

Feature: Surfactants 2005

John Woodruff

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Although almost everyone uses cosmetics in one form or another there has always been a movement against them, culminating in the Marriage Act passed by the British Parliament of 1670:

*"Be it resolved that all women, of whatever age, rank, profession, or degree; whether virgin maids or widows; that shall after the passing of this Act, impose upon and betray into matrimony any of His Majesty's male subjects, by scents, paints, cosmetics, washes, artificial teeth, false hair, Spanish wool, iron stays, hoops, high-heeled shoes, or bolstered hips, shall incur the penalty of the laws now in force against witchcraft, sorcery, and such like misdemeanours, and that the marriage, upon conviction, shall stand null and void."*

Currently we see movements not so much against the products themselves, but against various constituents. For decades there have been consumers who prefer not to use ingredients of animal origin, others who are concerned about allergic reactions to preservatives and those irritated by certain aromatic chemicals. This has given rise to new product launches to satisfy niche markets, some of which have become mainstream brands.

However other negative decisions are harder to understand and there is hardly a group of materials that does not have its anti-body, with chemical-free being the extreme example. Unfortunately rumours and scare stories can be started by anyone with access to the web and if widely circulated, it will only be a matter of time before they are given credence by the tabloid press. Surfactants are not immune to this process and we have all seen the negative comments about sodium lauryl sulfate (SLS) and sodium laureth sulfate (SLES) and, however many reasoned science-based rebuttals are produced, the general public only remembers the bad news. [**Surfactants 2004**] described many of the surfactants that were available as an alternative to SLES and its inseparable companion, cocamidopropyl betaine.

The movement against SLES is extended to all ethoxylated compounds, which includes the majority of effective solubilising compounds and a whole generation of emulsifiers. Fortunately non-ethoxylated emulsifiers are readily available and many of these are suitable for forming liquid crystals and lamellar structures within the emulsion, thus providing interesting sensorial textures and improved delivery vehicles. While not new, liquid crystal structures in emulsion formation have become increasingly important because of the unique properties that they confer. These organised systems are a mixture of amphiphilic compounds stabilised by the attraction of the molecules of a polar solvent, usually water. Liquid crystals are characterised by a very compact structure in which slightly longer formed molecules are arranged along parallel axes. The action of specific molecular interaction compacts and organises them in parallel. The temperature in a liquid crystal system is very important. The tendency to align is reduced by thermal agitation, while the cooling of the system increases the forces that cause the alignment, allowing the molecules to form a crystal state. [Ref 1]

Two structures are found in the emulsions: oleosomes and hydrosomes. Oleosomes are multilayers of lamellar liquid crystals surrounding the oil droplets that become randomly distributed as they progress into the continuous phase. The rest of the liquid crystals produce a viscoelastic gel phase. In the case of hydrosomes the lamellar liquid crystals produce a gel network in the continuous phase. The lamellar phase

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becomes swollen with water in between the bilayers. The network structure of liquid crystals extends throughout the emulsion and provides good suspending properties and it also improves emulsion stability by restraining the movement of droplets, thus reducing the tendency for droplets to coalesce. [Ref 1]

The stratum corneum consists of lamellar liquid crystalline structures of bilayers of ceramide, cholesterol and fatty acids. There are obvious similarities between the natural biological skin lipid system and the sub-microscopic bi-molecular membranes of oil-in-water skincare products. Emulsions based on liquid crystal technology hold more water in contact with the skin for a longer period and tend to penetrate the stratum corneum to a greater degree than other skin care products yet do not disrupt its bi-layer structure. They also have the advantage of being thixotropic, so spreading properties are considerably enhanced.

At the IFSCC Conference, Florence 2005, Johan Wiechers described the influence of liquid crystalline emulsion structures on the skin delivery of active ingredients. In a series of experiments Wiechers found that the rate of skin penetration of active ingredients can be influenced by the emulsifier system. Liquid crystal-forming systems enhance the skin delivery of both hydrophilic and lipophilic ingredients. For hydrophilic active ingredients, they permit longer dosage times and hence their delivery. For lipophilic active ingredients, they increase the speed of skin penetration and can therefore be used when fast efficacy of a lipophilic active ingredient is required.

There are many emulsifiers available that are able to form stable liquid crystalline structures, also called lamellar structures because of the arrangement of the micelles. Typical properties of these emulsifiers is their efficacy at low levels, often as little as 0.50% will stabilise an emulsion, and 2 – 5% is sufficient if used as the sole emulsifier. However they do vary in the way that they should be incorporated into an emulsion; some are added via the oil phase, others via the aqueous phase.

Mixing followed by homogenisation followed by slow stirring to ambient without further homogenisation is generally recommended but individual suppliers instructions should be followed. For lotion viscosity products it is usually beneficial to add a small quantity of a hydrocolloid like xanthan gum to improve stability. Cream-like consistency may be achieved by increasing the level of the emulsifier and/or of the oil phase or by adding a fatty alcohol, fatty acid or glyceryl stearate.

The author decided to make a simple evaluation of various non-ethoxylated emulsifiers that were on the sample shelf and which were claimed to form o/w emulsions with lamellar structures. They are listed below with abstracts of the supplier's descriptions.

- Olivem 1000, B&T, is a mixture of sorbitan olivate and cetearyl olivate. It is described as a self-emulsifying system forming liquid crystal networks, made from olive oil by esterification of fatty acids groups, with sorbitol and cetearyl alcohol. Emulsions formed with it have a light and silky texture, good spreading properties and easy skin penetration.
- Montanov 68, SEPPIC, a mixture of cetearyl glucoside and cetearyl alcohol, is described as a glucolipid co-emulsifier that is close to nature and an excellent promoter of liquid crystals. These act as genuine water reservoirs within the emulsion, helping to maintain moisturising of the skin over time. It gives creams with a rich texture for use on dry skin, for sun-care and for make-up products.

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- Arlatone LC, Uniqema, is a mixture of sorbitan stearate with sorbityl laurate that does not require additional emulsifiers to form stable o/w emulsions with a smooth, light skin feel. From 2 – 3% is used to form a lotion, 4 – 5.5% is recommended for creams although stearic acid, GMS or a fatty alcohol may also be used to give extra body.
- Arlatone 2121; a mixture of sorbitan stearate with sucrose cocoate, also comes from Uniqema. As well as forming o/w emulsions it can be used to form water-free emulsions based on an oil phase with a polyol and it forms stable emulsions with high ethanol content.
- Tego Care 450, Degussa, INCI: Polyglyceryl-3 methylglucose distearate, forms stable emulsions with all common oils and fats used for skin care products, including polar oils. Application properties of the emulsion are adjusted by the choice of oils: the better the spreading properties and the lower the viscosities of the oils are, the "lighter" the resulting emulsion.
- Tego Care CG90, Degussa, INCI: Cetearyl glucoside, forms liquid crystal structures in the presence of stearic acid or fatty alcohols. The oil phase components can be selected from mineral oil, vegetable oils and synthetic esters which enables the formulator to vary the application profile of the emulsion.
- Emulsiphos, Symrise, is a blend of potassium cetyl phosphate and hydrogenated palm glycerides, resulting in an efficient non-ethoxylated phosphate emulsifier for o/w applications.
- Eumulgin VL-75, Cognis, INCI: Lauryl glucoside & polyglyceryl-2 dipolyhydroxystearate & glycerin is a new, vegetable-derived and dermatologically highly compatible o/w emulsifier that shows a high emulsification potential for emollients of various structures. It is recommended for sun care applications because of its dispersing properties with inorganic screens and solubilising properties for polar organics.

A simple formulation was devised that would challenge the emulsifiers; it contained sweet almond oil and cetearyl alcohol, caprylic/capric triglyceride and glycerine but no additional stabilising additives or rheology modifiers were added. The emulsifier was added to either the oil phase or aqueous phase, according to the recommendations of the supplier.

<b>Oil Phase</b>	<b>%w/w</b>
Caprylic/capric triglyceride	7.00
Cetearyl alcohol	1.00
Prunus amygdalus dulcis (Sweet almond) oil	5.00
Tocopherol	0.10
<b>Aqueous Phase</b>	
EDTA, disodium salt	0.06
Glycerine	5.00
Imidazolidinyl urea	0.50
Aqua (Water)	To 100%
<b>Emulsifier</b> ; added as advised by supplier	3%*

\*Tego Care CG 90 was 1.5%  
 The oil phase was heated to 75C or as advised and added with mixing to water at a similar temperature. The mixture was briefly homogenised then cooled to ambient temperature with slow stirring. After 24 hours the product was divided and part was homogenised Samples of homogenised and non-homogenised product were stability checked at 40°C and also centrifuged at 3,000 rpm for 5 minutes, if stable they were also centrifuged at 5,000 rpm for a further 5 minutes. Samples were examined under a polarising microscope, with and without phase

contrast, for liquid crystal structures (LC) at 500x magnification.

All emulsifiers were present at 3% except Tego Care CG90, which was added at 1.5% yet still gave the highest viscosity. It must be stressed that none of the formulations were optimised for the emulsifier used. The effect of homogenisation on the emulsion 24 hours after formation varied considerably with the viscosity of some compositions being increased, some hardly changed and others were reduced. In most cases it improved the centrifuge stability but stability at 40C was generally adversely affected. There appeared to be little change in the numbers of LC present.

The samples used were a random selection and there are many others available that promote lamellar gel networks. Cognis recently introduced Emulgade PL68/50, a mixture of cetearyl glucoside and cetearyl alcohol and Eumulgin SG, INCI: Sodium stearoyl glutamate, that is effective at low levels and the viscosity of emulsions prepared with it are said to remain stable whereas the viscosity of many of the samples prepared by the author as described above increased with time. Tecomag supply an emulsifier based on hydrolysed wheat protein glutamate with cetearyl alcohol, glyceryl oleate and glyceryl stearate. Uniqema promote phosphosomes as an alternative to hydrosomes and oleosomes. They are based on Phospholipid EFA, a source of the linoleic acid, and said to provide an excellent after-feel on application, and allow prolonged moisturising.

The emulsifiers so far described are all non-ethoxylated. Cerulation H, Sasol, is based on the Gemini surfactant, sodium dicocoylthylenediamine PEG-15 sulfate in combination with behenyl alcohol, glyceryl stearate and glyceryl stearate citrate. The unique structure of Gemini surfactants is said to make them ideal carriers of ceramides and as dispersing aids for microfine oxide-type sunscreens.

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Ref 1. A new emulsifying system for liquid crystal structures: Dr Guido Bregaglio & Keith Harrison, Tecnico Res Pharma

Ref 2. Johan Wiechers *et al*, The influence of liquid crystalline emulsion structures on the skin delivery of active ingredients; IFSCC Conference, Florence 2005.

Emulsifier	pH	Viscosity	Centrifuge rpm		Stability @ 40C	Microscope
			3,000	5,000		
Olivem 1000	5.40	9,860	1	2	3	Droplets were small & evenly distributed. Few LC in either sample.
Ditto homogenised		7,100	1	1	5	
Montanov 68	5.30	15,580	3	N/A	1	Dense packing of LC observed. More varied distribution after homogenising.
Ditto homogenised		8,620	1	2	1	
Arlatone LC	5.89	5,680	3	N/A	2	Dense packing of LC observed in both samples.
Ditto homogenised		5,880	2	N/A	4	
Arlatone 2121	6.01	6,760	4	N/A	3	Uneven size distribution, improved by homogenising. Lots of LC structures in both samples.
Ditto homogenised		6,360	2	N/A	2	
TegoCare 450	6.00	18,000	1	2	1	Densely packed small LC in both samples.
Ditto homogenised		15,000	1	2	1	
TC CG90 @ 1.5%	4.81	31,800	1	1	1	Densely packed medium-size LC in both samples.
Ditto homogenised		40,800	1	1	1	
EU VL75 @ 3.0%	5.47	6,150	1	1.5	1	Uneven size distribution, improved by homogenising. Few signs of LC structures.
Ditto homogenised		5,500	1	2	3	
Emulsiphos	6.10	10,280	3	N/A	1	Loose packing of multiple LC, improved by homogenising.
Ditto homogenised		9,040	2	N/A	1	

Centrifuge & 40°C stability is compared on a scale of 1 to 5, with 1 being the most stable and 5 showing significant separation.