Feature; Surfactants1
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Introduction

An essay question set by the Society of Cosmetics Scientists (UK) in its prestigious Distance Learning Course started "Arguably surfactants are the single most important class of compounds found in cosmetics". It is a statement that is difficult to dispute as they are used as cleansing and foaming agents, emulsifiers and solubilisers, for wetting and dispersal of pigments and for skin and hair conditioning. They may have antimicrobial properties, add emolliancy; modify product rheology and impart texture and feel to product compositions.

This feature is going to focus on mild surfactants used in personal cleansing formulations and on some of the more recently introduced emulsifiers and solubilisers and will also suggest thickening aids for systems that do not respond well to the addition of electrolytes.

Mild Surfactants for Personal Care

Shower gels and body washes are invariably based on surfactants and the well established combination of sodium laureth sulphate [SLES] with cocamidopropyl betaine [CAPB] is still that in most common use. However for more expensive brands with claims to extra mildness, creamier foams and other positive attributes there are many more materials to investigate. The pursuit of more mild compositions may have been stimulated by a paper by Peter Dykes published in the International Journal of Cosmetic Science [IJCS] [Ref 1] in 1998.

In it Dykes described the effects of surfactants on the skin and wrote that when we clean the skin we remove not only the bacteria, dirt and grease which have accumulated, but also part of its natural barrier, the stratum corneum. Corneocytes, both singly and in clumps, are released from the skin surface by the action of detergents and mechanical stimulation. So too are the lipids and proteins which make up the inter-corneocyte region of the stratum corneum Dykes continued, changes in the physical properties of skin occur after washing, for example, changes in skin surface pH and transepidermal water loss (TEWL) are easily demonstrable. Also excessive exposure to surfactants results in repeated damage to the stratum corneum which can in turn lead to an irritant dermatitis.

In the pursuit of foam, which the majority of users perceive as a desirable product property, it is easy to overlook that when the bubbles are first formed they are spherical. There is enough space between each individual bubble for the presence of the surfactant-containing liquid, and the foam behaves like an emulsion and feels wet. However as the bubbles age the liquid drains from them and they assume a hexagonal shape, these bubbles are unstable and soon collapse. There is little liquid within the bubble walls and they have little wetting ability.

When formulating foaming products it is necessary to remember that sufficient wetting occurs only if the surfactant-containing liquid can drain from the foam to contact the skin, and drainage can occur only if the foam bubbles are spherical. Shampoos require a quick transition from spherical to hexagonal so that they can be readily rinsed away; shower gels need to be stable for two minutes or more while the user massages the product onto the skin and shave creams need to last the length of the wet shaving process.

The Cornelius Group has produced an interesting PowerPoint presentation [Ref 2] that shows micrographs of various foams produced by commonly used surfactants and how their stability can be controlled by the addition of certain surfactants from **RITA**. Because of its excellent foaming characteristics an 8% solution of sodium lauryl sulphate was used as the bench mark and comparable foams were produced using a blend of 0.8% acyl lactylate with 7.2% cocamidopropyl betaine. RITA claims that the addition of short-chain acyl lactylates results in high volumes of foam that remain stable for an extended time period and it is mild and biodegradable.

As well as the individual acyl lactylates RITA also supplies surfactant blends of various lactylates with cocamidopropyl betaine, decyl glucoside and various anionic surfactants. Supplying blends is becoming an increasingly popular method for suppliers to turn commodities into specialities, which are appreciated by users. They provide optimum mixtures for specific applications; mean holding less material inventory and avoid minimum order problems for lesser used ingredients.

Thus **Rhodia** supply Miracare SLB365 as a blend of sodium trideceth sulphate with cocamide MEA and sodium lauramphoacetate that make it possible to produce stable body washes with up to 30% oil content. It can support exfoliants and incorporate silicone oils using a simple cold mix procedure, which produces spherulites that are stabilised by the addition of guar derivatives. In use the oil content is deposited onto the skin giving a superb emollient effect.

The **Stephenson's Group** takes blends even further by supplying finished product concentrates. The Duroclens range of concentrated cleansing ingredients is derived from natural oils that have been developed to help formulate rinse-off products. They can be readily diluted in water and the concentrates are compatible with typical surfactant systems like SLES and CAPB or they can be used as the sole cleaning agent in a formulation. Stephenson's also market Durasoft polyglyceryl esters of natural oils that are water-soluble co-surfactants that may be added to shower gels to enhance foam and skin feel.

Ajinomoto supply Amisoft CS-22, a blend of sodium cocoyl glutamate and disodium cocoyl glutamate as an ultra-mild anionic surfactant mix that imparts a pleasant moisturised skin feel without drying the skin. Ajinomoto is well known for its amino acid based surfactants such as sodium cocoyl glycinate, sodium cocoyl alinate and various glutamates. Amisoft ECS-22SB [INCI: Disodium cocoyl glutamate] is suggested as an extremely mild surfactant system for delicate baby skin. Also if used as a tertiary surfactant in combination with SLES/CAPB it significantly reduces irritation and helps the skin to remain moisturised.

Sodium cocoyl glycinate is available as Hostapon SG from **Chemlink** and is a mild surfactant that gives a rich lather making it ideal for creamy body washes. Amino acids are also the basis of Liposine Glyglu/R from **Maycos Italia,** which is a lipo-amino acid obtained by the acylation of coconut fatty acids with amino acids from rice. This interaction forms a lipo-amino acid complex with cleaning and foaming properties. The foam obtained is creamy, fine and stable and the product is very mild to the skin.

Taurates are an alternative to alkyl ethoxylated sulphates and claim mildness and good foaming properties. **Nikko Chemicals** supply sodium N-cocoyl-N-methyl taurate as a 30% aqueous solution. It is trade named CMT-30 and Nikko claim that by minimising the salt level and by careful control of the alkyl chain in manufacture it is possible to make low viscosity shampoo and cleansing preparations that are clear and have excellent foaming characteristics.

It is difficult to find a more cost effective surfactant for foaming products than SLES and provided it is not excluded from use for marketing reasons there are many ways of reducing its negative effects while enhancing its performance and foaming properties. As an example **Kalichem Italia** suggest Olivoil Avenate Surfactant [INCI: Potassium olivoyl hydrolyzed oat proteins] as a poly-functional surfactant with mild cleansing power and emollient properties. It may be used alone in ultra-mild compositions or in conjunction with SLES to substantially reduce TEWL following showers and personal cleansing. Its structure is a balanced combination of whole lipids from olive oil and oat proteins.

Also from Kalichem and recommended for use in conjunction with conventional anionic surfactants is Olivoil PCa which is said to provide the skin with the moisturising effect of PCA with the benefits of the unsaturated fatty acids from olive oil. It is claimed that Olivoil PCA provides the skin with smoothness, a reduction of TEWL and renovation of the normal barrier function of skin. Another product range that adds exceptional smoothness when incorporated in shower gels are the Polyox high molecular weight polyethylene glycols from **Amerchol-Dow.**

Co-surfactants in cleansing compositions are usually either amphoteric like CAPB or non-ionic. Non-ionic surfactants are favoured because they are generally very mild to the skin and moderate the irritation and excessive cleaning that can be experienced with conventional anionic surfactants. Levenol H&B is a glycerine polyoxyethylene ester from **Kao**, [INCI: Glycereth-2 cocoate]. Described as a multifunctional and versatile non-ionic co-surfactant. it performs as a thickener and foam booster in rinse-off cleansers. Because it is a glycerine ester it has good skin conditioning and moisturising properties. **Respharma** markets the water-soluble olive oil polyglyceryl-4 esters as Resplanta PGF Olea with similar properties of foam boosting and skin conditioning.

Inulin obtained from chicory is the source material for two materials from **Beneo**. Inutec H25 is inulin itself and Inutec SP1 is inulin lauryl carbamate and both can be regarded as co-surfactants that improve foam texture and skin feel. Formulations incorporating these materials show excellent foaming even when containing up to 10% oils.

A product with cationic properties and compatible with anionic surfactants is Vegequat from **Sinerga.** It is a 30% solution of cocodimonium hydroxypropyl hydrolyzed wheat protein formed by the condensation of coconut fatty acids with hydrolyzed wheat protein. Although it’s principal application is in conditioning shampoos it can also be used in creamy body washes. Another product with cationic conditioning properties that is compatible with anionic surfactants is Silplex J2S from **Siltech** [INCI: Silicone Quaternary-20]. It is a water-soluble cationic silicone/anionic silicone complex that gives outstanding conditioning to skin and hair..

Whatever the cosmetic product category it is almost impossible to avoid silicone-based materials. Shower gels are no exception and **Koda** supply a number of polyethylene glycol modified silicones under its Hydrosil trade name. They are described as new and unique silicone urethane oligomers and are compatible with other silicone-based products and are readily soluble in water based formulations, adding lubricity and foam stability. They also show outstanding wetting properties for pigments and powders and 3-6% in water successfully wets fluoro-coated pigments and inorganic sunscreen actives, thereby aiding in their dispersal.

The principal use of silicones in surfactant compositions is in 2-in-1 shampoos but suspension of the silicone and achieving significant deposition onto the hair has always been a problem. An article in the IJCS [Ref 3] describes an increase in the deposition efficiency of silicone conditioning actives from a shampoo on colour-treated hair via liquid crystal colloidal structures, created with polyquaternium-6 and negatively charged surfactants such as ammonium lauryl sulphate and ammonium laureth-3 sulphate. This approach may be worth considering as a way to deposit silicones from shower products.

Emollients other than silicone are also incorporated in surfactant systems to improve skin feel and this is the theme of a paper by A. Mehling published in the same journal [Ref 4]. In this study, the effects of various tripartite systems consisting of SLES, a co-surfactant and an emollient were studied. The two different emollients tested; dibutyl adipate and a methylpropanediol monoester, adsorbed in varying amounts although the same surfactant/co-surfactant system was used. It was found that the deposition of both SLES and/or the emollient was also substantially influenced by the emollient component itself as well as by the co-surfactant used. Sensory assessments showed that although SLES has a negative effect on skin feel, adsorbed emollients improve skin softness and smoothness. Mehling concluded that the results show that optimisation of performance is possible when using a co-surfactant best suited for the emollient.

An emollient blend recommended for adding to shower gels is Nipseal PP21 from **Brasca**. It is a mix of C9-15 alkane with hydrated silica and polyquaternium-2 that is claimed to add skin feel and moisturising properties to the formulation. Amisol Trio from **Lucas Meyer** is a blend of phospholipids, glycine soja, glycolipids and glycine soja sterols that can be added to shower gels at 0.3% to reduce TEWL and improve skin hydration. Also from Lucas Meyer Detoxium is a mix of magnesium salts from sea water with phospholipids and stearoyl inulin, suggested as an additive for shower gels

Solubilising Perfumes and Essential Oils

Dissolving oils in water for such products as skin toners is difficult; made more so if the market does not want ethoxylated compounds, and various solubilising agents have been proposed to overcome the problem. **Sinerger** suggest Natisol [INCI: Cocoyl proline] for dissolving perfumes and essential oils. **Lonza** has the Polyaldo series of surfactants which are worth consideration; they are polyglyceryl-10 oleate and polyglyceryl-10 stearate. Sisterna L70-C is sucrose laurate in 40% aqueous/alcohol solution with good perfume solubilising properties.

Croda suggests the use of NatraGem S140 and NatraGem S150 as highly efficient natural solubilisers with counter-irritancy benefits. S140 is polyglyceryl-4 laurate/sebacate with polyglyceryl-6 caprylate/caprate and S150 is polyglyceryl-4 laurate/sebacate with polyglyceryl-4 caprylate/caprate, each in aqueous solution. The S140 is particularly effective for solubilising essential oils and a solubility table is available through Croda.

Symbio Sollv XC from **Dr Straetmans** is a PEG-free multi-component mixture of caprylyl/capryl wheat bran/straw glycosides, fusel wheat bran/straw glycosides, polyglyceryl-5 oleate, sodium cocoyl glutamate and glyceryl caprylate in aqueous solution recommended for solubilising perfumes and essential oils. Natpure SOL from **Sensient Technologies** is a mixture of sucrose esters that are all made from materials of natural origin. It has a combined HLB of 15.5 and shows outstanding solubilising properties, which are confirmed by many examples in its brochure.

Thickening Surfactant Systems

The viscosity of traditional anionic surfactant systems responds well to the addition of electrolytes and can be thickened to the desired level, even to a gel structure. However many of the surfactants described in this article do not respond to added salt and alternative systems are necessary. PEG-150 stearate is frequently used but its shear-thickening rheology is often a disadvantage. Other traditional thickeners include xanthan gum, carrageenan and various cellulose derivatives and there are many grades of these materials, each with different rheology profiles.

Guar derivatives also come under the heading of traditional rheology modifiers and are well known as hair conditioning agents but they are also useful for thickening difficult surfactant systems such as those based on amphoacetates. **Rhodia** supply a number under the Jaguar label and Jaguar C162 [INCI: Hydroxypropyl guar hydroxypropyltrimonium chloride] is worth consideration.

Versathix from **Croda** is an aqueous solution of PEG-150 pentaerythrityl tetrastearate with PPG-2 hydroxyethyl cocamide and described as an exceptionally versatile rheology modifier that provides viscosity building across a wide variety of surfactant systems, with a neutral effect on foaming. It provides viscosity in traditional, as well as sulphate free systems, coupled with shear thinning rheology which is especially important in bath and shower gels

More recent introductions are based on acrylate chemistry and Rheomer 33 from **Rhodia** [INCI: Polyacrylate-33] is a good example. It is a hydrophobically-modified alkali-swellable emulsion (HASE) polymer for personal cleansing solutions designed to provide efficient thickening with shear-thinning rheology and good suspension properties in low-to-medium surfactant systems.

Another example of a hydrophobically modified polymer is Aristoflex HMB from **Clariant.** This ammonium acryloyldimethyltaurate / beheneth-25 methacrylate crosspolymer is a pre-neutralised thickening additive for surfactant systems. Aculyn 28 by **Dow** is an acrylates/beheneth-25 methacrylate copolymer that is compatible with non-ionic and anionic surfactants and imparts pseudoplastic thickening to surfactant systems over a broad pH range.

Ajinomoto has prepared a very interesting presentation [Ref 5] showing the viscosity response of N-acyl glutamate to the addition of glyceryl laurate in the presence of magnesium chloride. The rheological behaviour is dominated by the change in micelle shape; initially these are spherical but the addition of glyceryl laurate changes their shape to rods and then added magnesium chloride changes their shape to worm-like and finally liquid crystals are formed. Disodium cocoyl glutamate can be used to control rheology of SLES/CAPB systems and this is the subject of a second presentation [Ref 6].

This article has focused on alternative surfactants to the traditional SLES/CAPB systems for use in personal care cosmetics. Many of them can form the basis of products for use in Spa treatments such as scrubs and bathing products with added benefits. This theme will be continued in the next issue.

NOTE: Many of the materials named are Ecocert approved and where INCI names are given this is for the principal ingredients only. Those interested are advised to contact the supplier for more information.

Ref 1 Dykes , P. (1998), Surfactants and the skin; Int. J. Cosmet. Sci, 20: 53–61

Ref 2 Acyl lactylate derivatives; The Cornelius Group

Ref 3 Brown *et al* (2010), Liquid crystal colloidal structures for increased silicone deposition efficiency on colour-treated hair; Int. J. Cosmet. Sci; 32, 193–203

Ref 4 A. Mehling *et al* (2010), Differential deposition of emollients from tripartite formulation systems; Int. J. Cosmet. Sci, 32, 117–125

Ref 5 Novel facial wash formulation based on the technique of wormlike micelles in aqueous n-acyl glutamate systems; Ajinomoto Amino Science Laboratories; available through Rahn UK.

Ref 6 Rheology control using viscoelastic surfactant solutions; Ajinomoto Amino Science Laboratories; available through Rahn UK.

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