Polymeric Surfactants-Its Evolution and Review

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Abstract: Hygiene has been increased in day to day life with increasing population the need of cleaning agents are highly demanded in the market. With the times, the formulation of soapy fatty matter to the various types of cleaning products; bars, soaps, liquid soap has evolved with time. The increasing demand and invention of technology and electronic goods the formulation of soap has also been changed and the form in it is being used. Invention of detergents lead to concept of cleaning of clothes, floor cleaning and many such similar activities. This lead to increase in the powder detergents. With time the competition increased with the market demand with cost effectives and maximum detergency performance. This lead to evolution of synthetic detergents, its used increased but the adverse effects were seen later on environment. These synthetic detergents has the constituents which are less biodegradable. This all lead to adverse effect on aquatic life. To overcome these, renewable form of source has been used and formulation of polymeric surfactants has evolved and hence was studied herewith. Eco-friendliness is desired portion of surfactant formulations whether if a purpose of uses is either domestic or industrial.

Keywords: surfactants, biodegradability, synthetic detergents, polymeric surfactants.

Introduction

'Surface active agent' - a surfactant (are also known as amphiphiles) is a molecule that lowers surface tension and has a distinct molecular structure that gives rise to their molecular properties. The word amphiphile was coined by Paul Winsor 50 years ago. It comes from two Greek roots. (amphi means ‘double’, ‘from both sides’).

The polar portion exhibits a strong affinity for polar solvents, particularly water, and it is often called hydrophilic part or hydrophil. The apolar part is called hydrophobic or lipophil. This would imply that surface activity is equivalent to tension lowering. Surfactants exhibit other properties than tension lowering and this is why they are often labelled according to their main use such as: soap, detergent, wetting agent, dispersion, emulsifier, foaming agent, bactericide, corrosion inhibitor, antistatic agent, etc.[1-5]

Madhura Bhalerao et al / International Journal of ChemTech Research, 2019,12(1): 183-190.
DOI= http://dx.doi.org/10.20902/IJCTR.2019.120121
Surface Active Agent or Surfactant: Chemical compound which, when dissolved or dispersed in a liquid is preferentially absorbed at an interface, giving rise to a number of physico-chemical or chemical properties of practical interest. The molecule of the compound includes at least one group with an affinity for markedly polar surfaces, ensuring in most cases solubilization in water, and a group which has little affinity for water.

**Historical Aspects**

The earliest recorded evidence of the production of soap-like materials dates back to around 2800 BC in ancient Babylon. [6] A formula for soap consisting of water, alkali, and cassia oil was written on a Babylonian clay tablet around 2200 BC.

American manufacturer Benjamin T. Babbitt introduced marketing innovations that included sale of bar soap and distribution of product samples. William Hesketh Lever and his brother, James, brought a small soap works in Warrington in 1886 and founded what is still one of the largest soap businesses, formerly called Lever Brothers and now called Unilever. These soap businesses were among the first to employ large-scale advertising campaigns.

Liquid soap was not invented until the nineteenth century; in 1865, William Sheppard patented a liquid version of soap.

Using glycerine and vegetable oils such as palm oil, rather than tallow, to manufacture soap, they produced a good, free-lathering soap, called ‘Sunlight Soap’.

In 1898, B.J. Johnson developed a soap (made of palm and olive oils); his company (the B.J. Johnson Soap Company) introduced ‘Palmolive’ brand soap that same year. This new brand of the new kind of soap became popular rapidly. At the turn of the twentieth century, Palmolive was the world's best-selling soap.

By 1900 Lifebuoy, Lux and Vim brands had been added and subsidiaries had been set up in the United States, Switzerland, Canada, Australia, Germany and elsewhere.

Lever Brothers Ltd also acquired other soap companies including A&F Pears, Crossfield's of Warrington, Hudson’s of Liverpool.

After William Lever's death in 1925 his enterprises were amalgamated as Unilever. Another wonderful factory was established during 1966 by Colgate-Palmolive factory in Balmain.

During the First World War, Fat and oil prices rose so highly that soap making became uneconomical. Due to this struggle and natural soap’s poor cleaning ability in hard waters, German scientists and engineers began experimenting with synthetic detergents. The products they developed, short-chain alkyl naphthalene sulphonates, were successful surfactants but second-rate detergents.

**Current Scenario of Surfactants**

Surfactant industries are growing very fast due to its wide application, new formulation and discoveries. Developments in the field of surfactant include silicone surfactants, fluorocarbon surfactants, gemini surfactants, nonionic types of surfactants having branched chain fatty acid alcohol, fatty amines etc.

The petroleum industry was rapidly developing in the 1930s, and refinery waste products were generally disposed of by combustion. It was discovered, however, that propylene, a kerosene fraction, could be converted to a long chain 2-alkene, which then could be reacted with benzene and sulphuric acid. The product of this was neutralized with sodium hydroxide to form alkylbenzenesulphonate (ABS), which quickly became the favourite surfactant in synthetic laundry detergents.

Nowadays, Does buying a high-priced detergent guarantee cleaner clothes or Grade 1 quality? What really is Grade 1? The detergent market is a highly competitive one where several brands vie with each other to get the customers attention.

Each brand claims to clean whiter and better, boasting of power pearls and of ability to fight granules, and so on. In all this, what consumers may end up overlooking are the chemical composition and quality of the
detergent powder they use, though their implications for personal health and the environment are critical enough to merit closer attention and action. Does anyone also boast about being eco-friendly? And if they are not doing that and are all synthetic, do they extend you the courtesy of at least warning that some precautions are in order?

The market for synthetic detergents was valued at about Rs 112 billion as of 2012-13, with a compounded annual growth rate (CAGR) of three percent. The machine or automatic wash sales has been dominated by powder detergents (vis liquid detergents), with 98 percent share in the market and a size of Rs18700 million.

However, a much bigger segment of the market is the non-automatic or the hand-wash category, which has a size of Rs 85,466.8 million. It is also dominated by powder detergents but by a smaller percentage compared to machine wash category, at about 68 percent. The remaining contribution comes from the bar detergents. Hand wash detergents have shown an impressive growth rate of 8.8 percent CAGR since 2005, which has contributed to the growth in the overall detergent market.

All present brands were found to have added phosphate in the range of 3.2 percent to 5.4 percent. Considering the amount of phosphate in these brands, these cannot be termed eco-friendly.

In India, most of the synthetic detergents are not phosphate free due to lack of mandatory legislations. Some manufactures tend to put in liberal quantities of phosphates in detergents to increase the cleaning efficacy.

An environmentally superior detergent is one that uses fewer chemical ingredients. The toxicity of detergents decreases if removal of additives like perfumes, colour and brightening agents is done.

Synthetic Detergents

Synthetic surfactants may be replaced by non-petrochemical surfactants or vegetable oil soaps; builders like phosphates can be replaced by sodium citrate and sodium bicarbonate; dyes and fragrances can be eliminated or minimised. Minimal packaging can also reduce environmental harm substantially.

Ingredients of Synthetic Detergents and its Adverse Effects

Animal and vegetable fats and oils were in short supply during the First World War, so the soap industry found itself in competition with the food and feed industries for limited resources. Fat and oil process rose so highly that soap making became uneconomical. Due to this struggle and natural soap’s poor cleaning ability in hard waters, German scientist sand engineers began experimenting with synthetic detergents. The products they developed, short alkyl naphthalene sulphonates were successful surfactants but second rate detergents.

In the 1960s, the commercialization of the Ziegler process for oligomerization of ethylene led to the development of linear hydrophobic molecules analogous to the branched hydrophobes used in ABS. The Ziegler process was devised in 1953 by a German chemist by the name of Karl Ziegler. Linear alkyl benzene sulphonate (LABS) was developed from these straight-chained molecules in 1964 as a biodegradable alternative structure to ABS. The new anionic surfactant readily breaks down in activated sludge wastewater treatment plants and all but eliminated the issue of foaming in surface waters. In addition to improved environmental performance, LABS foams and cleans better than ABS. These properties allow manufacturers to reduce the concentration of surfactants in detergents without compromising performance.

Alkylbenzene Sulphonate (ABS)

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In the years following the Second World War, carboxymethylcellulose (CMC) was added to synthetic detergents to reduce the redeposition of dirt, and orthophosphates were added to respond to calcium
and magnesium cations in hard water. However, ABS’s highly branched structure rendered it almost completely resistant to biological degradation, so only small amounts of the surfactant were removed in typical wastewater treatment facilities and remaining quantity remained in receiving waters and surfaces. This along with an increased use of the detergents caused natural surface water to foam.

Sodium tripolyphosphate (STPP)

Sodium tripolyphosphate (STPP) is mostly used as a phosphate ingredient in many detergents. It softens the water and prevents dirt particles from adhering to the garment. However, the use of STPP is also associated with environmental hazards. The Indian Standard specifies the minimum quantity of STPP in detergent powder at 9.5% and 6% for Grade 1 and Grade 2 respectively.

Common laundry detergent contains over 40% STPP, because it adversely affects the quality of the aquatic ecosystem and induces eutrophication (algal blooms, kills fishes and poor water quality). As per data compiled by India stat from central statistical organisation CSO about 817,933 tonnes of synthetic detergents were produced during 2009-2010. Almost all the laundry detergents in India contain STPP, ranging from 8% to 35%. Thus, the total amount of STPP use in detergents is estimated to be 0.16 million tonnes.

Alcohol Ethoxylates (AE)

Alcohol Ethoxylates (AE) is major non-ionic surfactant and its volume of use continues to increase. AE is one of the substances whose effects on aquatic organisms are of concern due to its ubiquitous presence in the aquatic environment in Japan. AE is non existent in the course of nature and is synthesised by adding polymerisation of ethylene oxide to higher alcohol. Normally, AE commercial products contain homologues with varying numbers of alkyl chains and molecules of ethylene oxide (EO). AE is used in various industries such as textile, pulp and paper, laundry, leather, cosmetics, photographs, rubber and plastic products, agriculture (agrichemicals), construction work, petroleum and coal and fuel, etc.

Linear AlkylbenzeneSulfonate (LABS)

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Undesirable Effects of LABS

LABS degrades readily, but only in aerobic conditions. Under anoxic conditions, LABS biodegrades very slowly; the surfactant is stable in anaerobic situations. In such cases, LABS can build up in receiving waters and cause foaming just as ABS does. If oxygen is reintroduced into anoxic waters, however, LABS biodegradation will resume. While most of the LABS remains in the aqueous phase, the same surfactant properties that make it effective in grease and dirt removal cause LABS to build up on sediments and in aquatic organisms. Further, sorption of LABS onto solid particles is an irreversible process. Anaerobic sludge with high levels of LABS can be rendered unsuitable for soil improvement and fertilization and must ultimately be incinerated or sent to a landfill. In areas with inadequate wastewater treatment, the sediments of receiving waters can accumulate high levels of LAS.

Health Effects

Laundry detergents and fabric softeners may cause acute effects such as respiratory irritation, headache, sneezing and watery eyes in sensitive individuals or allergy and asthma suffers. The National institute of occupational safety and health has found that one third of the substances used in the fragrance industry are toxic.
Protect water quality and aquatic life by refusing to purchase detergents containing phosphates, which may cause algal blooms, or alkylphenolethoxylates, including nonylphenol and octyl phenol.

**Emerging Avenues in Surfactants Domain**

Vegetable oil has a very wide role as surface active agent. They contribute to about 19 – 25% of total fatty raw materials used in soap making industry. The most important vegetable oil based surfactants are fatty alcohol sulphate, fatty alcohol ether sulphate, and fatty alcohol polyglycol ether. The main advantages are, no boiling is required, need less input of heat.

In the synthetic detergent industry, modified vegetable oil has been proven to be a very important surface active material. The majority of surface active agents used in synthetic detergent industries are sulphated alcohols, non-ionic detergents, cationic detergents, alkaloamides and sulphated acids esters and amides.

Recently sodium lauryl sulphate and sodium lauryl ether sulphate obtained from lauric acid of coconut are largely used as surface active agent in synthetic detergent industry.

Two relatively new vegetable oil based surfactants are fatty acid methyl ester sulfonate and alkyl polyglycoside, which are produced from fatty alcohol and starch or sugar, both renewable materials.

This research study examines opportunities for using methyl esters of the vegetable oils as surfactants in detergents. Hence replacing the petroleum based materials in the detergent like LABS with the renewable alternatives based on the vegetable oils.

**Polymeric Surfactants**

Polymeric surfactants serve all the same functions as ‘normal’ surfactants. Major differentiator is their greater molecular mass and higher order structural conformation. Polymerisation of vegetable oil fatty acids and their derivatives is seen to be leading to formation of polymeric surfactants. The polymeric surfactant is a new development in surfactants field. Currently polymeric surfactants are largely used as additives to improve the performance of detergents.

Despite the large variety of surfactant already available today, problem concerning colloidal stability and surface activity still arise which cannot be solved with conventional additives. Polymeric Surfactant is a unique class of high performance product for the emulsification of a wide range of disperse phases into a variety of continuous media. Additionally, some of them are capable of providing a powerful dispersing action under suitable conditions. Polymeric surfactants are therefore used as additives rather than active material.

Polymers such as cellulose, acrylates, acrylamides and pyrrolidones are currently being modified for special performance in commercial applications. In this regard, hydrophobically modified polymers are finding increasing use in the manufacture of consumer products and in industrial operations. Their performance is dependent upon the nature and degree of functionalization.

Polymeric surfactant should be considered as a means to achieve the development of colloidal system with performance characteristic that is currently unobtainable with conventional products. Polymeric surfactants are gaining increasing importance and their interest arises mainly from their low Critical Micelle Concentration (CMC) values and their low diffusion coefficients as compared to classical low molecular weight surfactants.

Polymeric Surfactants are mostly, amphipathic molecule and their mode of operation are by steric stabilization. Their amphipathic property is explained by the fact that they are built from at least two chemically bound groups having totally opposite characteristics.

Excellent stabilizing properties of polymeric surfactant are the direct consequence of the strong interaction between these moieties and both the dispersion medium and the insoluble phases that are being emulsified or dispersed. Anchoring groups are responsible for the strong adsorption of the surfactant molecule into the surface of the dispersed particle whilst stabilizing chains create protective layers of
sufficient thickness that approaching each other too closely. This interaction can be best exploited when the amphipathic molecule is of polymeric nature.

India has a very vast capacity of manufacturing Polymeric surfactant which are used in surface coating industries. The per capita consumption of detergent is higher than surface coating (paint industry). The use of polymeric additives in detergents is common since last 25 years. The important characteristics of polymeric surfactants are:

- Adsorption on fabrics
- Ca and Mg sequesterization
- CaCO$_3$ inhibition
- Fabrics anti incrustation and
- Soil disperancy and removal

Polycarboxylated polymers like styrene maleic co-polymer and acrylic maleic co-polymer have, been successfully used as detergent additives. It has been successfully viewed the use ofphthalic anhydride and sorbitol based polymers in liquid and powder detergents. The reduction and removal of polyphosphates for getting eco-friendly detergents are only possible because of polymeric surfactants.

Maleic vinyl ether was the first polymer used in detergent formulation as anti-redeposition agent in 1975. In last 25 years there is a systematic effort to produce low and zero phosphate detergents using various polymers and co-polymers. Worldwide consumption of detergent polymer is approximately 1,30,000 tonnes per year. The use of polymers has expanded in many countries and in many applications (viz. Fabric washing, dishwashing and industrial cleansers).

I) Polymers for improved soil removal

Special polymers are added to detergent formulation as soil-release that modifies the fabric surface to make it easier to clean. Soil release involves the modification of fabric to alter their polarity and decrease soil adherence.

II) Phosphate Reduction and Phosphate Substitution

In recent years restrictions were imposed in the use of STPP. So the interest in using polymers in detergents has historically coincided with an interest in reducing or eliminating sodium tripolyphosphate from the same detergents.

III) Clay Soil Dispersancy

Anti-redeposition agent (ARDA) helps to keep soil off the fabric by dispersing and stabilizing it in the wash water. ARDA adsorbs onto the soil particle and impart electrostatic repulsion, or both minimizing deposition onto fabric.

Biodegradability of Polymeric Surfactants

The polymers are finding extensive use in our day to day life. With increasing use of polymer, problem of disposal of waste of these products is also posing alarming curse. Since ordinary polymers do not degrade naturally by light, oxygen, water or micro -organism there is serious problem for their disposal. The main option is to produce biodegradable polymer which can be broken down rapidly by soil microorganisms and do not cause any serious effect on the environment. Thus, biodegradable polymers are degraded by micro -organisms within a suitable period so that biodegradable polymers and their degraded product do not cause any serious effect on the environment.

This study presents total replacement of LABS with polymeric surfactant, utilizes the surfactant based on polymer for detergency, and suggests an alternative product as a diversification for existing. Novel polymer plants without much additional investment. The polymeric surfactant based on methyl
esters of vegetable oils will be certainly biodegradable and eco-friendly as they are from renewable vegetable sources.

**Applications of Polymeric Surfactants**

The industries that use surfactant in large quantity are Textile industry, Leather industry, Detergent, Cosmetics, surface coating, paper and metal treatment industry. There are some miscellaneous applications of the Surfactant in the industry fire extinguisher, and insecticide powder, increasing the cover power of adhesive (Starch, gum).

**Applications of Polymeric Surfactants**

The polymeric surfactant is a new development in surfactant fields. The importance of polymers as detergent additives increased as sodium tripolyphosphate (STPP) was gradually removed from many detergent formulations. STPP is very important in detergent formulation due to its sequestering property. Nowadays, Zeolite are used in place of STPP. Polymers showing good sequestering ability and dispersive capacity are added to pick up some of the builder's task that Zeolite can do well.

Brief descriptions of a few important uses of surfactant are as follows:

1. Breaking of emulsion: in the separation of water from crude oil, the recovery of greases from wash water, treatment of crude oil is one of the most important field.
2. Corrosion prevention: The high polarity of modern detergents enables them to spread over metallic surfaces forming a film which hinders water gases dilute acids and other accelerators of corrosion from making contact with the metal.
3. Laundering: Surfactant reduces the surface tension of the water which will help in removing the dirt and stain on the cloths.
4. Metal cleaning: Synthetic detergents find a very important market in the cleaning of metal surfaces to prepare them for subsequent treatment and for cleaning before shipment. Their use is very extensive in wetting or anodic cleaning, polishing etc.

**Conclusion**

Surfactants specially bio-surfactants are one among those surfactants which are biodegradable and unharmed surfactants showing more attention due to its diversity, environment friendliness, possibility of their production through fermentation and their potential applications in the environmental protection, crude oil recovery, health care and food processing industries. One can say that future of surfactant science is very bright and one can notice tremendous discoveries in near future.

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