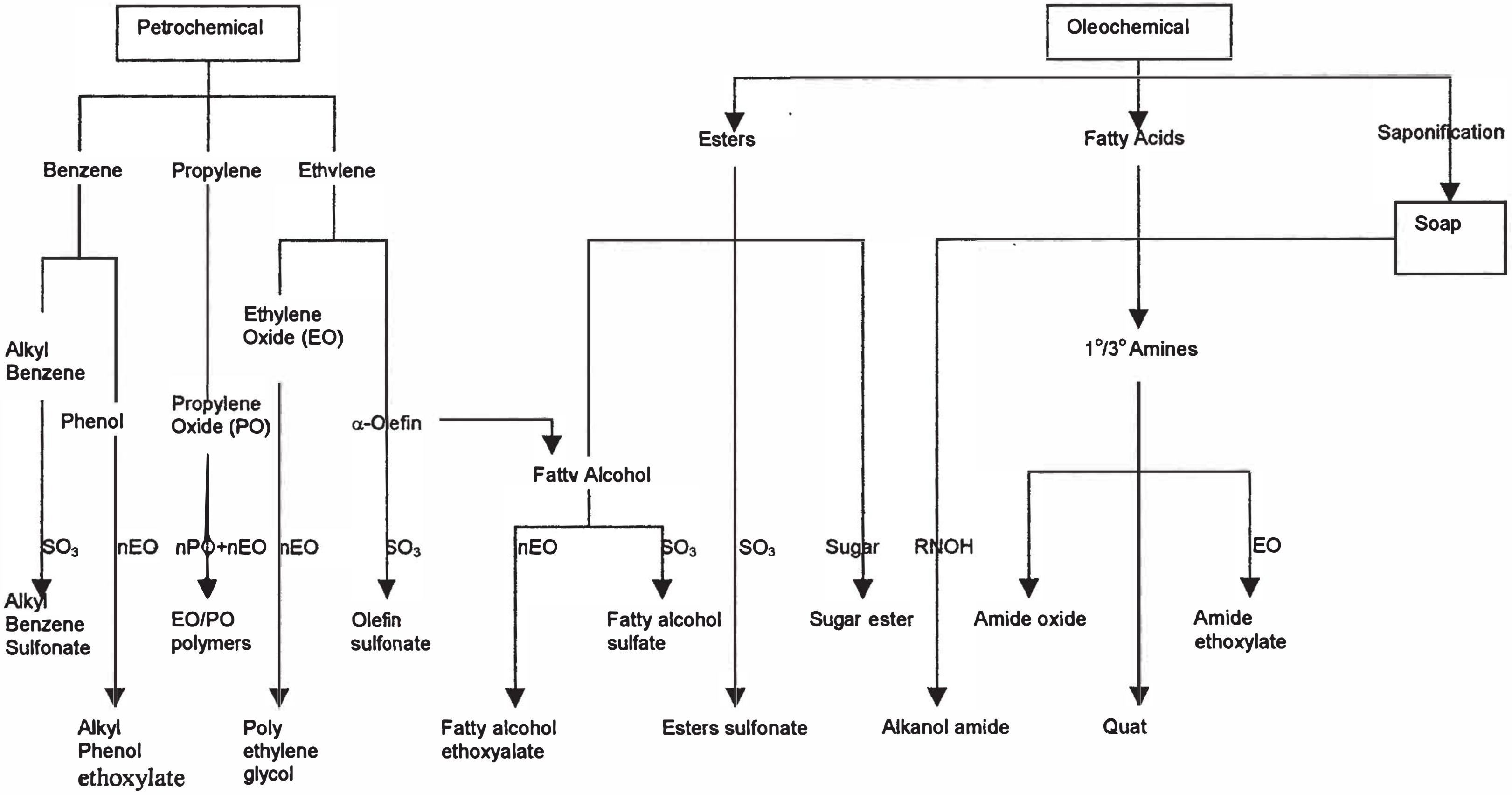


Figure 2: Chemical Origin of Surfactants

Abbreviation: SO_3: Sulfonation or Sulfation, nEO: ethoxylation, nPO: propoxylation, H_2: hydrogenation, NH_3: amidation or amination.
Source: Morpeth, 1995