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Brief history of surfactants, their applications, and research in Nepal

Rajendra Dhakal[1,2], Nabin Basnet[1,2], and Ajaya Bhattarai[3*]
[1]Department of Chemistry, Damak Multiple Campus, Tribhuvan University, Nepal
[2]Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal
[3]Department of Chemistry, Mahendra Morang Adarsha Multiple Campus, Tribhuvan University, Biratnagar, Nepal
**Correspondence: bkajaya@yahoo.com or ajaya.bhattarai@mmamc.tu.edu.np,*

Abstract

This article reviews on the origination and development of soaps (later called surfactants) and their applications in human civilization. It was reviewed that soaps were came in use in human life as earlier as 2200 BC in Babylon. In ancient time, soaps were prepared using tallow and ashes in most of the region of world, and in similar way China began to use plats and herbs to make soaps. The soaps later called surfactants were alkali metal soaps, which have been around for thousands of years. The first recorded reference to soaps as cleaning agents dates back to 200 AD, which was prepared by Galen (Greek Physician) using fat, ash lye and lime. Nowadays, the words soap, detergent and surfactant are synonymously used. These compounds are manufacturing in large amount using plants, animals and by synthetic method. These compounds have great importance in domestic, industrial, medicinal, and synthetic applications in our daily life.Currently, the global market value is about 40 Billion USD in 2024 and is expected to meet about 60 Billion USDby 2033. *Surfactants are widely used in the field of research in Nepal. A summary of surfactant research from 2009 to now is also included in this article.*

Key word: Amphiphiles, Soaps, plant extracts, cleanliness

Introduction

Surfactants, soaps, and detergents are the words that have been used frequently as their synonyms because of their similar mode of applications and their chemical physical and chemical properties. Soaps or surfactants are the surface active agents which has tendency to lower the surface tension property of liquids. Surfactants are widely used in our daily lives activities in the form of detergents , soaps , emulsifiers , foaming agent and dispersants and almost plays a significant role to wide spread their application in different industries like food and agriculture dyestuffs, cosmetics and personal care , detergents, paints, fibers, pharmaceutical, lubricants oil recovery etc.

Each surfactant molecule has a hydrophilic (water-loving) head that is attracted to water molecule and hydrophobic (water-hating) tail that hates water and simultaneously attached itself to grease and oils in dirt, also called lipophilic group.

Based on the presence of heteroatom and dissociation behavior on water, they are classified as cationic, anionic, amphoteric and non-ionic surfactants.

Anionic surfactants: A very large number of surfactants fall on this group, that account about 50% of world production. They possess a negative charge amphiphilic anion on their polar head and an alkaline metal like Na^+ or K^+ or NH_4^+ ions as cation, and have excellent water solubility, and have strong foaming capabilities. Primarily they are used as cleansing agents in numerous soap/detergent formulations and nowadays also used in industrial products. One of the mostly used examples is sodium dodecyl sulfate (SDS).

Cationic surfactants: These surfactants carry a positive charge on their polar head. Less than 5% of overall productions hold the market by cationic surfactants. Cationic surfactants shows specific behavior and have antimicrobial properties used to kill/ control bacteria at home and in medical facilities. They are utilized for sanitizing surgical equipment, food packaging bottles or containers and creating powerful disinfectants for tough cleaning tasks. Cetyltrimethylammonium bromide (CTAB) is a commonly used surfactant in this group.

Amphoteric Surfactants: A surfactant containing both anionic and cationic parts within the single molecule is called amphoteric or zwitterionic. . As the molecule of surfactant carries both cationic and anionic groups, the ionic behavior is affected by p^H level. Due to their limited uses and very special applications in the formulation of personal care cosmetics with their high biological compatibility along with low toxicity, and amphoteric surfactants are quite expensive. An example is Cocamidopropyl betaine.

Non-ionic surfactants: These **surfactants do not** notionized in water or any appropriate solvents thus not giving charge carrying species similar to above mentioned anionic, catationic or zwitterionic surfactants. These have both hydrophilic groups such as hydroxyl group (–OH), oxyethylene ($-CH_2CH_2O-$), ether groups (-O-) , or amide group ($–CONH_2$) etc. Similarly they have lipophilic groups such as natural fatty alcohols or synthetic alcohols, glyceryl esters/oils or acids etc. The solubility of such surfactant depends upon the strength of hydrogen bonding with water molecules. On increasing temperature, these surfactants form a milky/cloudy emulsion, and the temperature is known as the cloud point. The cloud forming property is very important for calculating the optimum use of such nonionic surfactants in the formulation of detergents emulsifiers and so on (*Salager, J. L. (2002).* An example of such surfactants is for example Brij -35.

Materials and Methods

The methodology for this review article involved a systematic evaluation of chronological articles including historical and contemporary literaturesthat mentioning the development and research of surfactants globally. For the review, primary and secondary data sourcesincluding peer-reviewed journal articles, archival documents, and conference proceedings were utilized. A comprehensive search was conducted using databases such as Google Scholar, and search engine googe.com to identify literature spanning 1958 to 2024. Keywords such as "amphiphiles", "surfactants," "history of surfactants," "applications of surfactants", "cleanliness", "surfactant research in Nepal," and related terms were employed to search appropriate literatures in various databases and search engines. Inclusion criteria prioritized studies documenting milestones in surfactant development, their applications, and research activities within Nepal. Selected articles were critically evaluated to trace the evolution of surfactants globally, their applications and research in Nepal, highlighting key trends, contributions, and challenges.

Result and Discussion

History of soap formulation

In ancient Babylon, around 2800 BC, there is evidence of the earliest known manufacturing of a material like soap. Around 2200 BC, a clay tablet from Babylonia had a recipe for soaps made of alkali, water, and cassia oil. The Ebers papyrus, which dates to Egypt circa 1550 BC, suggests that the ancient Egyptians took regular baths and mixed alkaline salts and vegetable and animal oils to make a product that resembled soap. A soap recipe was made of uhulu (ashes), sesame (seed oil), and cypress (oil) during the Nabonidus reign (556–539 BC) "for washing the stones for the servant girls"(Levey, 1958). Pliny (the Elder's Historia Naturalis), which addresses the production of soap from ashes and tallow, is where the Latin term "sapo", which meaning soap, first appears. Roman mythology states that soap was called after Mount Sapo, a historical location for animal sacrifices (Schumann & Siekmann, 2000). The animal ash and fat that accumulated beneath the sacred site would be washed to the banks of the Tiber River by rain following an animal sacrifice.

Ladies using the river to wash their clothing saw that after a particularly strong downpour, some sections of the river had washed their garments. Simply put, the Latin term sapo means "soap". It was probably taken from an ancient Germanic language and is similar with the Latin word sebum, which is Pliny the Elder's account of "tallow" (Poucher's Perfumes, Cosmetic and Soaps, 1999). Hence, the invention of soap, or at the very least, its use. Alkali metal soaps, the ancestors of surfactants, have been around for thousands of years. The first recorded reference to soaps as cleaning agents dates back to 200 AD and is found in the writings of Galen, the Greek physician who described making soap with fat, ash, lye, and lime. In ancient China, plants and herbs were used to make soap, or detergent, which is similar to soap. In China, real soap—which is derived from animal fat—did not exist until the contemporary age (Jones, 2011b). Ointments and lotions were more often used than detergents that resembled soap. In Italy and Spain around the eight century, soap production was well recognized. By 800, the countries of medieval Spain were among the top producers of soap, and around 1200, the Kingdom of England started producing soap (Fields, 2012). An Islamic manuscript from the 12th century explains how soap is made. It refers to the main component, alkali, which is derived from alqaly, or "ashes," and which subsequently turns out to be essential to contemporary chemistry.

With supplies in Nablus, Fes, Damascus, and Aleppo, the production of soap in the Islamic world had essentially reached industrial levels by the 13th century. France began semi-industrialized professional soap manufacturing in a few towns around the 15th century, and these hubs provided soap to the rest of France. English manufacturers expand their business sectors to focus in London. Later, from the 16th century onward, Europe made finer soaps by substituting vegetable oils, such olive oil, for animal fats. The Westminster Soap makers Society was given a 14-year monopoly by King Charles I in 1633. These soaps are still made in large quantities. One well-known example of a vegetable-only soap made from Italy's traditional "white soap" is Castile soap. England consumed more soap than any other nation in Europe during Elizabeth I's reign. The French chemist Nicolas Leblanc came up with novel methods in 1791 for separating soda from regular salt. Because of a growing awareness of the importance of hygiene in lowering the number of pathogenic bacteria, soap use has spread throughout industrialized countries in recent years. In the late 1700s, commercials in Europe and the US raised public awareness of the connection between hygiene and health, leading to the introduction of industrially produced bar soaps. Small-scale production of crude soap was the norm prior to the Industrial Revolution.

James Keir founded a chemical plant at Tipton in 1780 to produce alkali from the sulfates of soda and potash. This alkali was then added to a procedure used in the soap industry to manufacture soap. Following Keir's finding, the extraction procedure was carried out (Jones, 2011a). In London in 1807, Andrew Pears began producing transparent, superior soap. In 1862, Thomas J. Barratt, his son-in-law, established a business in Isleworth. From the 1850s onward, William Gossage made reasonably priced, high-quality soap. In 1837, Robert Spear Hudson started producing soap powder. At first, he ground the soap using a mortar and pestle. Sales of bar soap and product sample distribution were among the marketing ideas pioneered by American manufacturer Benjamin T. Babbitt. One of the biggest soap companies today, Unilever (previously Lever Brothers) was established in 1886 by William Hesketh Lever and his brother James, who taken the ownership by purchasing a small soap industry in Warrington. Some of the earliest companies to use extensive advertising campaigns were these soap manufacturers. In the 19^{th} century, William Shepphard abled to patent a liquid form of soap in 1865, however the invention of liquid soap did not occur until later. By purchasing a little soap factory in Warrington, UK, William Lever and his brothers got into the soap industry in 1885. They created a nice, free-lathering soap known as "Sunlight Soap" by using vegetable oils like palm oil and glycerin. The vegetable oils replaced tallow while making soap. The B.J. Johnson Soap Company launched the "Palmolive" brand of soap in 1898 after B.J. Johnson created a soap containing palm and olive oils, that's why the name "Palmolive". The new soap brand "Palmolive" gained popularity quickly, to the point where B.J. Johnson Soap Company rebranded itself as "Palmolive". As the 20th century began, Palmolive was the best selling soap company of the world at the beginning phase of 20th century. Several numbers of companies would started their own liquid soap businesses in the early 1900s. With the introduction of chemicals like PineSol and Tide to the market, washing surfaces other than skin (clothes, floors, and bathrooms) became considerably simpler. Liquid soap works better as a detergent than flake soap and typically leaves fewer residues on surfaces like washbasins and clothing. Traditional, non-machine cleaning techniques, such the use of a washboard, are also superior with liquid soap. On marshland at what would become "Port Sunlight," larger buildings were constructed. Subsidiaries had been established in the US, Switzerland, Canada, Australia, Germany, and other countries by 1900, along with the addition of the "Lifebuoy", "Lux", and "Vim" brands. Due to their widespread use, novel formulations, and discoveries, surfactant industries are expanding quickly. The domain of surfactants has witnessed advancements recently, encompassing nonionic surfactants containing alcohols of branched-chain fatty acid, fatty amines, fluorocarbon surfactants, silicone surfactants, and Gemini surfactants. Eco-friendliness is a desired feature of surfactant compositions, regardless of the application's home or industrial goal. Specialty surfactant production is rising in part due to growing authority pressure for the industrial sector to switch to biodegradable products.

Applications of surfactants

Surfactants play a pivotal role in a wide range of applications across various industries due to their unique ability to reduce surface and interfacial tension.In modern times, a large fraction of surfactants business focuses on elaborating the cleaning as well as industrial operations of surfactants to wide technological areas to enhance the role of surfactants. These promotes not only in the personal care products but also the formulation the effective medicine in pharmaceuticals , petroleum product recovery processes ,genetic science and engineering, so that a huge number of scientist and engineer divert themselves to synthesizes the unique characters of surfactants.In agriculture, surfactants improve the efficacy of pesticides and herbicides by enhancing their dispersion and adhesion to plant surfaces. Surfactants versatility and ability to modify surface properties make them indispensable in modern science and industry.

Surfactants research in Nepal

Surfactants are used in a variety of industrial processes, including metal treatments, colloid stability, mineral flotation, insecticides, pharmaceutical formulation, oil production, emulsion polymerization, particle growth, and many more. As a result, surfactants have been and continue to be a highly active area of scientific inquiry and commercial development for many years. Surfactants have an intriguing property: at low concentrations, they exist purely as monomers. The formation of micelles begins at a fixed surfactant concentration known as the critical micelle concentration (cmc) at mentioned above, at which point the physical properties of the solution, such as electrical conductivity, interfacial tension, and light scattering behaviors change abruptly due to the presence of micelles. The creation of micelles will enable the calculation of numerous thermodynamic parameters. These factors make surfactants not only an attractive and rich area for the discovery of novel phenomena, but also a research area with the potential to lead to new applications in a wide range of fields. However, the majority of past surfactant investigations have only focused on aqueous media.

Studies in mixed solvent media are particularly natural since the conformations of surfactants and their interactions can be easily modulated by simply changing the medium composition (Shah et al., 2009; Shah et al., 2016a; Shah et al., 2016b).

With this concept in mind, the Eastern Nepal research team began investigating the solution characteristics of surfactants in various mixed solvent media in the presence and absence of salts (Niraula et al., 2018; P. Bhattarai et al., 2021), electrical conductivity study of cationic surfactant in short-chain alcohol-water mixed solvents (Basnet et al., 2021)as well as the interaction of cationic and anionic surfactants in mixed solvents (A. Bhattarai, 2015; A. Bhattarai et al., 2017).

Furthermore, surfactant work involving single and mixed surfactants interacts with dyes (Kumar Sah et al., 2023; Prasad Tajpuriya et al., 2021; Sachin et al., 2019; Shahi et al., 2021; Shahi et al., 2023; Yadav, Shahi, Niraula, et al., 2024) and surfactants as corrosion inhibitors (Shahi et al., 2024; Yadav, Shahi, Adhikari, et al., 2024). The synthesis, characterization, and physicochemical properties of surfactant-based Schiff base transition metal complexes are investigated (Adhikari et al., 2022). The corrosion inhibition action of Co(II) and Zn(II) complexes of pyrrole-based surfactant ligands is worth investigating (Adhikari et al., 2023). Surfactant-polyelctrolyte (A. Bhattarai, 2019; A. Bhattarai, 2020) and surfactant-polyelctrolyte-dye (Narayan Yadav et al., 2022; Narayan Yadav et al., 2024) interaction investigations have recently been conducted.

Conclusions

The review found that, soaps have been used from Babylonia era and at that time soaps were used mainly for domestic purposes in cleanliness. Anciently, soaps were prepared from tallow and ashes and followed in china by plant and animal extracts, and the development of soaps faces many ups and downs in their formulations. Since ancient time the global market of soap or surfactants increases day by day and currently reaches about 40 billion USD in and is supposed to reach60 billion USD by 2033. Nowadays, surfactants can be by using solid methods of preparation using plant or animal extracts or by synthetic methods. Surfactants have been used in the research fields by studying the solution properties of surfactants in mixed solvent media as well as surfactants with salts, single surfactants and mixed surfactants with and without dyes. Surfactants and mixed surfactants as the corrosion inhibitors and surfactant-based Schiff base transition metal complexes are investigated. Surfactant-polyelectrolyte and Surfactant-polylectrolyte-dye are interesting area to study.

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