



UNIVERSITI PUTRA MALAYSIA

**PHASE BEHAVIOUR AND PHYSICAL PROPERTIES OF
SULPHONATED METHYL ESTER AND FATTY ALCOHOL ETHER
SULPHATE MIXTURES.**

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METHYL ESTER AND FATTY ALCOHOL ETHER SULPHATE MIXTURES.**

By

MOHD.ZAIHANIF BIN HUSIN

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Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**KELAKUAN FASA DAN CIRI-CIRI FIZIKAL CAMPURAN METIL ESTER
TERSULFONAT DAN ALKOHOL LELEMAK ETER SULFAT.**

Oleh

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July 2007

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Metil Ester Tersulfonat (SME) dan Lemak alkohol eter sulfat (FAES) merupakan surfaktan anionik. SME dan FAES banyak digunakan di dalam detergen tetapi tidak banyak yang diketahui tentang kelakuan fasanya. Kelakuan fasa bagi sistem fasa ternari telah di pelajari pada suhu 70°C di bawah pemerhatian pandangan dengan menggunakan lampu berkutub dan ianya disahkan dengan menggunakan mikroskop berkutub. Eksperimen mikroskop berkenaan komposisi melalui lampu berkutub membolehkan pengenalan kehadiran struktur mesomorphik di dalam sistem. Sistem fasa ternari telah dipelajari dari kombinasi di antara SME/ FAES/ Air, SME/ FAES/ 2% larutan NaCl, SME/ FAES (60/40)/ Propilen Glikol dan SME/ FAES (60/40)/ sabun pada suhu 70°C. Paten penglihatan bagi hablur cecair lamella menunjukkan rangkai silang maltes, garis berminyak dan tekstur bergaris apabila diperhatikan di bawah mikroskop berkutub.



Pembelajaran tentang sistem ternari membawa kepada kefahaman tentang aspek kimia-fizik dan membolehkan penyumbangan komponen berbeza pada formulasi detergen yang akan dibangunkan. Formulasi ini telah dirumus pada kawasan hablur cecair dimana telah disahkan melalui mikroskop berkutub. Hablur cecair selalunya sangat stabil menentang pemisahan fasa dan berkesan menanggalkan kotoran berminyak dan kotoran gris. Formulasi detergen cecair seperti cecair pembersih pingan, gel pembersih pingan, sabun cecair mencuci tangan, pembersih lantai dan detergen pembersih pakaian telah didapati mempunyai persamaan atau sedikit lebih baik ciri-cirinya berbanding sampel produk di pasaran dari segi pembersihan, kuasa pembasah, kuasa pembuihan dan kestabilan. pH dan kepekatan adalah setanding dengan produk dipasaran.



Abstract of the thesis presented to the Senate of University Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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Sulphonated Methyl Ester (SME) and Fatty Alcohol Ether Sulphated (FAES) are anionic surfactants produced from palm oil. SME and FAES are widely used in detergent but their phase behaviour in ternary phase system is little known. The phase behaviour in ternary system has been studied at 70°C under visual observation by polarizing light and they were confirmed by polarization microscope. The microspical study of the composition through polarized light enables identification of the mesomorphic structures present in the system. The study of ternary phase system in combination of SME/ FAES/ Water, SME/ FAES/ 2% NaCl Solution, SME / FAES (60/40)/ Propylene Glycol/ 2% NaCl Solution and SME / FAES (60/40)/ Soap/ 2% NaCl Solution at 70°C. The optical pattern of lamellar liquid crystals has shown a maltese crosses, oily streak and striated textures when observed under a polarizing microscope.



The study of ternary system leads to the understanding of physico-chemical aspects and allows the contribution of the different components to a detergent formulation to be developed. This formulation was formulated at the liquid crystalline region which was confirmed via polarizing microscope. Liquid crystal is usually highly stable against phase separation and effective in the removal of oily and greasy soil. The formulated liquid detergents, i.e. liquid dish washing, gel dish washing, hand liquid soap, floor cleaner and liquid laundry detergent were found to have comparable or slightly better properties compared to commercial samples in terms of detergency, wetting power, foaming power and stability. The pH and viscosity are comparable with the commercial product.



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I certify that an Examination Committee has met on 26th July 2007 to conduct the final examination of Mohd.Zaihanif Bin Husin on his Master of Science thesis entitled “Phase Behaviour and Physical Properties of Sulphonated Methyl Ester and Fatty Alcohol Ether Sulphate Mixtures” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the student be awarded the degree of Master of Science.

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which has been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Putra Malaysia, or other institution.

MOHD.ZAIHANIF BIN HUSIN

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TABLE OF CONTENTS

	Page
ABSTRAK	ii
ABSTRACT	iv
ACKNOWLEDGEMENTS	vi
APPROVAL	vii
DECLARATION	ix
LIST OF TABLES	xii
LIST OF FIGURES	xiii
LIST OF ABBREVIATIONS	xv

CHAPTER

1	INTRODUCTION	
	Basic Oleochemicals	1
	Surfactant	2
	Adsorption and Critical Micelle Concentration	4
	The hydrophobic Effect	6
	The hydrophilic Effect	6
	Micelles	7
	Liquid Crystal	10
	Lyotropic Liquid Crystal	10
	Classification of Lyotropic Liquid Crystal	11
	Lamellar Phases	11
	Applications of Liquid Crystal	14
	Surface Tension	16
	Ternary Phase Diagram	16
	Detergent Formulation	17
	Detergency	17
	Foaming	18
	Stabilization of detergent formulation	18
	Objective of the study	19
2	LITERATURE REVIEW	20



3	MATERIALS AND METHODOLOGY	
	Materials	29
	Methods	32
	Constructing the Ternary Phase Diagram's	32
	Measurement of Detergency Test	36
	Measurement of Surface Tension	40
	Measurement of Optical Microscopy	41
	Measurement of Foam Height	42
	Measurement of Washing Active Substance	42
	Measurement of Wetting	43
	Measurement of In-Vitro	44
	Measurement of pH	46
	Measurement of viscosity	46
	Measurement of Particle Size	46
	Measurement of Cloud Point	48
	Formulation	48
	Stability Test	48
4	RESULTS AND DISCUSSION	
	Ternary Phase Behaviour	49
	Optical Microscope	59
	Surface Tension	61
	Synergistic Effect	63
	Cloud Point	64
	Formulation	66
	Viscosity Test for liquid detergents	72
	pH for liquid detergents	74
	Foam Height for liquid detergents	75
	Cloud Point for liquid detergents	77
	Detergency Test for liquid detergents	78
	Wetting Test for liquid detergents	81
	Particle Size for liquid detergents	82
	Optical Microscope for liquid detergents	91
	In-Vitro Test for liquid detergents	95
	Stability Test for liquid detergents	96
5	CONCLUSION AND FUTURE WORK	98
	REFERENCES/ BIBLIOGRAPHY	100
	BIODATA OF THE AUTHOR	106



LIST OF TABLES

Table		Page
1.	The chemicals/ raw materials used	29
2.	Mixture ratios for each test tube (ternary phase diagram 1 and 2)	33
3	Mixture ratios for each test tube (ternary phase diagram 3)	34
4.	Mixture ratios for each test tube (ternary phase diagram 4)	35
5.	Summary of phase transition of the phase diagram 1	53
6.	Summary of phase transition of the phase diagram 2	54
7.	Summary of phase transition of the phase diagram 3	55
8.	Summary of phase transition of the phase diagram 4	56
9.	Formulation Liquid Dish Washing (LDW).	66
10.	Formulation Gel Dish Washing (GDW).	67
11.	Formulation Hand Liquid Soap (HLS).	68
12.	Formulation Floor Cleaner (FC).	69
13.	Formulation Liquid Laundry Detergent (LLD).	70
14.	Viscosity of liquid detergents.	72
15.	Particle Size of liquid detergent	82
16.	In-Vitro Test	95
17.	Stability Test	96



LIST OF FIGURES

Figure	Page
1. Adsorption at interfaces	5
2. Adsorption and concentration	8
3. Schematic diagram of normal and inverse micelles	9
4. Phase Behaviour of surfactant/ Water/ Oil System	12
5. (a) Schematic Structure of Lamellar Liquid Crystal and (b) Optical Patterns of Lamellar Liquid Crystal: (i) Maltese Crosses, (ii) Oily Streaks and (iii) Striated Pattern	13
6. Applications of Lyotropic Liquid Crystal	15
7. Mechanism for the formation of SME	30
8. Ternary phase diagram of SME/ FAES/ Water at 70°C	49
9. Ternary phase diagram of SME/ FAES/ 2% NaCl Solution at 70°C	50
10. Ternary phase diagram of (SME 60%/ FAES 40%) / Propylene Glycol/ 2% NaCl Solution at 70°C	51
11. Ternary phase diagram of (SME 60%/ FAES 40%) / Soap/ 2% NaCl Solution at 70°C	62
12. Optical Microscope	59
13. Surface Tension of SME at 25°C.	61
14. Surface Tension of FAES at 25°C.	61
15. Synergistic effect of mixed SME & FAES at 0.1% concentration.	63
16. Synergistic effect of mixed SME & FAES at 1% concentration.	63
17. Cloud point for mixed SME & FAES at 1% concentration.	64



18	pH of liquid detergents.	74
19.	Foam height of liquid detergents.	75
20.	Foam height of liquid detergents.	75
21.	Cloud point of liquid detergents.	77
22.	Detergency Test of liquid detergents.	78
23.	Detergency Test of liquid laundry detergents.	80
24.	Wetting Test of liquid laundry detergents.	81
25.	Size Distribution by Volume	90
26.	Optical Microscope	93



LIST OF ABBREVIATIONS

CMC	Critical Micelle Concentration
H ₁	Normal hexagonal
H ₂	Reversed hexagonal
L ₁	Isotropic micellar phase
N _c	small cylindrical micelles
N _d	planar disc micelles
BAS	branched alkyl benzene
LABS/ LAS	Linear Alkyl Benzene Sulphonate
SME	Sulphonated Methyl Ester
AOS	Alpha Olein Sulphonate
FAES	Fatty Alcohol Ether Sulphate
LDW	Liquid Dish Washing
GDW	Gel Dish Washing
HLS	Hand Liquid Soap
FC	Floor Cleaner
LLD	Liquid Laundry Detergent
RT	room temperature
F/T	freeze and thaw
S	stable



CHAPTER 1

INTRODUCTION

1.1 Basic Oleochemicals

Oleochemicals are chemical derived from oils or fats via the splitting of triglycerides into their constituent fatty acid derivatives and glycerol or via modifications of oils/fats. The oils/fats may be of vegetable, animal or marine origins while the splitting and modifications may be carried out using either chemical methods or biotechnology. Similar chemicals may be synthesized from petrochemicals, and they shall be referred to as petrochemicals. The most common basic oleochemicals are fatty acids, fatty methyl esters, fatty alkyl esters, fatty alcohols, fatty amines and glycerol. Currently, the oleochemical industry is well developed in Europe, USA, Canada and Japan.

The aim of intensive efforts being made in the oleochemical industry is to increase the share of oleochemical surfactants in world surfactant production. This is because, in contrast to petroleum, fats and oils are renewable, i.e. self-perpetuating , natural raw



materials which, because they are made up of linear fatty acid molecules with no branching or ring structures, can also be expected to provide the surfactants produced from them with favorable ecological properties from the outset (Baumann, 1991).

1.2 Surfactant

Surface Active Agents or Surfactants are the most common oleochemical derivatives used for cleaning. Surfactant is a substance that when present at low concentration in a system has the ability of absorbing onto the surface or interface of the system and thus altering the properties of those surfaces or interfaces (Arthur, 1990). The four types of surfactants are anionic (negatively charged head group), cationic (positively charged head group), nonionic (uncharged but water loving head group) and amphoteric (head group exhibits different behaviour depending on the condition the molecule is in).

In solvent such as water, the surfactants molecules distributed in such manner, that their concentration at the interfaces is higher than in the inner regions of the solutions. This behavior attributable to their amphiphilic structure. Amphiphilic structure consists of two structural parts, the hydrophilic and hydrophobic part with different solution characteristics. The hydrophobic is water insoluble because it interacts very weakly with water molecules in an aqueous environment meanwhile the hydrophilic is water soluble.



To understand how surfactants function and to select a surfactant for a specific purpose, it is necessary to classify surfactants according to their structural features (Adamson, 1990 and Porter, 1991). Surfactants have a very important role in our everyday life. Surfactants in industrial processes; our food, cosmetics, medicine and household items, such as soap and detergents, contain surfactants. The wide variety of surfactant applications has required different types of surfactants and a large number of surfactant structures are available for the specific need (Attwood and Florence, 1985 and Guteno, 1977).

When a soiled item is placed in a surfactant solution, the surfactants preferentially adsorb at the interfaces between the soil/ surface and soil/ water. The presence of surfactants at the interfaces reduces the interfacial tension and results in easy removal of the soil from the surface via a roll-up mechanism. The ability of a surfactant to remove soil from a surface depends on the nature of the head group, the carbon chain length, types of soil, types of surface, the temperature of washing and the quality of water used during the cleaning process.



1.3 Adsorption and Critical Micelle Concentration.

The major characteristic of surfactant is that it is at higher concentration at the surface than in the bulk of a liquid. This phenomenon is known as adsorption and occurs at a liquid/ solid interface, at a liquid/liquid interface and at an air/liquid interface as shown in Figure 1. In that figure, the surfactant molecule is pictured as a long straight hydrophobic group and a small round hydrophilic group. The adsorption of a surfactant at an air/water surface will result in pronounced physical changes to the liquid; the more surfactant there is at the surface, up to complete coverage of the surface, the more the change. A surfactant adsorbs because there are two groups in the molecule; a hydrophobic (water hating) group and hydrophilic (water liking) group.

Figure 1: Adsorption at interfaces



1.4 The hydrophobic effect

The reason for the insolubility of the hydrocarbon chain in the water is complex. The mechanism involves both enthalpic and entropic contribution and results from the unique multiple hydrogen-bonding capability of water. There is restructuring or re-orientation of water around nonpolar solutes, which disrupts the existing water structure and imposes a new and more ordered structure on the surrounding water molecules, giving a decrease in entropy (Clint, 1992)

1.5 The Hydrophilic Effect

While hydrophobic tend to increase the degree of order in water molecules around them hydrophilic molecules are believed to have a disordering effect. Thus, ion in solution is hydrophilic (e.g. sulphonate, carboxylate, sulphate). Polar with a highly electronegative character show strong electrophilic properties (e.g. primary amine, amine oxides, and sulphoxides). Other nonpolar molecules can be hydrophilic if they contain electronegative electron capable of associating with the hydrogen-bonding network in water.

The adsorption of a surfactant from a solution on to a surface depends upon the concentration. Figure 2 show the effect of the increasing concentration. At very low concentrations (1 and 11), there is no orientation the molecules lies flat on the surface. As the concentration increase (111), the number of the surfactant molecule on the



surface increase on the surface increase, there is not enough room for them to lie flat and so they begin to orient. The orientation depending upon the nature of hydrophilic group and the surface. At concentration the number of surfactant molecules available is now sufficient to form unimolecular layer. This particular concentration is important and known as the critical micelle concentration (CMC). At concentration (above CMC) there is no apparent change in adsorption at hydrophobic surfaces but hydrophilic surface more than one layer of surfactant molecule can form ordered structured on the surface of the solid. In addition, the surfactant molecules in the solution will form an ordered structure known as a micelle so long as the concentration is above the CMC.

1.6 Micelles

As mention above, micelles are formed above the CMC. Modern technique of measuring micellar sizes have shown that the aggregate numbers are in the region of 50-100 for most ionic surfactants. Micelles can be divided into two categories; normal and inversed (Hartley, 1936). Normal micelles are formed when surfactant are dissolved in water (polar solvent) the hydrophobic tails orient themselves towards the micelles interior while the head group remain hydrated (Figure 3). When surfactant is dissolved in nonpolar solvents, reversed micelles are formed. The polar head group reside in the micelle interior while the hydrocarbon chain in solvated.



Figure 2: Adsorption and concentration



Figure 3: Schematic diagram of normal and inverse micelles

