

## A Short History and Preamble of Surfactants

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### Abstract

Surface active agents (Surfactants) are a unique class of chemical compounds having dual characteristics of hydrophilicity and hydrophobicity. Surfactants are also known as amphiphiles or tensides. The applications of surfactants in science and industry are massive, covering every aspect of refined activity. The science of surfactants is rapidly growing with its wide applications in different industries, medical sciences, life sciences, chemistry, physics, engineering and pollution control etc. Although, surfactants in the present day rule massive cost-effective, significance and immense potential, hardly 70 years back, surfactant would have brought blank stares. The earliest recorded evidence of the production of soap-like materials dates back to around 2800 BC in ancient Babylon. A formula for soap consisting of water, alkali, and cassia oil was written on a Babylonian clay tablet around 2200 BC. The first authentic mention of soaps as cleansing agents appears in the 200 AD in the script of Galen, the Greek physician who has reported the preparation of soap from fat, ash lye and lime. This review provides information about early history, basic information and present scenario of surfactants.

**Keywords:** Surfactant, cmc, micelles, soap, detergent

### INTRODUCTION

'SURFace ACTive AgeNT' - a **surfactant** (are also known as amphiphiles or tensides) 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", "around", or amphibian and the root philos which expresses friendship or affinity). The polar portion exhibits a strong affinity for polar solvents, particularly water, and it is often called hydrophilic part or hydrophile. The apolar part is called

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**Anionic Surfactants** give rise to a negatively charged surfactant ion (hence anionic) and a positively charged counter ion upon dissolution in water. Examples of anionic surfactant groups include sulfonic acid salts, alcohol sulfates, alkyl benzene sulfonates, phosphoric acid esters, and carboxylic acid salts. Anionic surfactants account for about 50% of the world production.

**Cationic Surfactants** yield a positively charged surfactant ion (hence cationic) and a negatively charged counter ion upon dissolution in water. Cationic surfactants first became important when the commercial potential of their bacteriostatic properties was recognized by Domagk in 1935. These surfactants are in general more expensive than anionics, because of the high pressure hydrogenation reaction to be carried out during their synthesis.

**Amphoteric or Zwitterionic** When a single surfactant molecule exhibit both anionic and cationic dissociations it is called amphoteric or zwitterionic. This is the case of synthetic products like betaines or sulfobetaines and natural substances such as aminoacids and phospholipids.

**Nonionic Surfactants** are characterized by hydrophilic head groups that do not ionize appreciably in water. Examples include polyoxyethylenated alkyl phenols, alcohol ethoxylates, alkylphenol ethoxylates, and alkanolamides. Nonionic surfactants come as a close second with about 45% of the overall industrial production

## APPLICATIONS OF SURFACTANTS

Surfactants play vital role as cleaning, wetting, dispersing, emulsifying, and anti-foaming agents in many practical applications and products, including detergents, fabric softeners, emulsions, paints, adhesives, inks, anti-fogs, ski waxes, snowboard wax, herbicides, insecticides, cosmetics, firefighting, pipelines, leak detectors etc.

## HISTORICAL ASPECTS

The earliest recorded evidence of the production of soap-like materials dates back to around 2800 BC in ancient Babylon.<sup>[6]</sup> A formula for soap consisting of water, alkali, and cassia oil was written on a Babylonian clay tablet around 2200 BC. The Ebers papyrus (Egypt, 1550 BC) indicates the ancient Egyptians bathed regularly and combined animal and vegetable oils with alkaline salts to create a soap-like substance. In the reign of Nabonidus (556–539 BC), a recipe for soap consisted of *uhulu* [ashes], cypress [oil] and sesame [seed oil] "for washing the stones for the servant girls".<sup>[7]</sup> The word *sapo*, Latin for soap, first appears in Pliny the Elder's *Historia Naturalis*, which discusses the manufacture of soap from tallow and ashes.<sup>[8]</sup> Soap is mentioned twice in the Bible, but it is generally agreed that the Hebrew word "borith", which has been translated as soap, is a generic term for any cleansing agent. According to Roman legend, soap was named after Mount Sapo, an ancient site of animal sacrifices. After an animal sacrifice, rain would wash the animal fat and ash that collected under the ceremonial altars down the slopes to the banks of the Tiber River. Women washing clothes in the river noticed that if they washed their clothes in

certain parts of the river after a heavy rain their clothes were much cleaner. The Latin word *sapo* simply means "soap"; it was likely borrowed from an early Germanic language and is cognate with Latin *sebum*, "tallow", which appears in Pliny the Elder's account.<sup>[9]</sup> Thus the emergence of the first soap or at least the first use of soap. Zosimos of Panopolis, *circa* 300 AD, describes soap and soap-making.<sup>[10]</sup> Galen describes soap-making using lye and prescribes washing to carry away impurities from the body and clothes. Alkali metal soaps (predecessors of surfactants) were in use for several thousand years. The first authentic mention of soaps as cleansing agents appears in the 200 AD in the script of Galen, the Greek physician who has reported the preparation of soap from fat, ash lye and lime. According to Galen, the best soaps were Germanic, and soaps from Gaul were second best.<sup>[10]</sup>

Soap, or may be called as detergent similar to soap, was manufactured in ancient China from vegetation and herbs.<sup>[11]</sup> True soap, made of animal fat, did not appear in China until the modern era.<sup>[12]</sup> Soap-like detergents were not as popular as ointments and creams. In the eighth century, soap-making was well known in Italy and Spain.<sup>[13]</sup> The lands of Medieval Spain were a leading soap-maker by 800, and soap-making began in the Kingdom of England about 1200.<sup>[14]</sup> A 12<sup>th</sup> century Islamic document describes the process of soap production.<sup>[15]</sup> It mentions the key ingredient, alkali, which later becomes crucial to modern chemistry, derived from *al-qaly* or "ashes". By the 13<sup>th</sup> century, the manufacture of soap in the Islamic world had become virtually industrialized, with sources in Nablus, Fes, Damascus, and Aleppo.<sup>[16, 17]</sup>

Near around 15<sup>th</sup> century, France started semi-industrialized professional for the manufacture of soap in few centers which supplied to the rest of France.<sup>[18]</sup> English manufacture tended to concentrate in London. Finer soaps were later produced in Europe from the 16<sup>th</sup> century, using vegetable oils (olive oil) as opposed to animal fats. In 1633 King Charles-I granted a 14 year monopoly to the society of soap-makers of Westminster. Many of these soaps are still produced. Castile soap is a popular example of the vegetable-only soaps derived from the oldest "white soap" of Italy. In the reign of Elizabeth-I, soap consumption in England was greater than in any other European country.

In 1791, the French chemist Nicolas Leblanc discovered how to extract soda from common salt. In modern times, the use of soap has become universal in industrialized nations due to a better understanding of the role of hygiene in reducing the population size of pathogenic microorganisms. Industrially manufactured bar soaps first became available in the late 18<sup>th</sup> century, as advertising campaigns in Europe and the United States promoted popular awareness of the relationship between cleanliness and health.<sup>[19]</sup> Until the Industrial Revolution, soap-making was conducted on a small scale and the product was rough. In 1780 James Keir established a chemical works at Tipton, for the manufacture of alkali from the sulfates of potash and soda, to which he afterwards added a soap manufactory. The method of extraction proceeded on a discovery of Keir's. Andrew Pears started making a high-quality, transparent soap in

1807 in London. His son-in-law, Thomas J. Barratt, opened a factory in Isleworth in 1862. William Gossage produced low-priced, good-quality soap from the 1850s. Robert Spear Hudson began manufacturing a soap powder in 1837, initially by grinding the soap with a mortar and pestle. 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, bought 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. William Lever and his brothers entered the soap business in 1885 by buying a small soap works in Warrington, UK. Using glycerin and vegetable oils such as palm oil, rather than tallow, to manufacture soap, they produced a good, free-lathering soap, called "Sunlight Soap" [Figure 3]. 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, and to such a degree that B.J. Johnson Soap Company changed its name to Palmolive. At the turn of the twentieth century, Palmolive was the world's best-selling soap.<sup>[20]</sup> In the early 1900s, other companies began to develop their own liquid soaps. Such products as Pine-Sol and Tide appeared on the market, making the process of cleaning things other than skin (e.g., clothing, floors, and bathrooms) much easier. As a detergent, liquid soap tends to be more effective than flake soap, and tends to leave fewer residues on skin, clothes, and surfaces (e.g., wash basins). Liquid soap also works better for more traditional/non-machine washing methods, such as using a washboard.<sup>[21]</sup>

Larger premises were built on marshes at what became "Port Sunlight". By 1900 "Lifebuoy", "Lux" and "Vim" [Figure 4] 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, Crosfield's of Warrington, Hudson's of Liverpool. The picture of Lifebuoy factory which was established in Sydney during 1916 is shown in figure 5. MONKEY BRAND was the popular brand soap of Lever Brothers PVT. Ltd. and was first made in 1902. They used bright colours and the hard, glossy enamel finish meant that they defied the worst of outdoor conditions for many years. Lever rode the cresting late-Victorian consumer revolution to build a vast industrial empire spread across the globe<sup>[22]</sup>.



Figure 3: Various packaging of soap called Sunlight soap



Figure 4: Packaging of soap called Lifebuoy



William Street, Sydney 1916

Figure 5: Lifebuoy soap factory



**Figure 6:** Lever Bother factory at Balmain during 1928

Focus given to artists view towards infrastructure of factories and one of the best during those days was the factory of Lever Brother at Balmain [Figure 6]. The picture [Figure 7] is was of chemical laboratory setup used by Lever Brothers, Balmain. 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 [Figure 8].



**Figure 7:** Laboratory of Lever Brothers Balmain



**Figure 8:** Colgate-Palmolive factory, Balmain during 1966

During those days, women plead for soap in Sydney due to shortage of laundry soap in Sydney. Toilet soap was becoming scarce too. Film stars were used extensively worldwide to promote Lux as shown in figure 9.



**Figure 9:** Lux soap promoted by film star



Surfactant industries are growing very fast due to its wide application, new formulation and discoveries. Some of the very famous brand of surfactants are Kit, Omo, Surf, Jif, Breeze, Comfort, Huggie, Handy Andy, hair grooming (Vaseline petroleum jelly), dish-wash (Vim), transparent soap, baby powder, hair lotion (Pears), liquid soaps (Persil), Sunsilk, Oral care (Rexona strip tooth paste), detergent bar (Rin), hair colourant (Harmony), foam bath (Sunja), toilet cleaner (Domestos), floor cleaner or polish (Dual), baby soap (Softly), talcum powder (Rexona), Stick and roll on deodorants (Rexona), Shaving stick (Rexona), etc <sup>[22]</sup>.

Recent 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. Eco-friendliness is desired portion of surfactant formulations whether if a purpose of uses is either domestic or industrial. Increasing authority pressure for going towards biodegradable products in the industrial sector is contributing to the increasing in making of specialty surfactants.

## **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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