Design and Selection of Performance Surfactants

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Annual Surfactants Review

A series of annual volumes providing in-depth reviews of the most topical areas of surfactant science and technology. Written by authors from leading laboratories around the world, it is directed at surfactant researchers and manufacturers and users of surfactants: in particular, surfactant chemists; analytical chemists; environmental chemists; users of surfactant formulations in the fields of speciality chemicals, polymers and detergents; and health and safety personnel.

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Preface

Based on the premise that all commercially available surfactants are at best simple blends and that many in reality are a complex mixture of surface active species and minor non-surface active components, it rapidly becomes apparent that the prediction of performance-structure relationships is far from easy. The development of surfactants to meet specific performance criteria requires a fundamental knowledge of structural features and/or components which contribute to or possess one or more of the desired surface active properties. For example, a low foam wetting agent and emulsifier may contain a major component which is an excellent emulsifying agent and wetter with a tendency to foam, but a minor component may act as a defoamer, rendering the product 'low foam'. Structural aspects of each major component must be understood, while the possible influence of minor components should not be ignored. In addition to the basic factors influencing hydrophobicity (e.g. chain length, degree of chain branching) and hydrophilicity (e.g. poly(oxyethylene) content), the stereochemistry of surfactant molecules is a critical feature of surfactant design, as this in part will determine their interfacial behaviour. Simple 'monomeric' surfactants containing a single linear hydrophobe and a single hydrophilic 'head group' will pack closely at an interface, whereas a surfactant with a sterically very large hydrophobe will have far less molecules per surface area of the interface. Likewise, oligomeric 'comb' surfactants and polyfunctional surfactants, such as polyol-based EO/PO copolymers, provide effective surface coverage, due to the multiplicity of their hydrophilic groups.

Volume 2 of this *Annual Surfactants Review* series addresses some of these structure/performance considerations, from computer modelling through to a consideration of how to modify specific surfactants by adjusting carbon chain length distribution, by studying the influence of chain branching, by introducing reactive groups or fluorinated hydrophobes, or by replacing conventional hydrophobes (or hydrophiles) with natural feedstock derivatives. The latter include carbohydrate derivatives, natural hydrocolloids and biosurfactants. A detailed study of catalytic and kinetic effects in ethoxylation processes shows how nonionic ethoxylate compositions can be altered, and this is further illustrated by a consideration of narrow chain length distribution fatty alcohol ethoxylates and their properties. Influence of chain branching in fatty alcohol ethoxylates is also demonstrated, using secondary alcohol ethoxylates as an example. Two end-use applications are included, not only to report the latest developments in those areas but also to illustrate

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the performance/selection approach in identifying the most appropriate surfactants for a specific end use.

The Editorial Board and the Publishers have attempted to report back on some of the more recent and innovative developments in the field of surfactant technology. A single volume will provide only a fragment of the total picture but, as this *Annual Surfactants Review* series develops, it is hoped that the collected volumes will provide a valuable work of reference. The Editorial Board would welcome any constructive comments in relation to either the content or the presentation.

Dr David A. Karsa

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1 Sugar derived surfactants

H.S. Bevinakatti and B.K. Mishra

1.1 Introduction

Ever since the invention of ethoxylation by Scholler and Witter in 1930, the market for non-ionic surfactants has grown steadily [1]. Needless to say, the major share of this class of surfactants is constituted by polyoxyethylene surfactants due to the flexibility they offer. While the going has been good for the synthetic petrochemical-based surfactants in general until recently, growing environmental awareness is putting a lot of pressure on their continued use as surfactants. Keeping in mind that surfactants/emulsifiers have found inroads into a wide range of applications from use in detergents to more sophisticated applications such as the electronics industry, environmental friendliness and their biodegradability have become major issues [2]. The next millennium will decide the fate of these surfactants as the fear of tightened regulatory eco-toxicological appraisal systems becomes even more important.

Industrial surfactants are now required to be more environmentally acceptable, particularly where residual surfactants may find their way into aquatic or land environments. This has led to continuous, critical assessment of the use of long-established surfactants and a search for more cost-effective and environment-friendly alternatives. Moreover, due to the complex nature of even the most simple commercially available surfactants, the exact mechanisms of how they work are not often clearly understood and continue to be the subject of debates. This has led to a degree of empiricism while selecting surfactants for certain applications. Such issues may make it necessary to have a serious look at new safer and well-defined molecules and both surfactant producers and end-users have taken a voluntary, proactive approach to such changes in recent years [3].

One such class of surfactants which fits into the present-day requirements is carbohydrate derived surfactants, in short—sugar surfactants. Carbohydrates, in addition to being conjugates of renewable feedstocks, are also inexpensive and readily available. They are not harmful to the environment due to their complete biodegradability under aerobic and anaerobic conditions. They are non-toxic, non-skin irritants, odourless and tasteless, and they give normal food products after human and animal digestion. The presence of several hydroxyls and an aldehyde/hemiacetal group serves as good handles for their further modification to attach hydrophobes. In addition, if these hydrophobes are derived from

vegetable oils, another abundant natural resource, it further boosts the 'greener' image.

An attempt has been made in this chapter to bring together the information currently available on sugar surfactants. While chemical methods have delivered some of the widely used sugar surfactants as detailed in the next few pages, there may be scope for further improving the quality, contents and image of these surfactants through emerging biotechnological tools such as using enzymes for their preparation. Though such 'natural' processing conditions are being claimed to be vastly superior to the conventional present-day synthetic methods, only time will tell about their commercial viability in the long run.

1.2 Chemical synthesis and production

Currently available sugar surfactants fall into three distinctly different chemical classes—esters, acetals and amides. While esters are the oldest in the range of surfactants constituting well-known products such as sorbitans, including their ethoxylated counterparts, and sucrose esters which were introduced in 1940s and 1950s, respectively, acetals and amides are more recent. Alkyl polyglucosides belong to the acetal class and were introduced on the market in the 1980s. Amides are the most recent class of sugar surfactants to be marketed and alkyl glucamides were commercialized only in the 1990s. While it is beyond the scope of this chapter to cover all the excellent work done on carbohydrate-based surfactants of academic interest, an attempt has been made to look at molecules of commercial importance.

1.2.1 Sorbitan esters

Fatty acid esters of anhydrosorbitol, generally called 'sorbitan esters', are the second largest class of carboxylic ester surfactants and probably the first sugar surfactants to be commercially made and marketed. The first sorbitan ester synthesis was reported as far back as 1939 [4]. While sorbitan monoesters take the major share of the market in this class, the di-, and triesters are also commercially available. These are prepared commercially by the direct esterification of sorbitol with a fatty acid at 200–280°C in the presence of either an acid or base catalyst [1] as shown in Figure 1.1.

Though one would expect to see some sorbitol esters formed in this reaction, the product, however, contains none of them. Sorbitol undergoes dehydration at the high temperatures used for the reaction

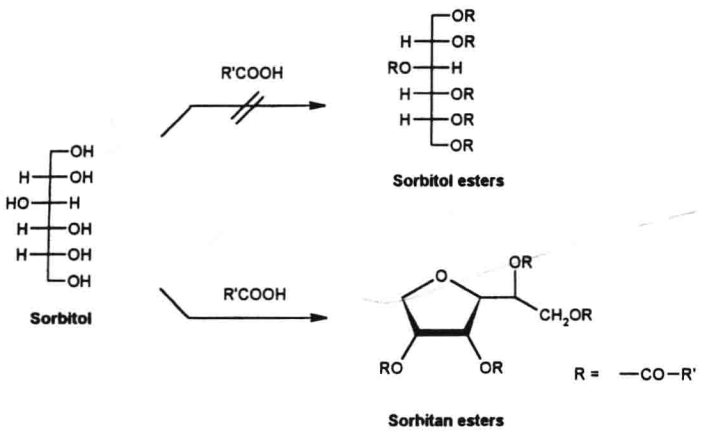

Figure 1.1 Chemical esterification of sorbitol leads to sorbitan esters.

to give internal cyclic ethers. While the monodehydration occurs predominantly to give sorbitans, double dehydration leads to isosorbide. Moreover, the monodehydration can take place in several ways due to the presence of multiple hydroxyls to give several isomers like 1,4-, 3,6-, 2,5- and 5,2-sorbitans [5, 6]. Thus, the commercial product not only is a mixture of several isomers, but also contains varying degrees of mono-, di-, and triesters. Analyzing such a complex mixture to pinpoint the exact number and identities of its constituents has been a difficult task as shown by the recent studies carried out using high-performance liquid chromatography (HPLC) and supercritical fluid chromatography [7, 8]. A more recent study using the GC–MS technique detected around 50–65 components in a commercial sorbitan ester [9]. They could detect up to ten sorbitan isomers in the product based on which the possible dehydration products as shown in Figure 1.2 were proposed.

Though the process is now well established and has been in operation for the last 50 years, the effect of various catalysts on the course of reaction was only recently studied [10, 11]. Rate of dehydration vs. esterification using catalysts such as *p*-toluenesulphonic acid, phosphoric acid, sodium hydroxide and sodium phosphates was observed. While it was found that monosodium phosphate led to the most effective dehydration of sorbitol, disodium phosphate was found to be less reactive and trisodium phosphate had no effect.

While it is believed that dehydrative cyclization in any high temperature chemical esterification of sorbitol is inevitable, some of the recent processes claim formation of sorbitol esters having essentially no anhydro compounds. One such process [12] claims rapid heating of a mixture of 2.5 mol of each sorbitol and coconut fatty acids containing 0.4% NaOH to 240°C for 35 min, allowing it to be stirred at this

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