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Surfactants From Renewable Resources: Applications In Modern Science And Technology.

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ABSTRACT

The valorization of surfactants, by the use of natural resources as basic raw material, is important in the environmental field. It is an alternative for the synthesis of new compounds respectful of the environment in order to replace petrochemical products, either as hydrophilic or hydrophobic building blocks. The study of their applications is also a solution to the major limitation of their use which was limited a long time due to the problems connected to their preparation and makes it possible to consider the commercial application of this class of useful compounds in almost every chemical industry. The following survey provides an introduction to surfactants derived from renewable natural resources. It goes on to look at their special applications in a series of practical application areas such as protein crystallization, transfection and even in nanotechnology.
Keywords: Surfactants, Valorization, Renewable Resources.

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INTRODUCTION

Worldwide production of surfactants amounted to 17-19 Mt in 2000 (including soap for less than 50%) **[1-3]**. The expected future growth rates is 3-4% per year globally and 1.5-2% in the European Union. The growth rate is closely related to the world demand in detergents, since this sector uses over 50% of surfactant production **[1,4]**.

Surfactants constitute an important class of chemical products, not only because they are commonly used but also because they have a great variety of applications in households, industry and agriculture **[1-3,5]**. They are used in the formulation of detergents (powders or liquid), of cosmetic products (shampoos, shower gels and toothpastes), and beauty products such as creams, milks, cosmetics and other products of care (as emulsionnant or fabric softener).

They are molecules that consist of one hydrophilic (water-loving) part and one hydrophobic (water-hating or oil-loving) part **[6]**. The production of a surfactant is essentially a question of joining different types of these two categories with one another **[6]**. Renewability refers to the sources for the hydrophilic and the hydrophobic groups. Many qualities including biodegradability and not toxicity make particularly interesting surfactants based on carbohydrates or glucidic alcohols (polyols).

It is mainly the amphiphilicity of surfactants that determines their ability to build complex supramolecular structures like micelles, liposomes, lyotropic liquid crystalline phases or microemulsions **[7]**. Of particular interest from a synthetic chemistry point of view is the fact that the amphiphilicity can be tuned via the molecular structure, i.e. via the balance of hydrophilic and hydrophobic parts **[7]**.

New molecular architectures have appeared at the borderlines between classical surfactants and hydrotropes and towards copolymers **[8]**. **Figure 1** focusses on new architectures of surfactants going from flexible hydrotropes or co-surfactants to very rigid diblock amphiphilic copolymers **[8]**.

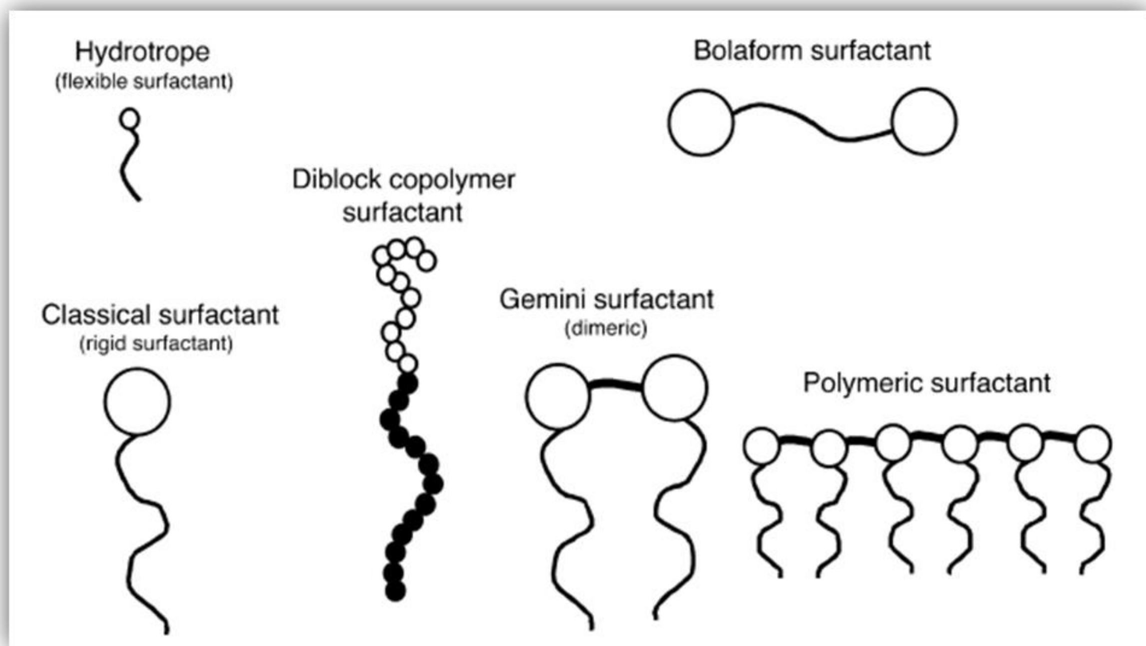

Figure 1: Different molecular architectures of surfactants [8]

Being an important group of products of the chemical industry, surfactants play a significant role in economic and socio-economic terms. Their production and use implies environmental and health impacts **[1]**. There is today a strong trend to replace conventional surfactants with more environmentally benign compounds **[9]**. Manufacturers and consumers demand novel environmentally friendly surfactants from renewable resources produced by clean and sustainable technologies (bio-based surfactants). The challenge is to find surfactants that are mild and biodegradable but meet performance and cost-benefit requirements **[9]**.

Surfactants from renewable resources

A surfactant can be categorised as anionic (negatively charged), cationic (positively charged), nonionic (no charge) and Amphoteric (containing both a positive and a negative group on a large pH scale).

Anionic surfactants are the most widely used type of surfactants for laundering, dishwashing liquids and shampoos. They are particularly good at keeping the dirt, once dislodged, away from fabrics.

Cationic surfactants are produced in much smaller quantities than the anionic. There are several types, each used for a specific purpose.

Nonionic surfactants are often used together with anionic surfactants. An advantage is that they do not interact with calcium and magnesium ions in hard water. Although they do not contain an ionic group as their hydrophilic component, hydrophilic properties are conferred on them by the presence of a number of oxygen atoms in one part of the molecule which are capable of forming hydrogen bonds with molecules of water.

Amphoteric (or zwitterionic) surfactants are produced by a range of methods, almost all of which contain a quaternary ammonium ion (a cation). The negatively charged group can be carboxylate ($-CO_2^-$), sulfate, ($-OSO_3^-$) or sulfonate, ($-SO_3^-$).

Surfactants can be derived from both petrochemical feedstock and renewable resources (plant and animal oils, micro-organisms). They were originally made from renewable resources like fats and oils, whereas today, the majority is of petrochemical origin **[3]**.

However, renewable resources play an important role in the market since they account for about one third of the total organic carbon fixed in surfactants, with two thirds of the organic carbon being of fossil origin **[1]**.

Renewable raw materials used

Fats and Oils as Raw Materials

Certain grades of vegetable oils and fats are industrially used and, together with carbohydrates and proteins, are important renewable resources compared to fossil and mineral raw materials, whose occurrence is finite **[10]**. Most fatty acids are obtained by hydrolysis of oils from various oleochemical sources (animal, marine and plant) and the composition of fatty acids in the oil is determined by its origin and production method. An exception to this is the widely used tall oil fatty acid products, obtained as free fatty acids together with rosin acid from paper pulping **[11]**.

Fatty Acid Soaps

Fatty acids and glycerol are the result of hydrolyze of fats and oils. The fatty acids can be purified by a range of methods, such as split distillation, before the saponification.

In contrast to the fatty acids, the soaps are generally water soluble and display strong surfactant properties. The solubility and surface-active properties can be tuned by the nature and combination of fatty acids, counterions and the extent of polarization **[11]**.

The ability of fatty acid soaps to adsorb selectively to solid particles in aqueous solution is used in many applications, for example lubrication **[12]**, flotation de-inking of paper **[13]** and purification of minerals **[14]**. The surface chemical aspects of the process of de-inking have been reviewed by Theander and Pugh **[15]**.

Polyethylene Glycol Fatty Acid Esters

Esters based on Polyethylene Glycol are classed as nonionic surfactants. The absence of acids or hard water in these compounds is considered as advantage over anionic or cationic soaps. They are known by their valuable surfactant properties in textile, agricultural, paper, personal care and cosmetics industries.

Fatty acids, fatty acids esters, diethyl sulfate, alkyl halides and aryl halides containing nitro groups and isocyanates can be reacted with polyethylene glycols. The reaction of polyethylene glycol with isocyanates results in the formation of polyurethane polymers.

Direct ethoxylation of fatty acids and fats with conventional catalysts yields a complex mixture of mono and diesters, as well as various polyethylene glycols as by-products, with a wide range in the number of polyethylene glycol units **[11]**. Despite the inhomogeneity of the composition of the final product, they have found a wide use as emulsifiers in food, feed and technical applications and detailed studies of their emulsification and solubility/dispersibility properties have been carried out **[16-18]**.

Polyglycerol Fatty Acid Esters

The use of natural glycerol as the hydrophilic part of the fatty acid surfactant is a novel attractive alternative environmental friendly to ethoxylation.

Partially hydrolysed triglycerides, with one glycerol moiety, represent the most widely used surfactant of this kind, found as emulsifiers in many food and cosmetic products **[11]**.

Several studies have placed the emphasis on polyglycerol fatty esters produced through a condensation reaction of fatty acids or partial glycerides with glycerol.

However, like the direct ethoxylation described above, this condensation reaction gives rise to a broad distribution in the hydrophilic head group, as well as a distribution of a number of fatty acids attached to the hydrophilic group and various glycerol oligomers as by-products **[11]**.

Nitrogen Derivatives of Natural Fats and Oils

Tallow, palm, soya bean, rapeseed and coconut are considered the raw materials of the manufacture of surfactants, especially amines and amine derivatives.

While the supply of vegetable oils can be adjusted to meet demand by further plantings, the supply of tallow is constrained by the consumption of beef and has remained fairly consistent from year to year **[19]**. Tallow is the animal fat most used in the industrial soaps. It gives a hard soap whose color varies from gray-cream to yellow cream. This animal fat is obtained after melting the fatty tissue of the animals of breeding and it is generally used in the soap factory to bring more sweetness and creamy.

Tallow is a by-product from the beef rendering industry and until recently has been an inexpensive feedstock; this is now changing with recent developments in alternative fuels technology, causing tallow prices to increase although the benefits of biofuels, for example CO_2 emission reduction, is already achieved by the use of these renewable resources to manufacture surfactants **[19]**.

Fatty amine ethoxylates are nonionic surfactants used as wetting and dispersing agents, stabilizers, sanitizers and defoaming agents in various industries like textile, paper, drilling, chemical, paint, metal etc. They play an important role as emulsifiers in agrochemical industries, cleaners in industrial processes especially in metal industry, oil field chemicals, fabric softeners, petroleum additives and for applications in textile and leather processing, paper de-inking, mining and drilling.

Fatty amines ethoxylate products is a result of reaction of amines like amino acids, tallow amines, oleyl amine, coco amine, stearyl amines etc with ethylene oxide in presence of a catalyst in ethoxylation process.

Amine alkoxylates are not the only nitrogen derivatives to find utility in agrochemical applications; quaternary ammonium salts **[19,20]**, amine oxides **[19,21]**, alkylamidoamines **[19,22]** and betaines **[19,23]** are also reported to have similar bioefficacy-enhancing properties to fatty amine alkoxylates. There has also been development of adjuvants with improved biodegradability and certain fatty esteramine and amidoamine deriviatives, for example, have been developed that exhibit enhanced biodegradability **[19,22]**.

Sorbitan Esters

Sorbitan fatty acid ester called sorbitan ester, are surfactants highly safe to use on human body and are widely used as a food additive in the production process as emulsifiers **[24]**.

The method most known for producing sorbitan esters is the direct esterification of sorbitol with fatty acids in the presence of acid or alkali catalysts in one step process. Another technique is used and consists in two step process: sorbitol is first dehydrated to sorbitan and then esterified with acid or alkaline catalysis. Both methods have been developed for industrial-scale production **[25]**.

Isosorbide Derivatives

Isosorbide (1, 4:3, 6-dianhydro-D-glucitol) is a V-shaped molecule consisting of two fused tetrahydrofuran rings having two hydroxyl groups with endo and exo orientations **[26]**. It is obtained by the double dehydration of sorbitol and it is used in household products, such as detergents, or in cosmetic applications. Preferably, this compound is used in personal cleaning applications, detergents and manual dishwashing detergents.

Sucrose Esters

Sucrose esters are versatile emulsifiers for food products and are approved for their dermatological properties. As a consequence these products seem to be perfect raw materials for food and cosmetic formulations and their use in those applications as a specialty emulsifier has a long tradition **[27-29]**.

The sucrose molecule is known that is very temperature sensitive and, due to its high functionality with eight hydroxyl groups, selectivity in the esterification reaction is difficult to achieve.

Alkyl Polyglycosides

Alkyl polyglycoside (APG) is a non-ionic surfactant made from vegetable oils and starch. New developments and increasing marketing for other sugar-based surfactants are the resultat of the Growing demand for (APG). These products could replace traditional petroleum and even other natural oils-based surfactants.

APG surfactants initially were developed for home care and body wash applications, but have been expanded to facial cleansing lotions, shampoos, oral care products, wipes, laundry detergents, hard surface cleaners and industrial and institutional cleaning applications. Manufacturing process for alkyl polyglycosides is detailed in the **Figure 2 [25]**.

Lysine-Based Surfactants

In general, the amino acid compounds can be classified as biocompatible surfactants. This biocompatibility makes them highly suitable for use as emulsifiers, detergents, wetting agents, foaming or dispersing compounds.

Lysine based surfactants are a chemical enhancers for two different local anesthetics, tetracaine and ropivacaine hydrochloride.

Results show that this class of surfactants strongly influences permeation, especially in the case of the hydrophilic and ionized drug, ropivacaine hydrochloride, that is not easily administered through the stratum corneum **[30]**.

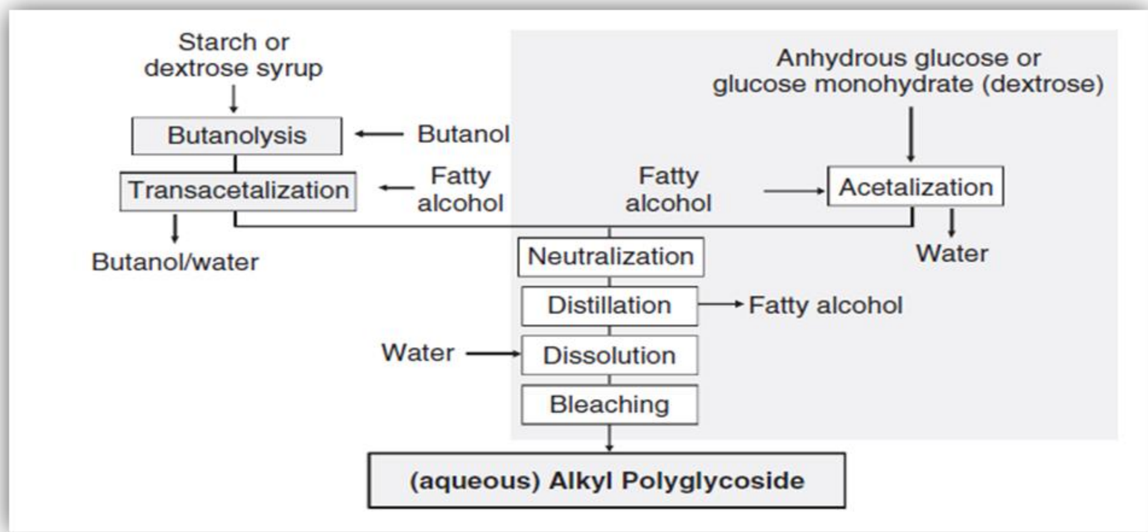

Figure 2: Manufacturing process for alkyl polyglycosides [25]

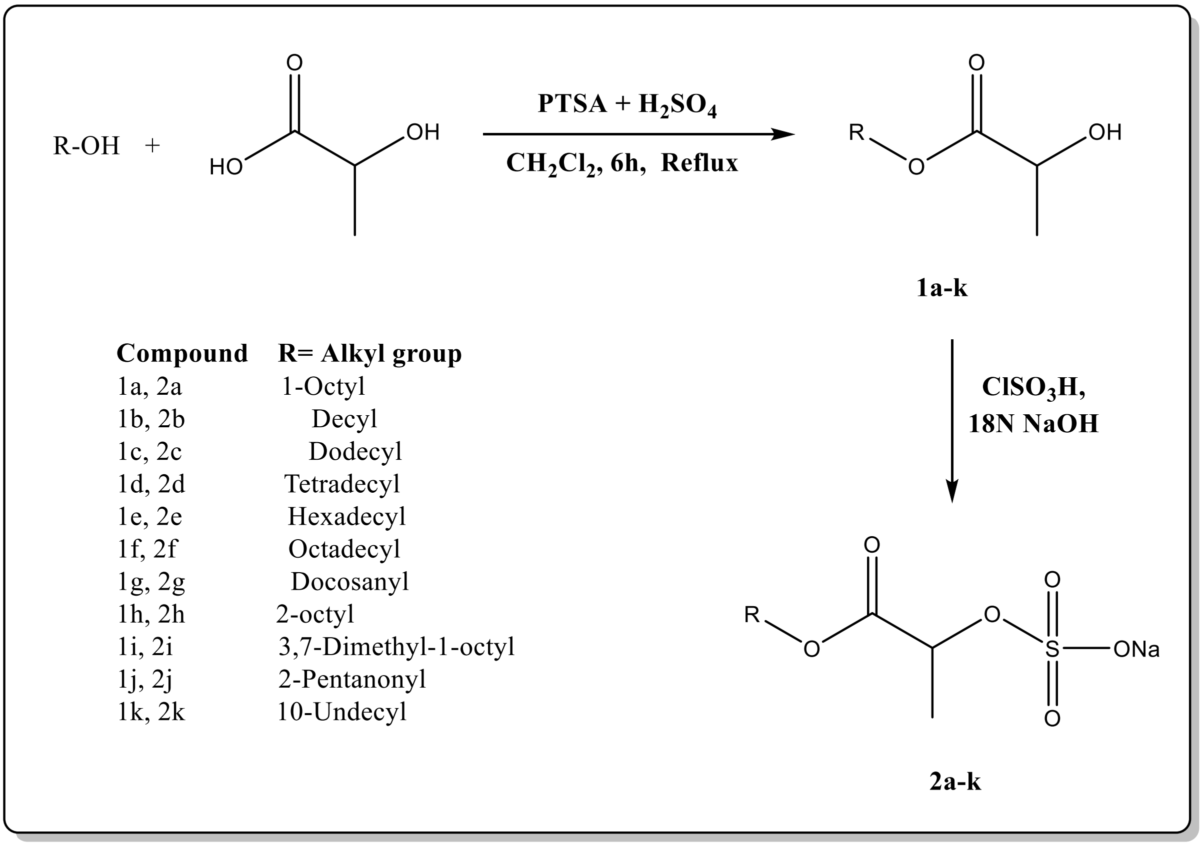

Figure 3: Synthesis of alkyl lactates and sulfated sodium salts of alkyl lactates [32]

Lactic Acid-Based Surfactants

Long-chain fatty acid esters of lactic acid, such as palmitoyl or stearoyl lactate, are ionic biocompatible surfactants widely used in the food industry **[31]**.

A new study was interested to synthesized lactic acid based anionic surfactants which are considered as promising candidates with biological functionality.

This series of lactic acid-based anionic surfactants were obtained by the esterification of lactic acid with a range of fatty alcohols differing in chain length as well as in branching and unsaturation. The resultant ester was sulfonated by treatment with chlorosulfonic acid followed by salt formation with aqueous NaOH solution **(Figure 3) [32]**.

Some of this synthesized surfactants exhibited good antimicrobial and anti-cancer activities against the tested microbial strains and cell lines **[32]**.

Lactic acid is also used in cosmetic industries as skin peels and emollients **[9]**. Cationic surfactants derived from lactic acid have been reported for increasing the skin absorbance of the lactic acid and decreasing irritating side effects **[33]**.

Ascorbic Acid-Based Surfactants

The vitamin C, one of the stereoisomers of the ascorbic acid, is known by its chemical instability what limits its use in the final production. It is a powerful, water soluble antioxidant this poor solubility in organic solvents has made its applications limited only in aqueous environments. However, surfactants from vitamin C increase the stability of the ascorbic acid and allow the use of these compounds in different environments **[9]**.

APPS (Trisodium Ascorbyl 6-Palmitate 2-Phosphate) is considered as the unique active ingredient vitamin C derivative known for its successful use in skin care by many cosmetics companies. This amphiphilic molecule acts as an antioxidative agent and an anti-melanogenesis agent (inhibition of melanin production) and it is more effective than other vitamin C derivatives.

Vitamin C amphiphilic derivatives seem to possess the main requisites to produce organogels. In fact, double-chain surfactants from ascorbic acid are a good candidate for the formation of organogels which can be considered one of the most interesting and promising examples of self-assembled soft matter **[34]**.

The presence of a redox-active polar head group in the surfactant adds an important and new functionality to the final organogel that extends their application and uses to the solubilisation, storage and protection of valuable but oxidable materials **[34]**. Nanostructures from alkyl vitamin C derivatives possess very interesting properties that make these compounds promising pharmaceutical derivatives for drug delivery systems **[35,36]**.

6-O-Ascorbic acid alkanoates (ASCn) have been investigated in order to evaluate the enhancing permeation effect of ASCn with different chain lengths and to correlate permeability changes with histological effects. No inflammatory cellular response was observed in the skin when ASCn coagels were applied, suggesting non-irritating properties **[37]**.

Special applications of surfactants

The most important applications for surfactants, however, are related to their self organisation in solution **[7]**. New surfactants with natural structural motifs can be classified and can be used in various highly specialized and interesting applications, far beyond the everyday utilization of surfactants in detergents.

Protein crystallization

As a result to the discovery of their involvement in various essential biological processes, the interest for the membrane proteins continues to grow. They represent the therapeutic target of privileged new drugs because approximately 50% of drugs have an interaction with membrane proteins.

Protein crystallization methods are very different. However, methods using surfactants is considered as innovative methods for the crystallisation of proteins. The strategy to crystallize is to decrease the solubility of the protein in order to obtain low specific interactions. These interactions make the possibility for the crystal to be formed but are also important for the quality of diffraction and consequently for the resolution.

An integral protein from a biological membrane is characterized by the presence of a hydrophobic part in their structure which makes them insoluble in water. The use of surfactants aims at solubilizing the protein by covering its hydrophobic surfaces. The natural and functional states of the protein are stabilized by the aggregation of the surfactant at his hydophobic parts.

Given a suitable size and uniformity of the resulting protein-surfactant complexes these may-under appropriate conditions-crystallise in an ordered lattice suitable for high-resolution structure determinations **(Figure 4) [7]**.

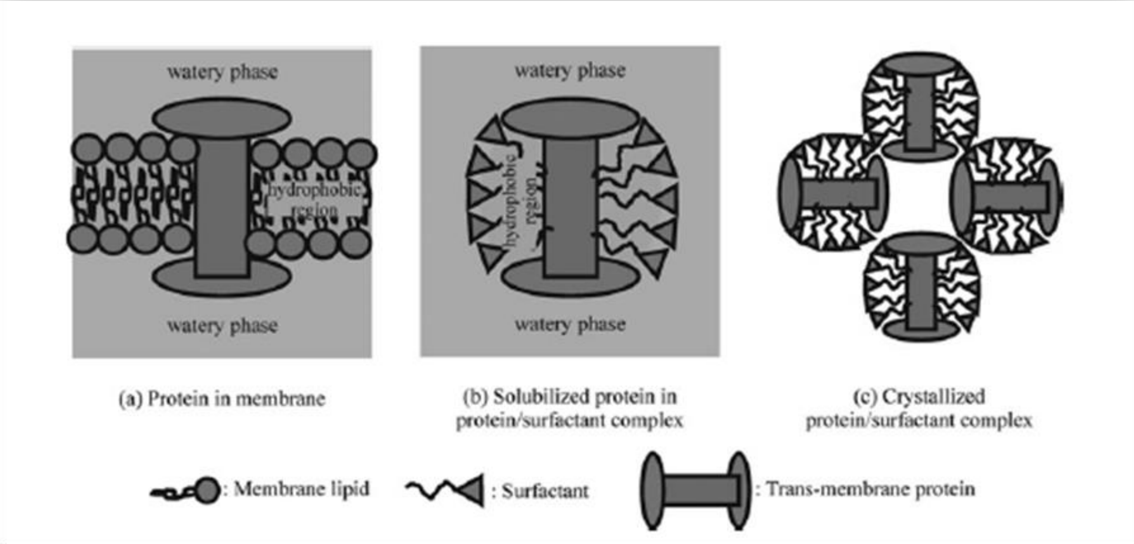

Figure 4: Steps of protein crystallization [7]

The main problems are that the membrane proteins can be denatured if they are solubilized with detergents what makes extremely difficult the realization of the functional studies, such as the spectroscopic analysis or the tests of crystallization on the IMP. For this reason, the choice of the detergents constitutes an important factor.

Amphiphiles with a quaternary central carbon which results of neopentyl glycol are developed. Since the hydrophilic groups are synthesized from the maltose they are called maltose neopentyl glycol (MNG) amphiphiles. Their performance compared to the classical detergents using proteins of various membranes in various applications is evaluated.

The ability of MNG amphiphiles to extract integral protein membrane of their biological membrane and to preserve the structure of proteins in order to produce high-quality crystals is also examined.

A super assembly photosynthetic protein obtained from the bacterial membranes has been used to show that the detergents MNG have been able to extract native assemblies from the intact membranes compared to other conventional detergents that have been less successful.

The amphiphiles MNG are therefore promising tools for research in biochemistry of membrane proteins and can be easily synthesized on a large scale.

Transfection

As opposed to the transduction, the transfection is the process of transfer of genes and introduction of exogenous genetic material in eucaryote cells, not using a virus as vector. Gene therapy is an experimental technique that uses genes to treat or prevent disease. Safe and efficient gene delivery vectors are needed in order to achieve successful gene therapy. As an alternative to viral vectors, the use of specialized surfactants (gemini surfactants) is another biochemical application.

In the basic design of gemini surfactants the central "spacer" bears pairs of identical long chain hydrophobic tails and cationic head groups derived from positively charged α-amino acids and/or amine-linked carbohydrates. All three components are based on natural metabolites, to minimize potential problems with toxicity. They are based on naturally occurring subunits fatty acids, α-amino acids, lipids, and carbohydrates to make them generally readily biodegradable **[38]**.

These surfactants, consisting of two surfactant monomers linked by a spacer group, are a thrust research area for gene therapy as non-viral vectors due to their high stability, longer storage on shelves, easiness to produce **[39]**. They are shown to bind and compact DNA efficiently **[38]** and to have better surface-active properties than corresponding conventional surfactants of equal chain length **[40]**. This choice has been motivated by some properties like their lower critical micelle concentration (CMC), and useful viscoelastic properties such as effective thickening.

The transfection ability and cytotoxicity of a series of phytanyl substituted gemini surfactants was evaluated in OVCAR-3 cells at the charge ratios (N^+/P^-) of (2 : 1, 5 : 1, and 10 : 1) **[41]** in order to create cationic surfactants that will improve transfection efficiencies of non-viral vectors.

For each gemini surfactant complex, the transfection efficiency and cytotoxicity are observed to go through a more or less well-evidenced maximum, occurring at different values of the charge ratio (N^+/P^-), depending on the surfactant structure **[41]**. The particle size decreased, while zeta potential increased with increasing N^+/P^- **[41]**. Analysis of SAXS profiles indicates that the ability of phy-3-m delivery system to adopt multiple phases correlated well with their higher transfection efficiency in OVCAR-3 cells **[41]**.

Much effort has been made to enhance the transfection efficiency using gemini surfactants and another report is established between the monomolecular condensation of plasmid DNA and efficient cell transfection by imidazolium gemini surfactants ([C_{12}-4-C_{12}im] Br_2), which could be a potential nonviral vector for efficient gene therapy **[42]**.

Highly efficient gene transfection in vitro and the low cytotoxicity of ([C_{12}-4-C_{12}im] Br_2) at transfection concentration region supports these gemini surfactants as an effective gene vector and could shed light on the rational molecular design of nonviral vectors for gene delivery systems **[42]**.

Surfactants in Nanotechnology

Nanotechnology has had an immense importance in almost every industry, from consumer electronics to pharmaceuticals and telecommunication.

Nanomaterials are an increasingly important product of nanotechnology which are used in healthcare, electronics, cosmetics and other areas because of their unique physical and chemical properties.

Surfactants, which are appreciated for human consumptions and veterinary therapeutic purposes, and which are very useful in many new technology areas due to their high effect on the dispersion, their self assembling amphiphilic nature and their role in lowering the interfacial tension, can be applied in the formation of nanoemulsions and related processes as stabilizers, growth control agents, templates, and modifiers.

Nanoemulsions are composed of oil droplets dispersed in an aqueous medium and stabilized by surfactant molecules **[43]**. They are formulated with oil, surfactant and co-surfactant and are considered as nontoxic and nonirritant. Generally, nanoemulsions are regarded as safe and are approved for human consumption.

The use of the minimum amount of surfactant in the formation of stable nanoemulsion continues to attract attention and it is considered a biggest challenge to mitigate due to their potential technical and economic benefits and the progress of their applications principally in agrochemicals, cosmetics, pharmacy, drugs, personal care, health care, film coating, carbon nano-tubes, and oil industries as a novel delivery system for drugs and lipophilic materials such as essential oils, flavours, colours and fatty acids.

The very small size of droplets improves the kinetic stability of the emulsion. Therefore, the problems of inherent creaming, weak flocculation, coalescence and sedimentation, which are commonly associated with macro emulsion, are prevented with nanoemulsions. Their transparent nature, their large surface area, their fluidity as well as the absence of any thickeners may give them a pleasant aesthetic character and skin feel **[44]**.

Nanoemulsions can be applied in agrochemical industry in order to minimize the side effects of excessive use of agrochemicals on the ecosystem. The ease of handling and lower requirement of smelly solvents go in favour of their use **[45]**. The formulation of agrochemicals using surfactants is advantageous due to the infinite stability of the nanoemulsion and the high concentration of surfactants generally needed for a formulation.

Nanoemulsions can also be applied for drug delivery due to their peculiar properties such as thermodynamic stability, increased surface area, preparatory ease, high bioavailability and optical transparency.

They are also known as submicron emulsions serving as vehicles for the delivery of active pharmaceutical ingredients as well as other bioactives. They are designed to address some of the problems associated with conventional drug delivery systems such as low bioavailability in order to reduce toxicity and irritant potency, to improve consumer compliance, to enhance absorption and to prolong stability **[46-49]**.

Nanoemulsions can be applied for delivery of fragrant, which may be incorporated in many personal care products. They could also be applied in perfumes which are desirable to be formulated alcohol free and as a substitute for liposomes and vesicles and it is possible in some cases to build lamellar liquid crystalline phases around the nano-emulsion droplets **[44]**.

Nanoemulsions can be administrated by intranasal drug delivery system which is considered as a reliable route for the administration of drugs because of the various problems of drug administration through oral, ocular, parenteral, and other routes of drug administration. This route is also painless, non-invasive and well tolerated and showed by pharmaceutical scientists. Nasal drug delivery system is commonly known for the treatment of local ailments like cold, cough, rhinitis, etc. **[50]**. It is considered as a promising approach which could offer simplified and more cost-effective protocols for vaccination with improved patient compliance **[51]**.

Nanoemulsions are proposed also for other interesting applications like in cancer therapy and in formulations for controlled drug delivery and targeting. They play a major role and they can easily be targeted to the tumor area due to their submicron size. They have the possibility to increase bio distribution of therapeutic agents to target organs and improve the pharmacokinetics, which will result in improved efficacy **[52]**.

Although nanoemulsions are chiefly seen as vehicles for administering aqueous insoluble drugs, they have more recently received increasing attention as colloidal carriers for targeted delivery of various anticancer drugs, photosensitizers, neutron capture therapy agents, or diagnostic agents **[53]**.

Nanoemulsions are also used for ocular drug delivery which is considered one of the most challenging routes due to the critical and pharmacokinetically specific environment that exist in the eyes. Nanoemulsions have been investigated for ocular administration, to dissolve poorly soluble drugs, to increase absorption and to attain prolong release profile **[54]**.

The cytosolic drug delivery system using nanoemulsions is also promising, which is an efficient route for the administering drugs that undergo a large cell efflux through the transporters like multi drug resistant proteins **[55]**. Nanoemulsions for cytosolic drug delivery are increasingly important due to stability to their concentrations at required levels for a longer time period during the process of targeting the drug to the action site.

Another interesting application, which is the application of nanoemulsions in cosmetics due to their own bioactive effects, has attracted considerable attention for the controlled delivery of cosmetics and personal care products including hair care products, moisturisers, make up, antiageing creams and sunscreen. It helps to give skin care formulations a good skin feels **[56]** and to treat fungal infection on internal body part **[57]**. Nanoemulsions can easily penetrate in skin because it has good sensorial properties with rapid penetration, merging textures and its biophysical properties especially the hydrating capacity **[58]**. Some of their properties such as the small droplet size, the absence of creaming and flocculation lead to a more elegant and stable product with different rheological behaviors, visual aspects, richness and skin feel. As an illustration, nanoemulsions have an effect on the dry hair aspect after several shampoos and a significant improvement is obtained with a prolonged use. Hair becomes more fluid and shiny, less brittle and nongreasy **[59, 60]**.

A relatively recent fast growing field of application of nanoemulsions is nanogel systems and emulsion-based wet wipes, nanoemulsions that are free from emulsifiers based on polyethylene glycol (PEG) **[61]**. It is a recent research topic and a fast growing field of application used in baby care and make-up removal.

Nanoemulsions have attracted also a significant interest in cell culture technology. They are a new method for delivery of oil-soluble substances to the mammalian cell cultures. The delivery system is based on nanoemulsions, stabilized by phospholipids **[44]**. The easy grip of nanoemulsions by cells increase the bioavailability of the encapsulated oil-soluble substances to cell in culture.

Research with nanoemulsions has shown promising results due to their antimicrobial activity. They are used as a prophylactic medication, a human protective treatment, to protect people exposed to bio-attack pathogens such as anthrax and ebola **[62]**. They have also been tested by US army on gangrene and *Clostridium botulinum* spores and can even be used on contaminated wounds to salvage limbs **[53]**.

Nanoemulsions have attracted a great deal of attention in every industry, but also they are considered as promising candidates for enhanced oil recovery (EOR) and as a medium for wellbore cleaning. The physicochemical properties of nanoemulsion and the small particle size distributions of the dispersed oil droplet in water phase, suggest that it can be successfully used to recover the residual oil which is trapped in the fine pore of reservoir rock by capillary forces after primary and secondary recovery **[63]**. This excellent property will improve the sweeping efficiency of the oil droplet in the reservoir and finally increase the oil recovery. It makes nanoemulsions suitable as superior wellbore cleaner as compared to conventional detergent-based cleaner **[64]**.

All these recent applications cited in this review, have made that the study of surfactants is very important and continues to attract significant interest, due to their special properties but also due to their role in the formation of nanoparticlcs by affecting the growth and particle characteristics significantly. Different surfactant systems can mediate to give different products even though the basic chemistry is the same **[65]**.
Template technology has the potential to have a positive effect compared with traditional synthetic methods, especially with respect to morphology, particle size, and structure during the preparation. Therefore, it is possible to design materials of required optical, magnetic, elastic and chemical properties by controlling the above factors **[66]**.

The ability of surfactants to self-assemble into well defined structures has been taken advantage of for the design and synthesis of inorganic materials with nanosized dimensions **[67]**. The structures formed by self-assembly of the surfactant are used as a kind of template for the synthesis **[45]**.

The use of partially water-miscible, biocompatible organic solvents through microemulsion as a template has been described for engineering drug nanoparticles especially for drugs that are soluble in either volatile organic solvents or partially water miscible solvents **[68]**. This technique is appreciated for the high drug solubilization, the long shelf life, the ease of production by controlling the emulsion droplet and easy scale-up but it is limited by the use of hazardous solvents and high amount of surfactants.

Interest in dispersed, amorphous and uniform silica nanoparticles was developed due to their simple preparation and potential applications in various industries **[66]**.

A series of the cationic surfactants, dodecytrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB) and cetyltrimethylammonium bromide (CTAB) are used in order to evaluate the effects of the chain length of cationic surfactant on the grain size of silica nanoparticles. Decreasing the particle size of silica nano particles resulted in increase in chain length of cationic surfactant **[66]**.

Nanostructures of polyaniline (PAni) and polypyrrole (PPy) with controlled morphologies have been synthesized on atomically flat surfaces using adsorbed surfactant molecules as templates. Such a technique in which one can engineer sub-100-nm-ordered nanoscale π-conjugated polymer structures of a desired shape by a simple self-assembly process presents potential as templates, sensors, and microelectronic devices **[69]**.

The key for the template method is to choose different templates, which are divided into hard template and soft template according to their different structures **[70]**.

The best example to illustrate this idea is the development in the preparation of mesoporous metals and related metal-based nanomaterials. Mesoporous metals are appreciated in a wide range of potential applications, such as in electronic devices, magnetic recording media, and metal catalysts, owing to their metallic frameworks. Mesoporous metals with highly ordered networks and narrow pore-size distributions have traditionally been produced by using mesoporous silica as a hard template. This method involves the formation of an original template followed by deposition of metals within the mesopores and subsequent removal of the template **[71]**.

Another synthetic method, which is considered as a new prospect for the production of mesoporous metals as well as related metal-based nanomaterials, is the direct-template approach from lyotropic liquid crystals (LLCs) made of nonionic surfactants at high concentrations.

Many mesoporous metals have been prepared by the chemical or electrochemical reduction of metal salts dissolved in aqueous LLC domains. As a soft template, LLCs are more versatile and therefore more advantageous than hard templates **[71]**.

CONCLUSION

Sustainable chemistry, continues progressively to gain attention in the society with not only their interest in preserving resources but also in supporting a development process in the chemical industry such as personal care, laundry detergent and home care cleaning products in order to preserve a sustainable future.

There is today a challenge to replace conventional surfactants with more environmentally compatible compounds nontoxic and biodegradable that must not impose an environmental threat but also must meet performance and cost-benefit requirements by environmentally friendly and sustainable technologies with new reaction conditions (cleaner solvents, biotechnological processes, etc.) and using bio-based raw materials from renewable feedstock such as cellulose, chitin, starch, fruits, lignin, waste proteins, fats and oils in order to conciliate sustainable issues with industrial development.

As with all chemicals and other colloidal species, and for an environmental risk assessment, it is very important also to understand the health hazards linked to surfactants both in normal applications and in accidental releases.

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