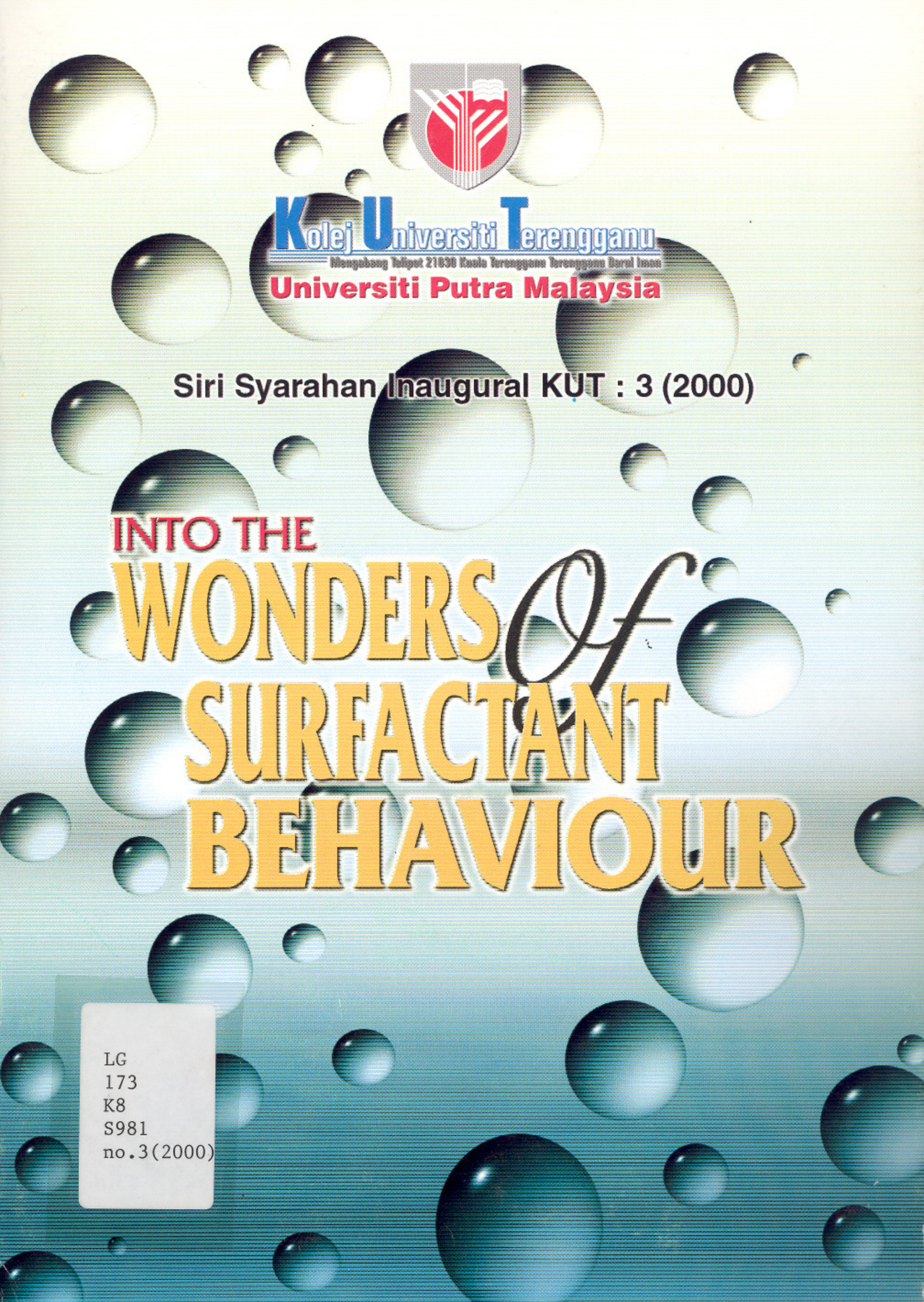

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INTO THE WONDERS *Of* SURFACTANT BEHAVIOUR

INTO THE WONDERS OF SURFACTANT BEHAVIOUR

By
Hamdan Suhaimi, PhD

INTRODUCTION

In the area of physical chemistry, a topic, which all chemistry undergraduates must encounter, is ***chemical equilibrium***. One very important aspect in this topic and is perhaps surprising, considering its great importance, that little or no attention is given in undergraduate courses is to teaching students the equilibrium between different phases. Even more irony is that the preparation of most commonly used chemical products needs the understanding of phase behaviour. The study of phase behaviour as an intensified research in priority areas undoubtedly offers vast potential for new, challenging and exciting discoveries. This is more so with the introduction of a group of chemical called ***surfactant***. In the industrial application the surfactants are used either as essential additives or processing aids or in many cases as only a minor part of a particular system or formulation. Here the surfactant may be regarded as a "performance" or "effect" chemical, whereby small changes in molecular structure can result in dramatic changes in its phase behaviour and performance.

Earlier confusion was due to the fact that the analysis of equilibria among phases was not clearly distinguished from the analysis of chemical equilibria. During most of 19th century, work was focussed on systems whose phase behaviour is very complex in comparison to many systems. The changes in state are accompanied by the changes in molecular structure. Hence, defining the parameter in such systems is cumbersome. However, the scenario began to take a different turn with the introduction of ***thermodynamics*** by J. Willard Gibbs in 1875 (Gibbs 1928). As usual, the science community was again slow in accepting this concept, perhaps because they did not understand the implications. After much convincing and many translations of Gibb's work, Roozeboom and Bancroft finally took up this idea and eventually, the ***"Phase Rule"*** was introduced (Bancroft 1897) i.e.:

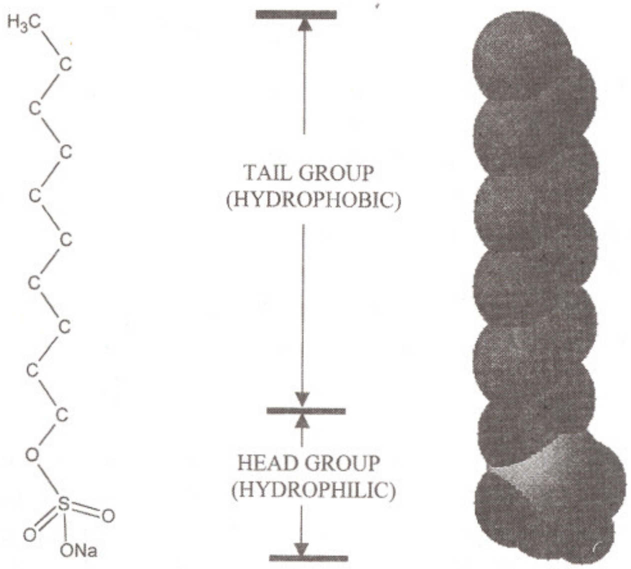
$$P + F = C + 2 \qquad [1]$$

This equation implies that, in a system having C components, the number of phases present (P) plus the number of degrees of freedom that exist (F) is a constant for any mixture of these components that is held at particular temperature, pressure and composition. With the Phase Rule in place the phase behaviour of all class of chemical system could be explored and an explosion of research on phase science occurred in the first several decades of the 20th century.

What is a surfactant?

"Dissolve 50 ml of water in 70 ml of palm oil".

Such an instruction would leave most chemists with the impression that there is a misprint, or if instructed by a professor would give rise to doubt about his/her mental stability. No matter how sophisticated the solubility theory is, one would know that the mutual solubility of water and oil is small if not any at all. How then can one overcome this problem and turn two "insoluble" compounds into a solution that is "clear to the eye" and is furthermore, thermodynamically stable? The answer lies in the ability of the so-called third compound to dissolve both of the insoluble compounds and hence must possess both of the water and oil loving properties in one molecular structure. The answer is **SURFACTANT**. The ability to mix oil and water has an obvious industrial applications and especially, in the detergent industry. A classic example of a surfactant is soap. The recognition of phase equilibrium and phase behaviour in surfactant systems and in particular, to the complex phase equilibria, which exist in soap-water system, owes much to J.W. McBain (1950). With the synthesis of new surfactants in recent development, has challenged the science community to understand the behaviour of these fascinating molecules and the thermodynamic changes that are accompanying them.



Schematic illustration of surface active substance, surfactant

Surfactant, an abbreviation for surface-active agent, is a class of compounds, which are unique in their own right. Due to their hydrophilic (water-loving) and lipophilic (oil-loving) moieties, they are soluble in water and organic solvents. The dual structures tend to orient the hydrocarbon chain into the non-aqueous environment at an aqueous interface and thus altering the properties of the interface. Academically, surfactants are generally categorised, depending on the nature of their polar head group (Table 1), into four types namely:

- Anionic
- Cationic
- Nonionic
- Amphoteric

Table 1: Classification of surfactant

Surfactants	Illustration	Examples
Anionic		Sodium dodecyl sulfate
Cationic		Quaternary ammonium halides (R_4N^+C1)
Amphoteric		Sulfobetaines
Nonionic		Dodecylacohol ethoxylate

These compartmentalisation are for convenient and ease in grouping according to their physical properties but are not relevant when it comes to choosing the right surfactant for a particular end use. Therefore, realistically in industrial applications, to describe a surfactant some of the more important factor need to be address in choosing a surfactant are:

- Is it commercially available?
- Does it perform the function required?
- Is it stable to long storage?
- Is it expensive to use?
- Is it safe to manufacture and transport?
- Is it environment-friendly?

Of late, the safety and ecology concern are becoming increasingly important requirements. No matter how good or cheap the finished product, if the surfactant poses a danger to the consumer and environment then the product is not saleable. Presently, there is also a shift by consumers and surfactant producers changing from petroleum-base feedstocks to that animal fats, vegetable oils and carbo-hydrates (Figure 1). The reason being surfactants synthesised from these natural and renewable feedstocks, has the following advantages (Yoneyama 1996).

- It is easy to produce
- It is found to have good detergency behaviour (Figure 2)
- It shows excellent detergency in hard water and in the absence of phosphates (Figure 3)
- It has excellent biodegradability and hence poses little or no danger to the environment (Figure 4)

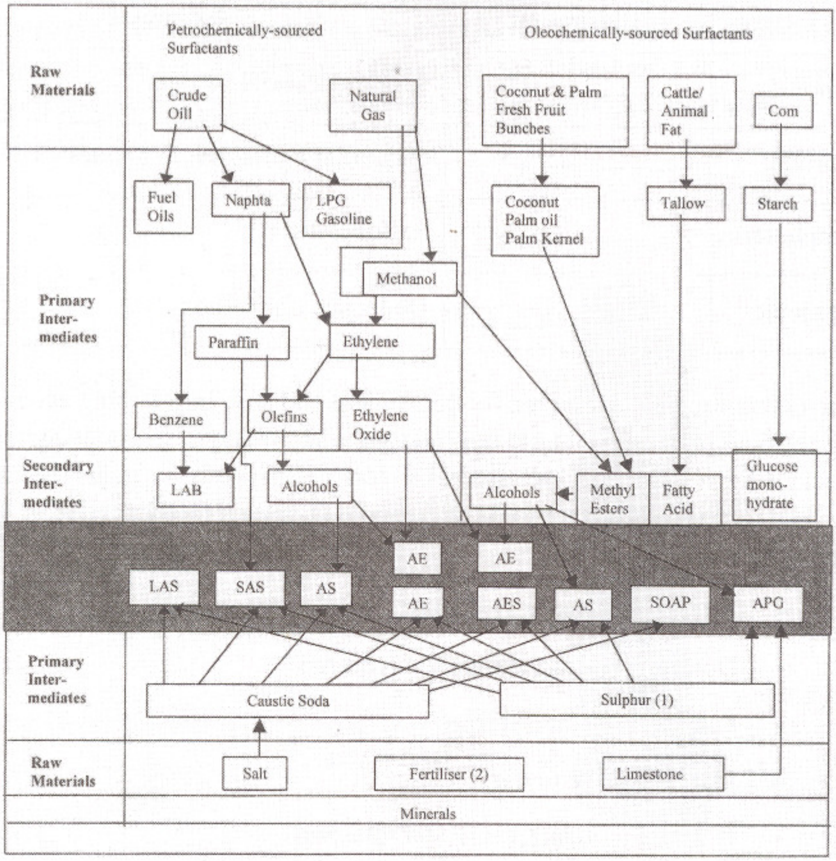


Figure 1: Sourcing Diagram for Surfactants Production (Material Flow)

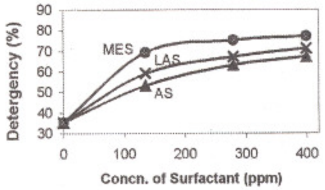


Figure 2: The relation between detergency and the concn. of the surfactant

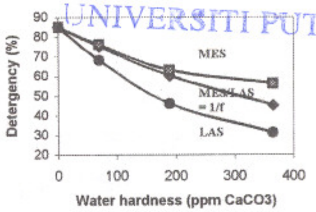
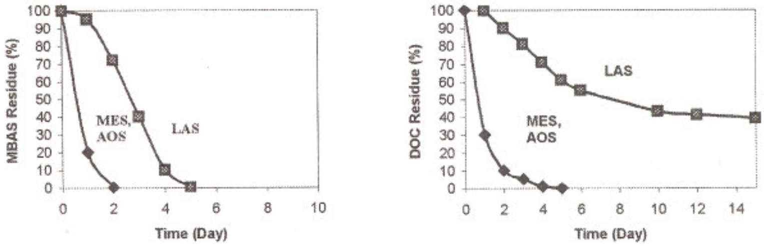


Figure 3: Effect of water hardness on detergency of MES/LAS mixed system



(a) Detected by MBAS method

(b) Detected by DOC method

Figure 4: Biodegradation of surfactants by shake culture method

Oils and Fats (Oleochemical) Surfactants

Oils and fats are mainly used in food applications and only a small portion is used in non-food and technical applications. In 1993, worldwide fat production amounted to 88.5 million tonnes, of which 20% or about 17 million tonnes were used for non-food and technical applications (Figure 5). A major application of technical fats is the production of oleochemical surfactants (Table 2). It is estimated that in the year 2000 a total of 110 million tonnes of oils and fats would be available of which 15 million tonnes available for oleochemical consumption. Oleochemical surfactants accounted for about 40% of all the surfactants produced, which corresponds to about 1.4 million tonnes. Figure 6 shows the production of detergent, which are the most important end use for oleochemicals and the consumption of surfactants in industrialised countries in 1992. Asia however, has a low consumption of detergents (Figure 7). Looking at the enormous consumption by the industrialised countries and an expected increase in the world population from 6 billion in 1999 to 7 billion in 2010, one can envisage the huge growth potential for surfactant consumption in this region. One would also expect Malaysia with its ready availability of palm oil and oleochemical processing know-how to be a major player of the development to produce aleochemical surfactants.

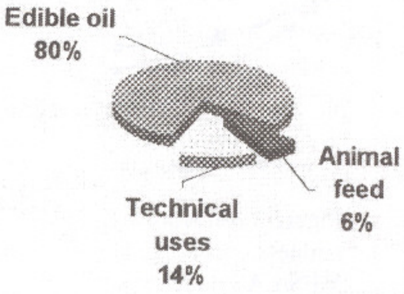


Figure 5: World usage of fats and

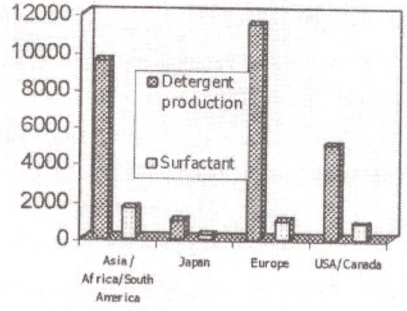


Figure 6: Detergent production and surfactant us e worldwide 1992 ('000 MT)

Table 2: Production of oleochemical surfactants

Surfactant	Surfactant used
Fatty alcohol derivatives	1100
LAS	1850
BAS	500
MES	50
Other	100

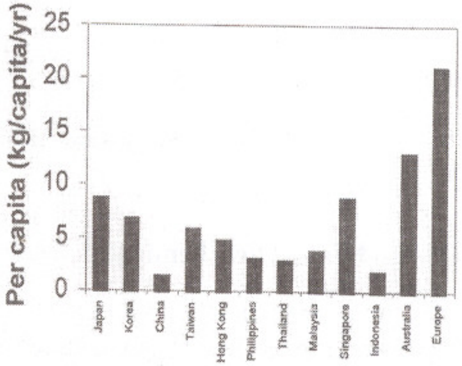


Figure 7: Detergent consumption in the Asia-Pacific region

Palm Oil: Malaysia's Gift to the World

Malaysian palm oil products continued to maintain their share in the global oils and fats market. The world production of oils and fats increased from 79.8 million tonnes in 1990 to 102.4 million tonnes in 1998, registering an average annual growth of 3.6% as shown in Table 3. Out of the 102.4 million tonnes of oils and fats produced in 1998, palm oil contributed 18.9 million tonnes or 18.4% of total global production compared to 15.5% in 1990.

Malaysia produced 52% of the world palm oil production, contributed 8% of the world production of oils and fats and 20% of the world oleochemicals. The World Bank has projected that palm oil production will surpass soybean oil production after the year 2000. As mentioned earlier, world oils and fats production is expected to reach 110 million tonnes this year of which about 22.6 million tonnes of palm oil and 22.4 million tonnes of soybean will be produced, respectively. These figures and numbers simply illustrate that Malaysia is in a better position to contribute actively and competitively by not only continuing to be the leading supplier of palm oil but also a giant player in the production of oleochemical surfactants.

Table 3: World Production of Major Oils And Fats (Mil. T.)

Year	PO	SBO	SFO	RSO	Total V-Oils	Animals	Grand Total
1980	5.1	13.3	5	3.5	38.3	18.2	56.5
1990	12.4	16.1	7.8	8.1	49.6	20.2	79.8
1997	19.5	20.8	9.5	12.8	79.1	21.1	100.2
1998	18.9	24	8.6	12.3	18.0	20.6	102.4
2000	22.9	22.4	10.3	15.0	87.9	21.5	109.4
2010	33.5	28.1	12.9	23.6	119.1	22.9	142.0
2020	40.2	34.3	15.8	34.7	150.3	24.0	174.3

Biosurfactants

A background on the developments of surfactants is by no mean complete without mentioning about biosurfactants and especially sugar-based surfactants and natural surfactants found in our body system.

Sugar-based Surfactants

Sugar-based surfactants or alkyl polyglucosides (APG) (Figure 8) are a class of nonionic surfactant. The first idea and realisation on the use of saccharides especially for surfactants began in the early 1990's. By simply conjugating the hydrophilic sugars with hydrophobic fatty acids, these "biosurfactants" are formed which nicely satisfy the needs of the industry and the environment, today as well as tomorrow. It is worth mentioning that synthesising different compounds that exhibit the hydrophilic-hydrophobic character necessary for a surfactant is not a difficult task, but to synthesise a "world-class" commercial surfactants (like those of LAS, MES and AE) would be an experience of a lifetime. Sugar-based surfactants offer this challenge and coupled with oleochemical surfactants, I am a confident major discovery and breakthrough will be waiting at the end of the tunnel. For all we now it could be a Noble Prize winner!!!

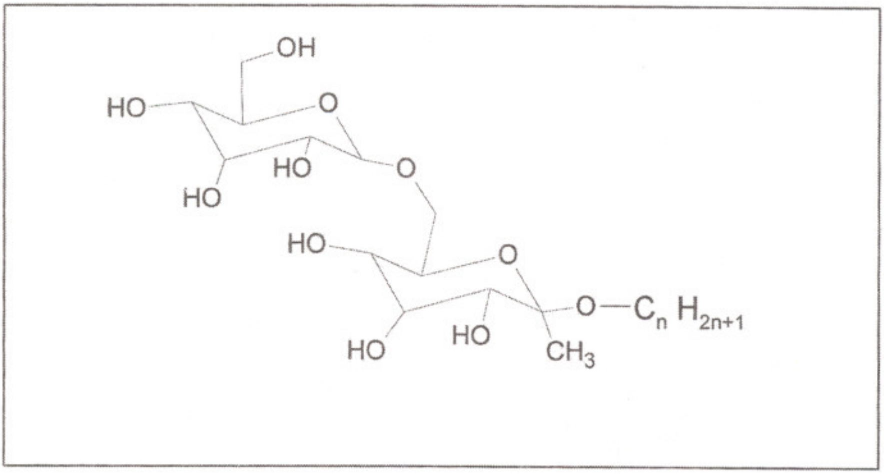


Figure 8: Typical structure of alkyl polyglycoside

Natural Surfactant in Human Body

I would like to share with you a newspaper article about baby Monika Dryburgh. Normal babies are born at the usual time of forty weeks but for baby Monika she was ten weeks early. She was very premature. For the next nine weeks after she was born, she was fighting for her life. She was very weak and having difficulty in breathing and was dependent on the respirator for 3 weeks. The chances of survival were slim and her parent thought that they would loose their precious baby.

But today at the age of 18, Monika is just like any other teenagers. She is breathing normally, excels in her studies and led a healthy life. Thank you to SURFACTANT. She was given a special surfactant treatment. This surfactant called **pulmonary surfactant** is a chemical produced in the lungs. It makes them much easier to expand, by reducing the surface tension in the millions microscopic air sacs which make up the bulk of the lung. Without surfactant, air sacs tend to collapse. Those baby born very prematurely, before enough surfactant has been produced, find breathing much more difficult. This could develop to lung problem called respiratory distress syndrome, which could result in death. Examples of pulmonary surfactants are pumactant and beractant. Other examples of natural surfactants are bile salts and lipids of human skin.

Surfactant Association Structure

I hope that in this short introduction or scenario setting I have been able to convince you of some of the wonders, the flavours and the beauty of surfactant behaviour. To uncover the secret of these wonders, I shall now proceed to the surfactant association structures.

As I have mentioned earlier, surfactants are among the most demanded products in the chemical industries today. They appear in such diverse products (Figure 9) as the detergents used for laundry, the lubricants, the pharmaceuticals and cosmetics, the drilling muds used in petroleum exploration and the list goes on and on... The question now arises is how and why does surfactant fits into all these applications that is very dear and close to our daily living. To answer, one must therefore, understand the phase behaviour of surfactants and the association structures or aggregates, which underlie them.

In order to understand the phase behaviour in surfactant systems, it is imperative that one is able to provide answers to four questions below:

1. How many phases exist?
2. What is the composition of each phase?
3. What is the structure of each phase?
4. What is the boundary of each phase?

Correct answers to all these four questions mean that the phase behaviour is known and understood.

Most surfactants have crystalline structures and when a solvent, commonly water, is added to the surfactant molecule, the crystalline molecules create their own interface by forming monolayers, micelles, vesicles and lyotropic liquid crystal in order to remove a portion their structure from contact with the solvent. Surfactant aggregates on the other hand, can form separate thermodynamic phases such as emulsion, microemulsion and coacervates (Hamdan et al 1995: 1996: 1997). The phase behaviour in a typical ternary phase diagram of a surfactant/water/alcohol system illustrates this variation in behaviour (Figure 10). Much of the contributions in the construction of ternary diagrams was attributed to Ekwall (1975), who has meticulously established numerous ternary diagrams of surfactants systems.

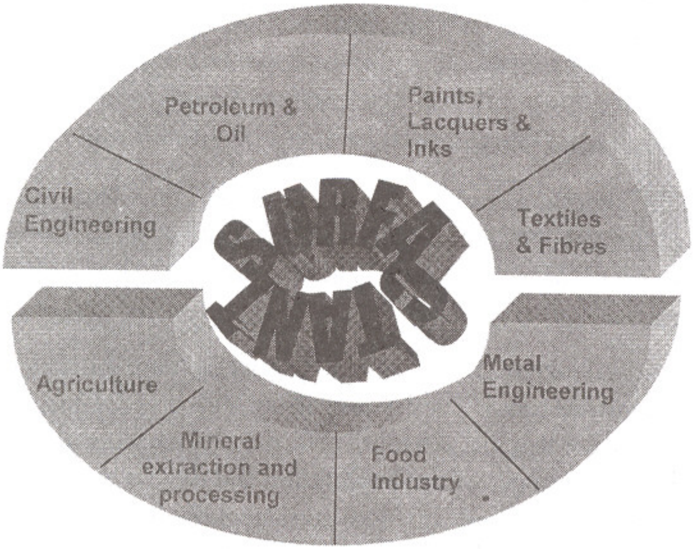


Figure 9: Some applications of surfactant

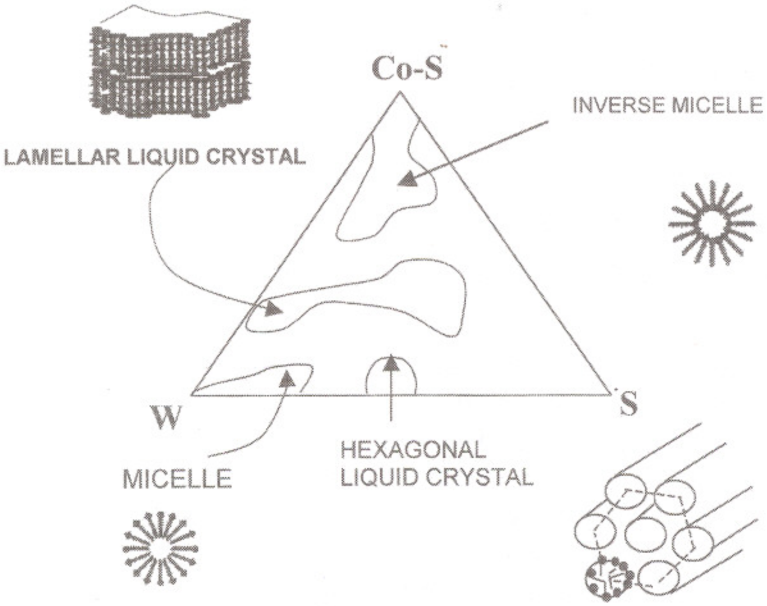


Figure 10: Surfactant Phase Behaviour

It is these association structures/aggregates that is responsible for the vast application of surfactant. It has been shown that micelle structures are responsible for the cleaning process while liquid crystal, an important structure in biological membrane such as human skin, provides information on the stability of the end product. I have the opportunity to be involved in a research group headed by Friberg to understand the chemical aspects of cell membrane and especially human skin, from model systems based on surfactants (Friberg et al. 1988: 1991, Hamdan and Friberg, 1990). This is simply because cell membrane lipids are natural surfactants. In 1985, the group succeeded in deriving a **Skin Epidermal Lipids Model** to be used and served as a basis in many cosmetic formulations. Friberg won the Kendall Award for this achievement and the secret underlie it is in the formation of liquid crystal.

Surfactant Research in UPM

Realising the vast potential in this particular area, the need to expand the downstream activities of palm oil and the miracles performed by natural surfactant, I have initiated a fundamental research on the physical aspect of surfactant properties with special emphasis on the association structures in surfactants systems. My first attempt was to investigate the location of palm oil and the penetration of water in the liquid crystalline structure of ionic surfactants (Hamdan 1991). This is because it has great relevancy in many palm-based cosmetic formulations. Then as the year goes by I have managed to convince a few of my colleagues and formed a group called **Surfactant Research Group (SRG)**. The group consists of five chemists in different chemical discipline. Through SRG and the synergistic blends of ideas, the research has blossomed and mushroomed into what it is today. We have ventured into numerous possible venues and have successfully established phase behaviour of many surfactants systems; be it petroleum-base or oleochemical-base or natural-base surfactants (Anuar et al., 1998, Ambar et al., 1997, Dzulkefly et al., 1994; 1997 & 1999, Faujan et al., 1995; 1997 & 1998, Zaizi et al., 1996). Even though the facilities were limited and the financial support was little that did not stop nor deter us from working. SRG's philosophy is to turn shortcomings into opportunities. SRG is just like a surfactant. Though small in quantity, but exhibit a massive performance.

Finally, in 1996, the Ministry of Science, Technology and Environment (MOSTE) awarded SRG with a handsome IRPA grant of about to RM500,000.00 to undertake a national project on the *"formulation of cosmetic and toiletries products from oleochemical and their derivatives"* for the Seventh Malaysia Plan. In this limited time and space, it is not possible to discuss all of the projects. I shall only concentrate on three of the projects undertaken whereby the findings have not only given great satisfaction to SRG and provide new insight into the studies of surfactant systems but also was recognised by several agencies as an award winning project.

New and simple method to detect the structural change in microemulsions

A characteristic property of surfactant molecules is their tendency to form aggregates. At a certain concentration called the **critical micelle concentration (cmc)**, the surfactants will create their own interface and formed micelles. These micelles will in turn form separate thermodynamic entity called **microemulsion**. Above the cmc value a number of solutes which would normally be insoluble or slightly soluble in water dissolve extensively in surfactant solutions. A phenomenon called **solubilization**. It is this phenomenon and its structural change that became the main thrust in this project. In order to elucidate the location and the structural changes in such systems, techniques such as fluorescence spectroscopy, electron spin resonance (ESR), nuclear magnetic resonance (NMR) and laser light scattering (LLS) are employed. Those techniques require high cost equipments. Take for instance a good NMR will cost around RM 1.5 million.

A newly developed method from our laboratory, a natural flavour, is used to detect the structural change (Hamdan e al. 1995). The method in not only cheap but also, very rapid and reliable. With the usual titration to turbidity of the natural flavour into the microemulsion solutions, graph as in Figure 11 is obtained. Figure 12 shows the result reported by other workers using laser light scattering. Eventhough the method lacks the information on the location of the solutes (Laili et al. 1997); it is nevertheless a useful method to detect the presence of micelle, which is an important phenomenon in detergency.

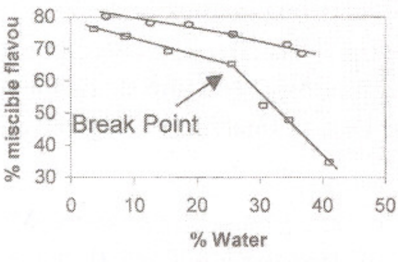


Figure 11: Variation of miscible flavour content with water content

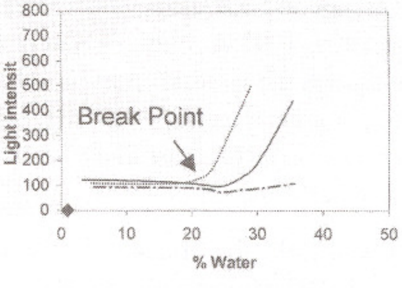


Figure 12: Variation of light intensity with water content

Phase behaviour of mixed surfactants system in nonaqueous environment

Mixed surfactant systems are inevitable in nearly all practical application of surfactants. These mixtures arise from:

- The already mixed nature of the feedstocks such as feedstocks with variable hydrocarbon chain length
- The difficulty in producing chemically pure surfactants
- A single surfactant cannot provide all the properties required
- The relatively lower cost in production
- The superior performance compared to those of single surfactant

The growing interest and practical importance of mixed surfactant system has seen much research activities in the late 1980's and early 1990's. Several books and review articles have been published devoted to mixed surfactants systems. My contribution (Hamdan et al. 1992; 1993; 1994; 1995 & 1996) in this area has been directed to the nonaqueous system of mixed surfactants an obvious impediment to the progress in this field but surprisingly, attention was only given on single surfactant systems. There was no report published anywhere on the nonaqueous system of mixed surfactant. Seeing this opportunity to be a pioneer, I quickly published the first comparison of the phase behaviour of mixed surfactant in aqueous and nonaqueous systems in 1995 (Hamdan and Laili) as shown in Figure 13. This pioneering contribution won me the **1996 National Young Scientist Award** from MOSTE and the **1996 Young Scientist Lectureship Award** from S & T NAM, India.

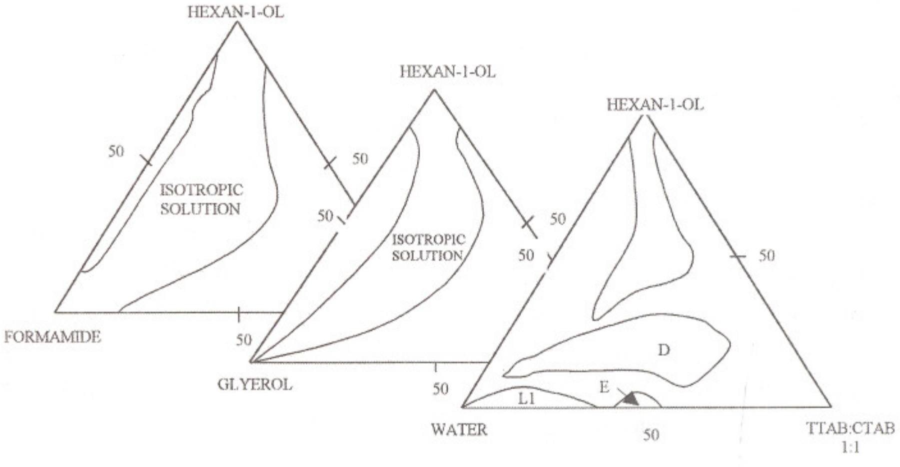


Figure 13: Comparison of aqueous and non-aqueous in mixed surfactant system

In Search of Novel Surfactant: Synthesis of sugar-base surfactant via solvent-free esterification

To start off with, recently, this project was selected as the top ten researches in the **"2000 UPM Research and Invention Award"**. The project also won the **"1998-1999 Lever Brother Award"**, for outstanding research in Surfactants and Detergents and the **"2000 Best Graduate Student Project"**, both awarded by the American Oil Chemist's Society, USA. If I may, I would like to share with you one of the comments made by the reviewer:

"The paper reports an interesting method for assigning structures and the composition of mixtures of mono and difatty acid esters of peracetylated α*-D-glucopyranoses. The use of HMBC as a tool to probe the induced shifts on the carbonyl carbon is **very novel**. This work will make an excellent contribution to JOACS."*

The words "very novel" are underlined and bolded because this project was launched as a PhD project in a pursuit to search and synthesise new and novel surfactants (Obaje et al. 1999 & 2000). As mentioned earlier, the sugar-base nonionic surfactants have demonstrated prospects for meeting the current demand of environment concerns, safety of use and renewability of raw material resource. However at present, esterification methods for producing sugar-base fatty esters have been facing with many problems such as:

- Low yield and uneconomical
- The solvents used (pyridine, DMF, DMSO, benzene etc) are toxic and unsafe for food applications
- High temperature needed in the process

In this project, a solvent-free, low temperature chemical interesterification, yielding up to 90% product (mainly mono - and di-fatty acid substituted, acetylated glucopyranoses) was developed. The reaction scheme for the interesterification is shown in figure 14 and the major products are shown in Figure 15. The structural elucidation of these products has always remained difficult and not as straight forward which sometimes led to ambiguous conclusions. However, by systematically combining the ^{13}C-NMR technique with heteronuclear shift correlation, Hetcor and heteronuclear multiple bond correlation (HMBC) data (Figure 16) to assign chemical shifts of the pyranosyl ring-proton and carbon atoms and those of carbonyl carbon atoms, a novel method was developed. The molecular structure was successfully characterised as shown in Figure 15.

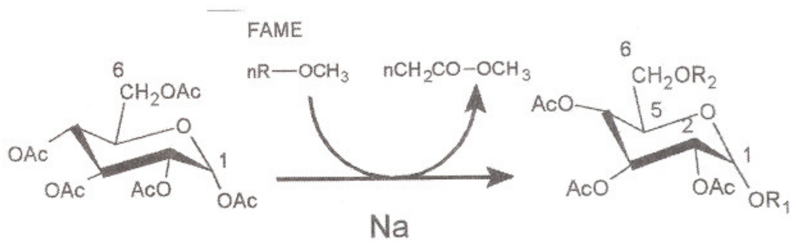
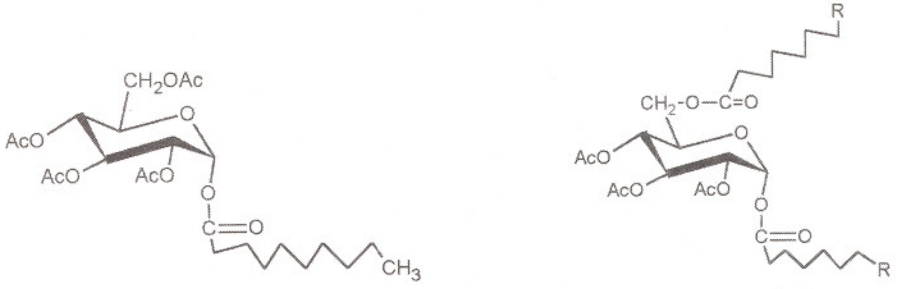


Figure 14: Reaction scheme for interesterification



Product A: 1~O~fatty acid 2,3,4,6-
acetyl α-D-glucopyranose
(~R = the fatty acid group)

Product B: 1,6-O-fatty acyl 2,3,4-
acetyl α-D- glucopyranose
(~~R = the fatty acyl group)

Figure 15: Molecular Structures of the major Products

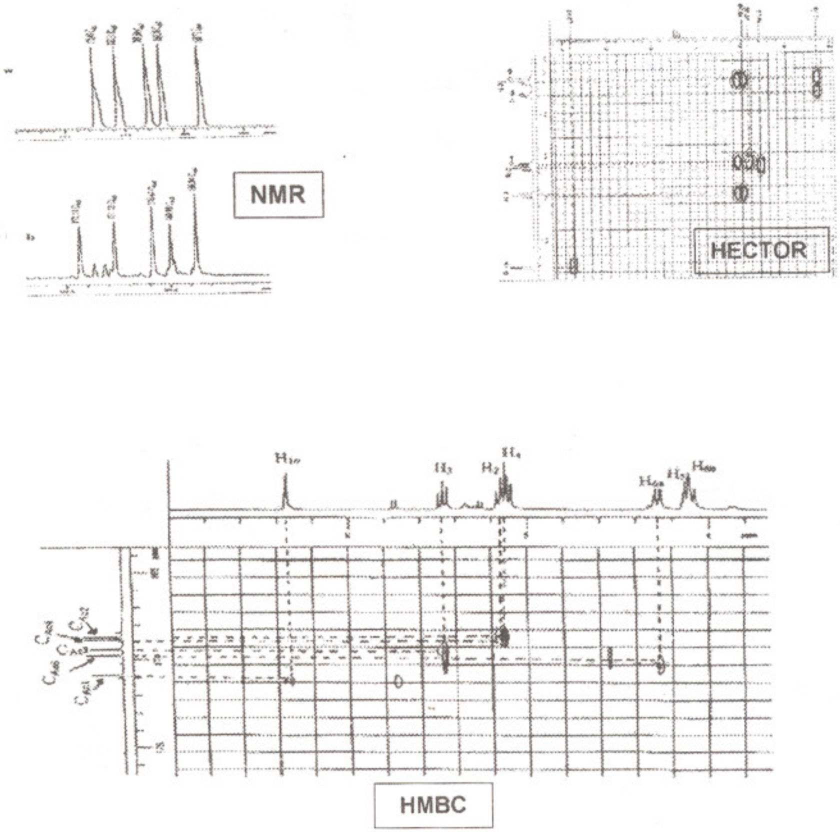


Figure 16: The spectra of NMR, Hector and HMBC for assigning molecular structure

Future Direction

The examples given above show that major progress has been made in the area of surfactant behaviour. I have to admit that when I started off with this research my focus was not very clear. Now with the availability of so many behaviour of surfactant systems and ease in accessing information, one can make an educated guess to which cases merit an in-depth study. This type of effort requires the collaboration of chemists from different disciplines. For larger applications, engineers have to be included to develop scale-up procedures and techniques for continous processing. I am happy to say that SRG has all of the above. It is time to move forward and be more focussed and directed towards the commercialization of our findings without of course sacrificing the fundamental groundwork which is the underlying forces responsible for the phenomenon of surfactant behaviour. Fundamental research is still an integral part of the program in order to provide firm basis for applying knowledge to practical problems.

Another challenge is a factor of **sustainability**. Being up there is easy and not much of a problem, but staying up there could be a difficult task. In addressing this factor, I foresee 4 key elements to sustainability, i.e.: i). Research grants, ii). Infrastructure, iii). Reward system and iv) economic. If all the challenges and requirements surrounding these elements, are either overcome or fulfilled, I am confident this area of research offers tremendous opportunity for both academia and industry. It is truly fascinating, intriguing and rewarding.

Indeed, I conclude that the many wonders of surfactant behaviour, as old as it may be, is presently in a state of rebirth.

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