From soap to high-tech emulsifiers

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There are two basic needs that are as old as mankind – hygiene and skin care. Both of them deal with the transport of lipid substances. In order to work most effectively while being gentle on the skin, modern cosmetic products make use of powerful tensides and emulsifiers. Recent emulsifying systems even are oriented towards biological structures.

The cleansing is intended to remove more or less fatty residues while the skin care is focused on providing the skin with lipid substances. Isn't it natural then just to combine lipids and water? But how can it be done? In order to mix such dissimilar phases like lipids and water there is need for an additive which basically reduces the surface tension of water and combines with both superficial lipid as well as water layers. This characteristic is called "amphiphilic" which literally means "loving both". In other words: the substance simultaneously is lipophilic (likes lipids) and hydrophilic (likes water).

Saponins

How had this problem been solved in times when there was no chemical industry yet? Well, people were orientated towards Mother Nature. They used appropriate vegetable components like saponins (sapo is the Latin term for soap) for cleansing. These substances are contained in the bark of the Latin American soap bark tree, in Indian soap nuts, leguminous plants and horse chestnuts. The roots of the soapwort (saponaria officinalis) contain 2 to 5 % saponins. They consist of a lipophilic steroid or triterpene structure and a linked hydrophilic sugar – they are basically simple precursors of today's sugar tensides.

Sodium carbonate, potassium carbonate

Hence, people experimented with a multitude of different substances and, among others, mineral ash (potash) gained in log fires. It mainly consists of potassium carbonate (potassium salt of carbonic acid). Potash has a high pH-value and reacts with acids while it releases carbon dioxide. Also the fatty acids on the skin surface as for instance palmitic acid react in the same way and form fatty acid salts – potassium palmitate.

K_2CO_3 (potassium carbonate) + 2 x $C_{16}H_{33}COOH$ (palmitic acid) ==> 2 $C_{16}H_{33}COOK$ (potassium palmitate) + H_2O (water) + CO_2 (carbon dioxide)

Potassium palmitate is composed like a typical soft soap. Soft soap is amphiphilic and can emulsify triglycerides (lipids) and hydrocarbons as for instance squalene of the skin. Sodium carbonate, the sodium salt of carbonic acid which naturally occurs in saline lakes, is similar to potash. The cleansing effect of carbonic acid salts is excellent, and today they are used in floor cleaning products among others. Yet, they are rather skin-unfriendly since they quickly leach out the skin.

Soft soaps and curd soaps

Later it was found out that the boiling of watery soda or potash solutions with vegetable oils or animal lipids resulted in comparably mild soapsuds. After sodium chloride or potassium chloride has been added to the stable viscous emulsions, soaps can be separated – the chemical term for this process is "salting out". These soaps are still on the market in form of soap bars. In combination with soda, the rather hard curd soaps are formed whereas the above mentioned soft soaps result from a combination with potash. The term "saponification" comes from this process, and has become the technical term for ester hydrolyses since triglycerides of the vegetable oils and animal lipids are the fatty acid esters of glycerin which are hydrolyzed into glycerin and three fatty acids by reaction with water. In this process the fatty acids – as described above – are transformed into the corresponding sodium or potassium soaps. Soaps are universally usable to do the laundry or for body cleansing purposes. They are particularly mild when they contain a sizable residue of unsaponified oils and lipids or even free fatty acids ("super-fatted soaps").
The Medieval soap boilers used to be an important profession. However, as soon as sodium and potassium hydroxide have become industrially available, they replaced soda and potash. They made saponification processes a

lot faster and less expensive. Today, superfatted soap bars made of vegetable oils have become increasingly popular again.

O/W Emulsions

If the soap amount in soap oil mixtures is further reduced so that only a low percentage is left, the cleansing activity takes a back seat. Resulting then are stable O/W cream emulsions with skin caring features. From the physiological point of view, they have good skin caring properties as the comparably low amounts of soaps are transformed into the corresponding free fatty acids in the skin. In other words: the soaps as such do no longer exist which means that the washout effect of the skin care oils after subsequent skin cleansings is relatively low, a fact which stands in marked contrast to many modern synthetic emulsifiers. These are not transformed in the skin and activated again as soon as the skin gets in contact with water with the effect that skin care and barrier lipids are transported out of the skin.
Furthermore, it turned out that partly saponified triglycerides, hence diglycerides (glycerin with two fatty acid residues) and monoglycerides (glycerin with one fatty acid residue) also have emulsifying properties. If they contain traces of soaps, they are called "self-emulsifying". Ester hydrolyzing skin enzymes then complete the transformation of these glycerides into glycerin and free fatty acids.

Emulsifiers & tensides

A disadvantage of soaps is their sensitivity towards the water quality. Hence, they form ugly grey flakes when they come in contact with hard water. These are non-soluble calcium or magnesium salts which form grey, yellowy to brownish spots on textile fibers. For a long time these spots have been compensated with additives in complementary colors (washing blue).
Detergents today have complicated formulas. They contain alkyl polyglycosides (sugar tensides) as surface-active agents and sulfonates for which hard water is no longer a problem. Sulfuric acid esters of alcohols and ethoxilated alcohols (sodium lauryl sulfate, sodium laureth sulfate) are frequently used in simple liquid soaps. In addition to that, emulsifiers with most diverse structures are used for cleansing and skin care purposes.
The frequently found differentiation between emulsifiers and tensides (detergents) rather refers to their application than to their chemical structure. In both cases we are dealing with the same surface-active compounds. They are called **emulsifiers** in lipid-containing systems like skin care creams (leave-on products), food and metal working fluids, and **tensides** if they are surface-active, fat-free or low-fat detergents (skin care: rinse-off products). In case of anionic emulsifiers like soaps and sulfuric acid esters, the lipophilic part is negatively charged, whereas the lipophilic molecule area in the rarely occurring cationic emulsifiers (quaternary ammonium salts) is positively charged. Amphotheric emulsifiers (amphotensides, betaines) have a positive and a negative charge which means that they appear neutral on the outside. Non-ionic tensides (niotensides, nonionics) to which the above mentioned sugar tensides, the frequently occurring polyethylene glycols (PEG), polypropylene glycols (PPG), polyglycerins and many of their derivatives belong, also are neutral.
In the narrower sense, **microemulsions** are no longer emulsions but highly concentrated tenside systems. In these systems, the water and oil phases can no longer be differentiated under the electron microscope. Due to the side effects of tensides respectively emulsifiers they have no bearing in cosmetic products except for cleansing products like shampoos.
Besides the O/W emulsions in which the oil droplets are stably emulsified in water, W/O emulsions (water droplets in an oil matrix) and so called multiple W/O/W and O/W/O emulsions are used. In **multiple emulsions,** droplets of the inverse phase are again found in the emulsified droplets. They are very finely dispersed and show an excellent stability.
O/W emulsifiers often have their hydrophilic group located at the end of a linear molecule. W/O emulsifiers, by contrast, frequently have it in the center area of a possibly also branched molecule. During the warming up process, O/W emulsions often turn to W/O emulsions. This also happens vice versa. The phase inversion process is used to produce finely dispersed O/W emulsions via cooling down process.
Besides the droplet structure, there are also emulsions with lamellar areas which can be detected as streak-like structures under a low resolution microscope. They are characteristic for some stearate-containing compositions and should not be confused with lamellar structured and emulsifier-free liposomes (bilayer) or Derma Membrane Structures (planar multilayers). The latter mentioned are only visible with an electron microscope.

Emulsifier free systems

There is one problem, however, that cannot be solved with modern emulsifiers (tensides). Due to their surface active effects emulsifiers do not only disperse the cream components but also the lipid components of the skin barrier. This

leads to skin barrier disorders, above all when applying emulsifiers which, unlike glycerides (see above), do not integrate into the homeostasis of the skin. Rather often, it is attempted to compensate the emulsifier impact on the transepidermal water loss (TEWL) by adding filming paraffins and long chained silicones.
There are still emulsifier free suspensions for the sensitive skin – particularly as pharmaceutical preparations. Water and oil phases are separated here and that is the reason why the suspension needs shaking before use. From the physiological point of view, this is a quite reasonable solution, but in terms of applicability it is rather inconvenient. Systems like the Derma Membrane Structure or liposomes are orientated towards biological structures like the skin barrier itself or the structure of skin cells. They have a lamellar-like structure and are emulsifier free. The ingredients are copied from Mother Nature and consist of phosphatidylcholine (main component of cell membranes), ceramides and sterols (components of the skin barrier). All the raw materials can be gained from vegetable sources. Monolamellar and biologically degradable nanodispersions based on phosphatidylcholine can also be formed from these components. The skin care products based on these components have minimal wash-out effects only.

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