Emulsifiers enable mixtures

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Emulsifiers are indispensable wherever lipids, oils and waxes are mixed with hydrophilic media with the objective of obtaining a stable mixture over a certain period of time. They are, among others components of food and cleaning agents, lubricants and cosmetics.

Under normal circumstances lipids and aqueous substances can no be mixed – emulsifiers are needed as additives. In general, there are hydrophilic substances which dissolve in aqueous solutions and lipophilic substances dissolving in oils and lipids. In cases where a hydrophilic substance is combined with a lipophilic one within the same molecule an amphiphilic substance is formed with an affinity to aqueous media as well as to oily and fatty substances. Amphiphilics are surface-active which means that they float within the interfaces between aqueous and oily phases and thus form links - the essential precondition for emulsifiers.

Emulsions

Are an aqueous and an oily phase mixed in combination with an emulsifier droplets will form with the emulsifier in the interfaces which avoids the merging of the droplets. Dependant on the structure of the emulsifiers oil in water emulsions (O/W) or water in oil emulsions (W/O) are formed. In the cosmetic and dermatological field emulsifiers are primarily used for creams, lotions and ointments with the objective to combine aqueous as well as oily skin-caring substances and active agents in one single product.
Mixtures of emulsifiers and water are able to absorb lipid substances even later in the process, a specific feature which is used in detergents. In these cases we speak of surface-active agents due to the specific structure of the emulsifiers. These substances are highly surface-active and thus have increased dirt-removing properties.

Soaps & allies...

The oldest known synthetic emulsifiers are soaps, i.e. the sodium and potassium salts of fatty acids. They were first produced from natural lipids with the help of a chemical reaction with sodium carbonate or potash. Still today sodium and potassium palmitate resp. stearate can be found as components of skin care creams and detergents.
As a rule stearate creams are distinguishable by a so-called "slowing down" sensation as soon as the creams are applied on the skin. Used in combination with free palmitic acid or stearic acid as well as glycerol mono and glycerol diesters soaps still belong to the emulsifying systems with the closest affinity to the physiology of the skin as the low pH value of the skin causes the release of the palmitic or stearic acid from the soaps. A precondition here is that the soap dosage is low and the buffer systems of the skin will not be strained. Palmitic acid is a main component of the barrier layers of the skin.

Specific types of emulsifiers

Soaps belong to the so-called **anionic** emulsifiers: they are provided with a negative electric charge. Used in higher concentrations for skin cleansing purposes (soap bars) they cause a pH-value above 7 on the skin which will lead to barrier disorders in cases of long-term influence and subsequently to an unintentional swelling of the skin.
Salts of the fatty alcohol sulfates however as e.g. lauryl sulfate and cetyl sulfate or fatty alcohol phosphates like cetyl phosphate are almost pH-balanced. They are used in O/W products. In contrast to soaps they will stay in the horny layer with hardly any chemical modification which leads to the fact that a new emulsification will take place as soon as there is contact with water, causing lipid substances to be transported out of the skin which also is known as wash-out effect. High dosages of short-chained representatives here like lauryl sulfate may be irritating for the skin which is the reason why this substance is used as the standard irritant in comparative skin tolerance studies. A frequent companion of anionic emulsifiers is triethanolamine used instead of sodium or potassium hydroxide in order to neutralize and activate emulsifiers. Alternative amines are far less frequently added.

Among the **cationic emulsifiers** which have a positive electric charge, quaternary ammonium salts are the most important. As a rule, however, cationic emulsifiers rather are an exception. They are an interesting alternative for hair treatment products e.g. as they gather on the hair and have anti-static effects.
Whenever a positive and a negative charge are combined in a single molecule and thus neutralize each other we speak of **amphoteric emulsifiers** or amphotensides and betains. They are used in shampoos and other hair cleaning products and also frequently leave an anti-static effect on the skin.
By far the most often used type of emulsifier are **non-ionic emulsifiers**. These non-ionics may be synthesized to order, as their basic structure, just to explain it in a simplified way is the linking of a polyethylene glycol (PEG) with a fatty alcohol ("ethoxilated alcohol") or a fatty acid ("ethoxilated fatty acid"). In this process the chain length of the PEGs, the fatty alcohols and fatty acids may be modified in any way in order to receive the intended function. Instead of PEG also polyglycerol ethers may for instance be used. Depending on the respective fatty alcohol O/W or W/O emulsions can be synthesized.
In the INCI they can be detected either by the abbreviation PEG or the ending "...eth" as for example ceteareth-8 which is a compound of cetyl and stearyl alcohol with an ethoxilate chain and 8 ethylene oxide units on average. Further advantages are the low price and their insensibility against electrolytes (salts) and hard water which is important for detergents. Dependent on their structure ethoxilates lead to a more or less intense wash-out effect as they remain in the skin without any modifications. The consumers frequently feel that that their skin becomes dehydrated especially if the creams applied contain mineral oil products with occlusive effects.

...and what about their tolerance?

Their tolerance depends on various factors. An important role here plays the penetrability into the skin. Non-ionic emulsifiers e.g. penetrate easier than ionic ones, short-chained better than long-chained emulsifiers. Short-chained emulsifiers like **lauryl sulfate** e.g. may denaturate proteins or have haemolytic effects. The so-called critical micelle concentration in water (CMC) which indicates in which concentration the dissolved emulsifier molecules aggregate to micelles closely correlates with the tolerance of an emulsifier. The lower the CMC value the better the tolerance of the emulsifier.

Exposed to solar radiation the atmospheric oxygen easily may affect the **ethoxilates**. In this process highly reactive peroxides will develop which may cause the so-called Majorca acne on sensitive human skin. These effects frequently are adjusted by even further additives as e.g. antioxidants, complexing agents and UV filters.
The emulsifier concentration influences dispersion i.e. the size of the emulsion droplets. The smaller the droplets, the better the stability of the emulsion. Along with the concentration of emulsifiers however also the risk of skin barrier disorders is increasing and it is quite a challenge for the manufacturer to find an adequate compromise here.
Microemulsions in this connection are emulsions in which discrete particles are no longer to be identified. Due to their limited tolerance, microemulsions have not gained broad acceptance and can at best be found in rinse-off products as e.g. in cleansing products.
Regarding the tolerance glycerol mono and glycerol diesters are recommended as emulsifiers as they adapt very well to the physiology of the skin. Their handling however is somewhat complicated as they need further additives to emulsify and they may chemically modify during the manufacturing process or the storage of a cream. This frequently includes modifications of the consistency of the product particularly in combination with soaps.

Different types of emulsions

Emulsifiers which dissolve easier in watery phases generally develop O/W emulsions and those with specific affinity to oily phases rather develop W/O emulsions. Frequently emulsifier compounds or so-called co-emulsifiers are used to optimize the stability of the respective emulsion. Cetearyl alcohol is regarded to be one of the typical co-emulsifiers. Other substances may also be helpful in this process as e.g. adding magnesium soaps like magnesium stearate stabilizes W/O emulsions.
A parameter which is very important for manufacturing and stability is the so-called phase inversion temperature (PIT) at which a W/O emulsion converts to an O/W emulsion. A very simple method to determine the emulsion type is to add a product sample on filter paper and see whether a ring of water forms around the sample (O/W) which disappears after evaporating or whether a grease mark shows up (W/O). Besides the O/W and W/O emulsions there are still multiple systems like W/O/W and O/W/O.

Alternatives

Besides the emulsions in the meantime further systems have gained acceptance in which membrane forming substances like ceramides and phosphatidylcholine act as links between water and oils. These systems excel by their double membranes which can be naturally found in form of cell membranes and in the barrier layers of the horny layer. The regular droplet structure which can be identified with a normal microscope however is missing here. Only with the help of the electron microscope structures can be recognized which are formed like cells (liposomes) or layered (derma membrane structure creams). With considerable energy input oil-containing droplets may be produced (nanoparticles) which also are only visible with the electron microscope. As a rule, these systems are not adaptable to conventional emulsifiers. Compared to emulsions their wash-out effect is insignificant and their tolerance is excellent due to their physiological composition. They are particularly suitable for the sensitive and problem skin. Membrane systems can be used for skin care as well as for skin protection purposes. With the exception of a few specific products, emulsifiers are still indispensable in today's cleansing products.

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