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A REVIEW ON RHEOLOGY OF FACE CLEANSER

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ABSTRACT

Skin, the largest organ of the human body, serves as a protective barrier and plays a vital role in maintaining physiological balance. To preserve its health, cosmetic products are widely used with facial cleansers being one of the most essential categories. A cleanser is a topical formulation developed to clean the skin surface without causing irritation or disrupting the natural moisture barrier. An ideal cleanser should balance cleaning efficiency with skin compatibility, ensuring it removes impurities while maintaining hydration and pH balance. Rheology, the science of flow and deformation of materials plays a crucial role in the development and performance of face cleansers. Rheological behavior determines the product's viscosity, spread ability, stability, and user sensory perception. Parameters such as shear-thinning behavior, thixotropy, and viscoelasticity influence how the cleanser is dispensed, how it spreads on the skin, and how easily it can be rinsed off. Understanding rheology also assists in optimizing formulation components such as surfactants, thickeners, humectants, and preservatives to ensure both physical stability and desirable texture. In this review, we primarily focus on the rheology of face cleansers and its significance in developing formulations that offer effective cleansing, enhanced stability, and improved consumer acceptance.

KEYWORDS: Cleanser, Surfactants, Rheology, CMC.

INTRODUCTION

Cosmetics means any article intended to be rubbed, poured, sprinkled or sprayed on or introduced into or otherwise applied to the human body or any part thereof for cleansing, beautifying, promoting attractiveness or altering the appearance and include any article intended for uses as a component of cosmetics.[1] Cosmetics and other personal care products provide barrier function and improve skin appearance. The selected product should be appropriately formulated; poorly formulated products can damage the skin and also increases transdermal water loss.[2]

Skin is the largest protective organ of the body that continuously exposed to environmental pollutants, sebum, dust and cosmetic residues. Healthy skin depends on an intact stratum corneum, an appropriate lipid and protein matrix all these are influenced by both intrinsic and extrinsic factors.[3]

Poor hygiene causes a wide range of skin diseases. Insufficient removal of dead skin cells, debris, and other impurities can promote microbial overgrowth, acne, and other inflammatory conditions. Proper facial cleansing plays an important role in maintaining skin health by removing the impurities. A cleanser is a topical formulation that helps in solubilizing dirt, excess oil and other impurities from the skin surface, thereby preventing clogged pores, acne, dullness and irritation. An effective cleanser not only clean the skin but also maintain its physiological balance, leaving the face refreshed, hydrated and free from all the residues. Modern cleanser aims to balance effective removal of the impurities with preservation of barrier lipids and skin hydration.[4]

In modern cosmetic science, the rheology of face cleanser has gained importance in product development and consumer acceptance. Rheology determines the key

characteristics of a cleanser such as viscosity, spreadability, thickness and ease of dispensing. Rheological behavior also affects the stability of suspended ingredients, ensuring uniformity and preventing phase separation throughout the shelf life of the product. Face cleansers exhibit shear thinning property. Shear thinning pseudoplastic behavior is a rheological property in which the viscosity of the formulation increases by applying a shear force. Gels, creams and liquid cleansers exhibit shear-thinning property. This property is mainly achieved by incorporating rheological modifiers and surfactants into the formulation. Shear thinning formulations provide ease of dispensing, spreadability, and pleasant skin feel. So, in a face cleanser shear thinning is highly desirable not only for manufacturing efficiency but also consumer performance.[5,6]

1. SKIN

The skin, also known as the cutaneous membrane covers the external surface of the body and is the largest organ of the body in weight. In adults, the skin covers an area of above 2 square meters (22 square feet) and weighs 4.5-5Kg (10-11b), about 7% of total body weight. It ranges in thickness from 0.5mm (0.02in.) on the eyelids to 4.0mm (0.16in.) on the heels. Over most of the body it is 1-2mm (0.04-0.08in.) thick.

The skin is the largest organ of human body. It consists of two main parts:

a) Epidermis: The superficial, thinner portion. It is the outer protective layer, formed by stratified, squamous epithelium composed mainly of keratinocytes (90%) and dendritic cells, including melanocytes, merkel cells and langerhans cells.

b) Dermis: Second deeper part of the skin. Composed of dense irregular connective tissue containing collagen and elastic fibre Deep to the dermis, but not part of the skin is the subcutaneous layer. Also called hypodermis, this layer consist of areolar and adipose tissues.[7]

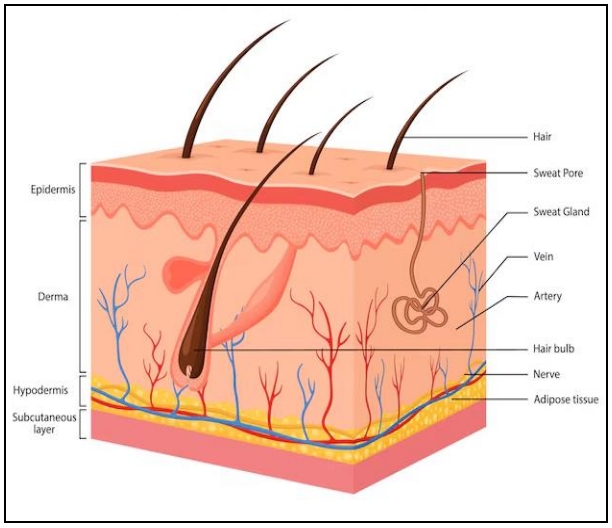

Fig. 1.1: Structure of skin.

1.1. EPIDERMIS[8,9]

It contains four principal type of cell: keratinocyte, melanocyte, intra-epidermal macrophages, and tactile epithelial cell. Keratinocytes produce a protein called keratin that helps in protecting the skin and underlying tissues from abrasions, heat and microbes. Keratinocytes also produce lamellar granules which release a water-repellent sealant that decreases water entry and inhibit the entry of foreign materials. Epidermis consists of five layers:

1.1.1. Stratum basale

Stratum basale also known as startum germinativum is the innermost layer of epidermis that sitting directly on top of dermis. It consists of stem cells that produce keratinocytes and melanocytes. The nuclei of the cells are perpendicular to the basement membrane.

1.1.2. Stratum spinosum

Stratum spinosum also known as prickle cell layer. It is the thickest layer of epidermis that comprises of 8-10 cell layers. And situated between stratum basale and startum granulosum.

1.1.3. Stratum granulosum

Startum granulosum is the third layer of the epidermis, located above the stratum spinosum and below stratum corneum. It has 3-5 cell layers and contains diamond shaped cells with keratohyalin and lamellar granules. The lamellar granules maintain cellular cohesion.

1.1.4. Stratum lucidum

Startum lucidum is the thin layer of epidermis that comprises of 2-3 skin layer. It is present in thicker skin on the palms and soles. It contains protein rich substance called eleidin, which is transformation product of keratohyalin.

1.1.5. Stratum corneum

Stratum corneum is the outermost layer of epidermis that consists of 25-30 layers of flattened dead keratinocytes. It is composed of keratin and dead keratinocyte that forms horny scales. Dead keratinocyte release defensins within this layer, which are part of our first line of immune defense mechanism.

1.2. DERMIS

Dermis connected to epidermis by the basement membrane, and has the ability to stretch and recoil easily. It is much thicker than epidermis and consist of 2 connective tissue layers, papillary and reticular. The papillary layer is the upper dermal layer which is thinner and composed of loose connective tissue. Reticular layer is the deeper layer, which is thicker and less cellular. It consist of dense connective tissue that composed of collagen fiber bundles. Dermis helps in supporting epidermis by providing strength and flexibility to it and also helps in producing sweat. Dermis also keeps our skin moist due to the presence of sebaceous glands. Dermis contains cutaneous appendages or adnexal

structures. These are sweat glands, sebaceous gland, hair follicle, arrectores pilorum and nails.

1.2.1. SWEAT GLAND

These are widely distributed throughout the skin and are most numerous in the palms of the hand, soles of feet, axillae and groins. They are formed from epithelial cell. There are 2 types of sweat glands.

1.2.1.1. Eccrine gland

Eccrine glands are the most common type and open onto the skin surface through tiny pores. These start to develop on the palms and soles at about 3 months, but not over the rest of the body until the fifth month. They are simple, coiled tubes that open directly onto the skins surface. Eccrine glands helps in regulating body temperature by releasing sweat. The glands are lined by two main types of secretory cells: basal, acidophilic, clear or chief cells and the superficial, basophilic dark granular cells.

1.2.1.2. Apocrine gland

Apocrine glands are larger than eccrine glands and located in the armpits, groin and around the nipples and areolae. Unlike eccrine glands they become active at puberty and secrete a viscous, milky substance of fats, proteins, and sugars that can cause body odor when broken down by bacteria. They release their secretions through a process called decapitation where the tip of the cell buds off into the duct.

1.2.2. SEBACEOUS GLAND

Sebaceous glands are found everywhere on the skin except on the palms and soles. These are holocrine glands that secrete via disintegration of the glandular cells into the upper portion of the hair follicles, which is then distributed onto the skin surface. The number and activity of the gland differ by anatomic location, sex and age. Sebaceous gland function is responsive to stimulation by sex hormones and adrenal corticosteroids. Sebum lubricates the skin and hair.

1.2.3. HAIR FOLLICLE

Hair follicles are complex structure formed by the epidermis and dermis. They are found over the entire surface of the body except the soles of the feet, palms, glands penis, clitoris, mucocutaneous junction, and portion of the fingers and toes. Hair follicle consists of epithelial and connective tissue components. The hair shaft is made up of outer sheath and pigmented cortex and inner medulla. These are small bundles of smooth muscle attached to each hair follicle.

1.2.4. NAILS

Nails are hard, protective structures made of keratin that helps in protecting the finger tips, assisting with tactile perception and aiding in daily tasks like grasping and scratching. These are thickenings of the deeper part of the stratum corneum that develop at specifically modified part of the skin called nail bed.

1.3. TYPES OF SKIN[10]

Skin is classified according to several factors related to its balance: sebaceous secretion, hydration and sensitivity level.

There are five types of healthy skin

- Normal skin
- Dry skin
- Oily skin
- Sensitive skin
- Combination skin

1.3.1. NORMAL SKIN

This skin is neither too dry nor too oily. It has regular texture, no imperfections and a clean, soft appearance, and does not need special care. At cosmetological level, normal skin is structurally and functionally balanced and it has fine pores. This skin has a balanced sebum and moisture level and also has healthy glow and uniform complexation.

1.3.2. DRY SKIN

Dry skin is a skin type that occurs due to lack of moisture or reduced sebum production. Dry skin is characterized as scaly, rough and dull which can lead to tautness and itchiness. This skin type tends more toward premature aging and is likely to have more wrinkles. Excessive cleansing or use of harsh soap and dehydration can cause dry skin. And environmental factors like low relative humidity, cold weather and sunlight in addition to repeated contact with water, surfactants, and solvents plus numerous skin diseases can cause dry skin.

1.3.3. OILY SKIN

Oily skin is a skin type that is characterized by excess sebum production. It has enlarged pores and gives a shiny appearance on the T-zone (forehead, nose and chin). This skin type is prone to acne, blackheads and whiteheads. Oily skin usually develops with onset of puberty and affects a large percentage of young people. Factors like genetic inheritance, overactive sebaceous glands, hormonal changes (puberty, menstrual cycle), hot and humid climate improper diet high in fats and sugars cause dry skin.

1.3.4. SENSITIVE SKIN

Sensitive skin gets reacts easily to external factors like cosmetics, temperature changes, pollution etc. it is a complex dermatological condition defined by abnormal sensory symptoms for example tingling, chafing, burning or pricking and possibly pain or pruritus by various chemicals (cosmetics, soaps, water, pollution) physical factors (UV light, heat, cold and wind), microorganisms, psychological factors (stress), and hormones (menstrual cycle). The term “sensitive skin” refers to facial skin, but it can also concern other body areas, such as hands, scalp or genital area.

1.3.5. COMBINATION SKIN

Combination skin, as its name implies, it is the combination of normal and oily skin or of oily and dry skin. This type of skin has a tendency to be greasy in the central T-zone of the forehead, nose and chin. Occasional acne or black heads in oily areas are seen in this type of skin type. Factors like uneven sebum production across different parts of the face, genetic factors, and hormonal changes affecting oil gland activity, environmental conditions like humidity etc causes combination skin.

Fig. 1.2: Types of Skin.

1.4. SKIN DISORDERS

1.4.1. ACNE[11]

Acne is a chronic inflammatory disease of the pilosebaceous unit resulting from androgen-induced increased sebum production, altered keratinization, inflammation, and bacterial colonization of hair follicle on the face, neck, chest and back by propionibacterium. The appearance of lesions around puberty is related to physiological hormone variation. The condition affects the hair follicle, the opening of which is blocked by keratin material resulting in formation of comedones. Comedones may be open having central black appearance due to oxidation of melanin called black heads, or they may be in closed follicles reffered to as white heads. A closed comedones may be get infected and result in pustular acne.

Pustular acne has been cited as the cause of acne because it is typically present in teenagers with acne and not those without acne. P. acnes are seen as small, red bumps with a distinct white or yellow tip. The presence of the bacteria is likely not a direct cause of acne breakouts though it is more likely that the inflammation seen in acne is caused by free fatty acid that results from the breakdown of triglycerides in the sebum owing to bacterial lipases. Other extracellular enzymes proteases and hyaluronidases may also play a important role in inflammatory process.

Fig. 1.3:Acne.

1.4.2. ROSACEA[12,13]

The exact etiology of rosacea remains unclear, but several mechanisms have been implicated, including innate immune system dysregulation, demodex mite overpopulation, neurovascular hyperactivity, genetic predisposition, and environmental triggers. Sunlight, heat, alcohol consumption, and spicy foods are main reason to rosacea symptoms. Flushing and telangiectasia are major symptoms in patients with rosacea. Intestinal inflammation and bacteria may cause hyper sensitization of facial sensory neurons via the plasma kallikrein‐kinin pathway and production of bradykinin. Although rosacea is a chronic, incurable condition, appropriate treatment and lifestyle modifications can improve symptoms and enhance quality of life. Rosacea is a chronic inflammatory skin disorder characterized by facial redness, flushing, visible blood vessels, and sometimes acne‐like bumps, commonly affecting the central face and triggered by various environmental and lifestyle factors. It primarily affects the central facial skin, presenting with persistent erythema, telangiectasia, papules, and pustules, often exacerbated by vascular hyper‐reactivity and environmental triggers.

Fig. 1.4: Rosacea.

1.4.3. WRINKLED SKIN[14]

Skin changes with age and wrinkles emerge and become more pronounced. Wrinkle formation depends on the nature of the skin and on muscle contraction. Wrinkles

are the most important macro‑structures of aging skin. Two types of wrinkles are considered: expressive wrinkles and age‑related wrinkles. Expressive wrinkles, also referred to as temporary wrinkles, appear on the face during facial expressions at all ages and may become permanently visible over time. In addition to their visual effect, expressive wrinkles serve as an important cue for understanding and interpreting facial expressions, while permanently visible wrinkles are a cue to a person's age. The pathophysiology involved in skin wrinkling is collagen loss, elastin degradation and telomere shortening. With age collagen fibers degrade and synthesis diminishes which in turn cause to reduce skin tension and loss of structural integrity.

Elastin fibers gives skin its elastic recoil after stretching, with age, UV radiation and smoking the elastic recoil losses. This causes skin to loss their ability to return to original shape which results in formation of permanent fold and thus forms wrinkles.

Telomeres are thermal portions of mammalian chromosomes which is composed of hundreds of short sequences of repeat base pairs. Telomeres cap chromosome ends and shorten with each cell division, leading to cellular senescence. In skin fibroblasts, shortened telomeres reduce proliferative capacity, decreasing collagen synthesis and resulting in a thinner, weaker dermis that promotes wrinkle formation. Oxidative stress from UV exposure and smoking accelerates telomere shortening, causing premature skin aging and wrinkles. Telomerase activity declines with age, further shortening telomeres, inducing skin cell senescence, and reducing skin renewal, which contributes to wrinkle development.

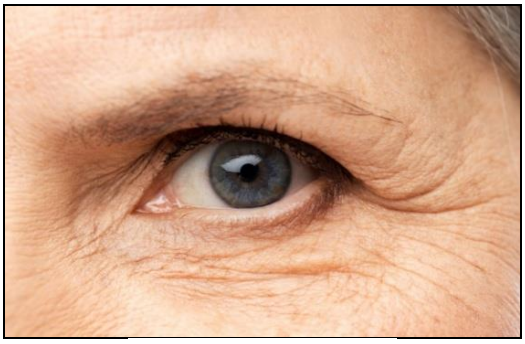

Fig. 1.5: Wrinkled skin.

1.4.4. IMPETIGO[15]

Impetigo is a skin infection mostly seen in children and it is transmitted easily from one person to other. It is highly contagious infection that affects outer layer of epidermis. Impetigo is caused by Gram-positive bacteria. Bacteria form a complex biofilm on the skin surface. There are two types of impetigo called non-bullous and bullous impetigo. Impetigo is commonly caused by Staphylococcus aureus. Non-bullous is classified into primary and secondary impetigo. Primary impetigo is due to the direct bacterial penetration into the skin. Secondary impetigo is due to the preexisting skin lesions such as eczema, insect bites, cuts or abrasions. Poor hygiene, infrequent washing, dirty skin and unclean nails can promote impetigo. The skin is continuously get exposed to dust, sweat, sebum and pollutants. Poor facial hygiene disrupts the normal skin barrier. Bacterial colonization can lead to impetigo.

Fig. 1.6: Impetigo.

1.4.5. SEBORRHEIC DERMATITIS

Seborrheic dermatitis is a chronic, relapsing, non-contagious inflammatory skin condition that causes oily, yellowish scales, redness and itchiness. It mainly affects sebum rich areas of skin like face, chest, scalp and ears. Scaly flakes of skin are considered as a typical symptom of this disease. This scaly flake forms a reddish appearance on light colored skin. Though this disease isn't contagious it comes back in adult. The exact cause of seborrheic dermatitis isn't known, but it is associated with overgrowth of malassezia species, increased sebum production, abnormal immune response, genetic predisposition and exacerbating factors like stress, cold weather, poor hygiene and neurological disorders. Malassezia yeast metabolizes skin lipids, producing inflammatory by-products that irritate the skin, leading to scaling and erythema. The rashes spread to other body parts.[16] This diagnosis of this disease is based on pattern and lesion distribution and by analyzing the characteristics of scaling and erythema.[17] Regular cleansing with mild and non-irritant cleanser will help to prevent this condition and frequent hair washing with medicated shampoos will also help. Maintaining proper facial and scalp hygiene is very important to prevent this condition.[18]

Fig. 1.7: Seborrheic dermatitis.

2. FACE CLEANSER[19]

Skin care is an important of patient care. Conditions like xerosis, eczema, dermatitis, acne, rosacea, psoriasis are caused as a result of barrier dysfunction. Two of the most important skin care categories are cleansers and moisturizers which have a significant dermatological activity. Many of the cosmetic products and other impurities are difficult to remove by normal washing as they are insoluble in water, so washing with substances that can emulsify, this water insoluble impurities into fine particles are recommended.

A face cleanser is a cosmetic preparation formulated to remove dirt, oil, makeup, dead skin cell, and other impurities from the skin of the face. A good quality face cleanser should have gentle surfactants and moisturizers to cleanse the skin. Cleansers composed of alkaline soaps or less barrier damaging synthetic detergents known as syndets.

Fig. 2.1: Face cleanser.

2.1 Types of Cleansers[20]

Now a days variety of cleansers are available in market, but all the available cleansers fall into two categories: soap based and syndet cleansers. Both these cleansers wash off the impurities from the skin and surfactants are the main constituent, but they differ in their chemical properties and physiological effects.

2.1.1. Soap Based cleanser

These are the oldest and most commonly used cleansing agent. They are produced by saponification reaction between fatty acids or triglycerides and a strong alkali like sodium hydroxide or potassium hydroxide or magnesium hydroxide that result in the formation of alkali salts of fatty acids. Thus formed fatty acid chain has a length of C12-C18. Soap based cleansers have a alkaline pH that range from 9-10 which is a very high pH than natural pH of the skin. Frequent use of soap based cleanser cause skin dryness, irritation, increased transdermal water loss (TWEL) and barrier damage. The rheological property of these cleansers are relatively simple compared to synthetic cleansers. Soap based cleansers are popular because of their low cost, anti-microbial properties and ease of manufacture. Though due to their alkalinity, soap based cleansers are getting replaced by syndet based cleansers.

2.1.2. Syndet Based Cleanser

Syndet cleansers are modern cleansers that are chemically synthesized using petroleum, fats or oil based products. These cleansers are produced by combination of different chemical process and not by saponification. Anionic, amphoteric and non ionic surfactants are most commonly used surfactants in these cleansers. Syndet cleansers are more mild in skin than soap based cleansers and they effectively remove the impurities from the skin surface. The pH range of this cleanser typically range from 5.5-7, which is a main advantage of syndet cleanser as it maintain a pH range with skin. Syndet cleansers cause less protein denaturation and lower transdermal water loss (TWEL). And these cleansers are ideal for sensitive, dry and acne prone skin. Syndet cleansers are widely recommended by dermatologist due to their mildness and skin compatibility.

2.1.3. Gel Cleanser

Cleansers that are transparent, gel like in form that give a deep cleansing and these are ideal for oily or acne-prone skin.

2.1.2. Cream Cleanser

Cleansers that are thicker and more hydrating are cream cleansers. Ideal cleanser for dry and sensitive skin.

2.1.3. Foaming Cleanser

These cleansers effectively remove excess oil and suitable for combination or oily skin.

2.1.4. Oil Cleanser

These cleansers dissolve makeup and impurities without stripping moisture. This type of cleanser can be used for all type of skin types.

2.1.5. Exfoliating Cleanser

These are cleansers that contain chemicals like glycolic acid to remove dead skin. This cleanser is ideal for dull skin.

2.1.6. Clay Cleanser

This cleanser helps in removing oil and toxins, leaving skin fresh. Ideal for oily and combination skin.

2.1.7. Micellar Water

Cleansers that are gentle and contains tiny molecules called micelles suspended in soft water that act like a magnet to attract and lift dirt oil and other impurities from face.

2.1.8. Hydrating Cleansers

Cleansers that maintain skin moisture and perfect for dehydrated or sensitive skin.

2.2. Properties of Face Cleanser[21]

- A quality cleanser should remove dirt, oil, makeup and impurities without losing skin moisture.
- Should maintain skin pH.
- Should be available for all skin type.

- Should leave the skin soft, hydrated and prepared for other products.
- Pore unclogging: Clears out debris that can lead to breakouts
- Non-irritating: A good cleanser should be free from harsh alkalis (high pH soaps) and fragrances that can trigger redness or allergic reactions.
- Cleansers should be free of surfactants that disrupt lipid bilayer to maintain barrier function.

2.3. Uses of Face Cleanser

- Cleanser clears surface debris, pollutants, and excess sebum that accumulate throughout the day.
- Dissolves foundation, sunscreen, and mascara and other makeup products for a clean canvas before skincare or makeup reapplication.
- Clears follicular openings, reducing the risk of comedones (blackheads/whiteheads) and acne breakouts.
- Gentle formulas preserve natural lipids while clearing away irritants, helping the barrier function stay intact.
- Opens up the stratum corneum so that serums, moisturizers, and treatments penetrate more effectively.
- Regulates excess sebum production, especially with formulations tailored for oily or combination skin.
- Face cleanser is essential for daily skin hygiene, keeping the skin clean, clear, and receptive to subsequent skincare steps.

2.4. Advantages

- A face cleanser helps in removing dirt and other impurities
- Helps in preventing acne and breakouts
- Maintain skin hydration
- Improves absorption of skincare products
- Refreshes and revives the skin
- Balances skin pH

2.5. Disadvantages

- Over cleansing can damage skin barrier
- Fragrances, preservatives or certain surfactants can trigger contact dermatitis in susceptible individuals
- May cause dryness or tightness
- Requires regular use
- Give only temporary result
- Cleansers with high pH can raise skin surface pH temporarily and increasing susceptibility to microbial overgrowth.

3. SURFACTANTS[22]

Surfactants or surface active agents are principal constituent of cleansers that provide cleansing action. Surfactants act by lowering the interfacial tension by moving to the interface after dissolving in water. They are amphipathic molecules that consist of a non-polar hydrophobic portion and a polar hydrophilic portion. The hydrophobic portion is a straight or branched hydrocarbon or fluorocarbon chain that having 8-18 carbon atoms, these atoms are attached to the polar portion. Hydrocarbon chain has a weak interaction with the water molecules whereas the polar head has a strong interaction via dipole-dipole or dipole-ion reaction. Surfactants are commonly used in chemical industry like detergents, dyestuffs, cosmetics, fibers, agrochemicals, plastics and also in pharmaceuticals surfactants are used in drug delivery system and to solubilize poorly water soluble active pharmaceutical ingredients. Surfactants are also used in shampoos, body washes and facial cleansers and these are also used in oil industry in recovering tertiary oil.

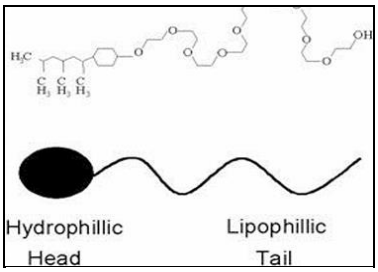

Fig. 3.1: Structure of surfactant.

3.1. Types of Surfactants

3.1.1. Natural surfactants

Natural surfactants which are also known as bio surfactants are amphiphilic biological compounds derived from renewable resources like plants, animals or microorganisms. Plant derived natural surfactants include glucosides, saponins etc. Lecithine that obtained from egg yolks is an example of animal derived surfactants. Bio surfactants are molecules that produced by bacteria, yeast or fungi is an example for microorganism produced surfactants. Natural surfactants are less toxic and have functionality under extreme conditions. These surfactants are used in the field of petroleum, medicine, agriculture, food and cosmetics. Natural surfactant perform as same as synthetic surfactants in case of cleansing, foaming, emulsifying and wetting. They are often termed as 'green' due to their low toxicity and biodegradability. The production and purification of the natural surfactants are expensive and also the separation and purification process are complex as they are present in small quantities

3.1.2. Synthetic surfactants

Synthetic surfactants are synthetically produced using nonrenewable sources. These surfactants are man made chemicals obtained from petrochemical feedstock through various chemical process like alkylation, ethoxylation and sulfation. Synthetic surfactants are used in personal care products like shampoos, body washes and conditioners and also they are used as wetting agents, paint additives and emulsifiers. These surfactants are widely used in products like detergents and cleansers. Synthetic surfactants can be categorized based on their ionic charge as anionic, cationic, non ionic, zwitter ionic.

3.1.2.1. Anionic surfactants

Anionic surfactants are made up of anionic functional groups like sulphate, sulfonate, phosphate and carboxylate. These groups have negatively charged head that makes them excellent cleansers also they have good lather characteristics. They are known as primary surfactants and used along with cation surfactant. Anionic surfactants when compared with non-ionic and amphoteric surfactants they are termed as secondary surfactants. Anionic surfactants are widely used in soaps, shampoos, laundry detergents etc. Eg: Sodium lauryl sulfate, Sodium dodecyl sulfate, Ammonium laureth sulfate.

3.1.2.2. Cationic surfactants

Surfactants that have positively charged hydrophilic portion is called cationic surfactant and they are the smallest group of surfactants. These surfactants doesn't have any wash activity but used for conditioning, softening and disinfecting. This group has more antimicrobial activity than anionic surfactants. Cationic surfactants are incompatible with anionic surfactant but compatible with non-ionic surfactant. Eg: Alkyl ammonium chloride, Bezalkonium chloride, Cetyltrimethyl ammonium bromide.

3.1.2.3. Non-ionic surfactants

Surfactants that contain hydrophilic portion that has no charge are called non-ionic surfactant. They have both water attracting and oil attracting parts and they will not dissociate into ions in aqueous solution. These surfactants have poor cleansing and lather characteristics and are excellent emulsifying, wetting and cleaning agent and they remain uncharged in water. Non-inonic surfactants are found to have tendency to dissolve stearic acid than anionic surfactants. Eg: Alkyl phenol ethoxylate, Fatty acid alkoxylate, cetyl alcohol.

3.1.2.4. Zwitterionic surfactants

Zwitter ionic surfactants are made of anionic and cationic groups having diametrically opposite charge that is both positive and negative charges on the same molecule thus resulting in a net charge of zero. This surfactants are referred to as amphoteric surfactants that undergoes a pH change from low to high. They are less irritant to skin than anionic surfactants and have good cleansing and lather characteristics. Zwitter ionic surfactants are used to improve foam quality and viscosity in products like shampoos amd body washes. Eg: Coccamido propyl betaine, Lecithine, Glyceryl laurate.

4. RHEOLOGY[23]

Rheology is derived from the Greek words 'rheo' means to flow and 'logos' means science, that introduced to describe the flow of liquids and the deformation of solids. Rheology is the science studying the relationship between deformation and stress caused by various reasons. It has been widely used in chemical industry, biological engineering, food industry, petroleum and other disciplines. Fundamental principles of rheology are used to study paints, inks, doughs, road building materials, cosmetics, dairy products and other materials. In pharmaceuticals rheology is widely used to study polymers. Also rheology examines viscosity and elasticity. It encompasses the study of solid, liquids and gases. For solids, understanding deformation laws is key, why liquids require knowledge of flow laws. Important aspects include creep stress relaxation, yield values and rheological models. Rheometers are used as a tool to measure responses to stress. Rheometers applies a stress or a stain to a sample then measures the material's response ie. deformation or stress overtime. Thus obtained data provides viscosity elasticity and time dependent behavior of the sample. Rheology of face cleanser deals with their texture flow and stability. Polymers and surfactants are added to control viscosity, provide foam and to create smooth gels.

Rheological properties of pharmaceutical system can influence the selection of processing equipment used in its manufacture. While classifying the materials in accordance with their flow and deformation they come under any of these two categories: Newtonian or non-Newtonian systems. This classification is based on whether or not their flow properties are in accord with Newton's law of flow.

Newton's Law of Flow: Shear stress (force) between fluid layers is directly proportional to the rate of shear strain (velocity gradient) between them. ie, shearing stress (F) is directly proportional to shearing rate (G).

$$F \alpha \ dv/dr$$

$$F = \eta \ dv/dr$$

Where F is shearing stress = f/A force per unit area
Unit = newton per meter^2
G = dv/dr = Shearing rate = change in velocity/change in distance
Unit = sec^{-1}

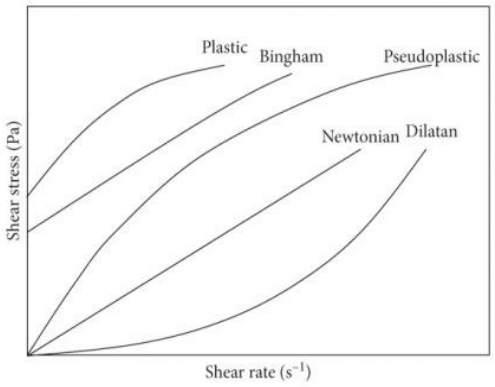

Fig. 4.1: Rheology.

5. CRITICAL MICELLAR CONCENTRATION (CMC)[24]

The concentration at which micelles first form in solution is termed as critical micelle concentration. When amphiphiles present in liquid medium at low

concentration, it exist in sub colloidal size and separately. As the concentration increases aggregation occurs, these aggregates contain 50 or more monomers are called micelles.

Critical micelle concentration is the concentration of the monomer at which micelle form. Below CMC, the concentration of amphiphile undergoing adsorption at air-water interface increases as the total number of amphiphile is raised. Eventually a point is reached at which both the interface and the bulk phase become saturated with monomers, this is the CMC. At CMC there will be a change in the slop of the viscosity curve due to the formation of micelle, disrupting the monomer-solvent structure. Above CMC, the surface tension remains constant, showing that the interface is saturated and micelle formation has taken place in bulk phase.

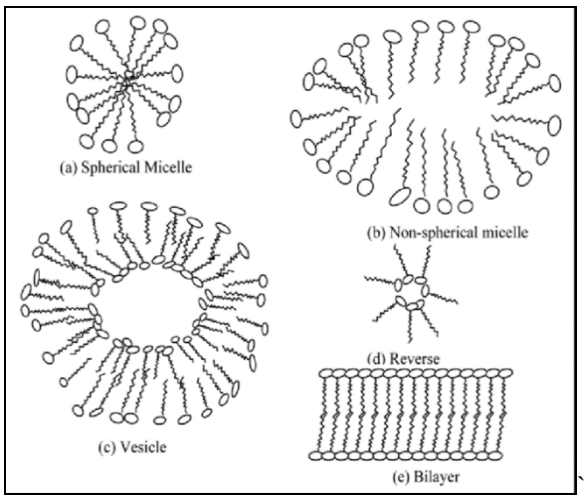

Fig. 5.1: Critical micellar concentration.

5.1. Effect of Electrolyte on Critical Micelle Concentration[25]

Addition of electrolyte to ionic surfactants decreases the CMC and increases the micellar size. The effect decrease in CMC is primarily attributed to the reduced thickness of the ionic atmosphere surrounding the surfactant head-groups, which leads to a drop in electrical repulsion between them within the micelle. This allows the micelles to grow and also reducing the work required for their formation. Clearly, an increase in electrolyte concentration in the solution enhances this effect, resulting in a larger reduction of the CMC.

5.2. Viscosity Changes With CMC[26]

Below the critical micelle concentration (CMC), viscosity typically increases as individual surfactant molecules interact. Above the CMC, viscosity often raises more due to the formation of spherical micelles and with further increases in concentration, may transform into larger, ordered structures such as cylindrical micelles or network assemblies.

5.3. RHEOLOGY MODIFIERS

Rheology is concerned with investigating how materials deform and flow when subjected to external force. Rheology modifiers also called thickeners or viscosity modifiers are polymers that used to alter and control the viscosity, flow, and spread ability of the product without affecting its chemical stability. It plays a crucial role in the manufacturing and performance of topical and injectable pharmaceutical formulations, as semisolid formulations like ointment, gels and toothpaste should have a shear dependent property for the smooth pumping. And they should also possess a shear-thinning property for easy extrusion and spread ability upon application. Rheology modifiers help in adjusting the product thickness and flow, it prevents phase separation and sedimentation in emulsions and suspensions, also it enhances spread ability of the product and keep insoluble particles evenly dispersed. Mechanism of action of rheology modifiers involves network formation of high molecular weight polymers and clays, they form a three-dimensional network by forming hydrogen bond or cross links, that increase resistance to flow.[27]

Classification[28]

Types of rheology modifiers	Examples
Natural polymers	Xanthan gum, Guar gum, Agar
Synthetic polymers	Carbomers, Polyvinyl alcohol, Polyacrylamide derivatives.
Inorganic thickeners	Bentonite, Magnesium aluminium silicate, Colloidal silica

5.3.1. Comparison of natural and synthetic modifiers[29]

Natural Rheology Modifiers

Advantages

- Derived from renewable sources, making them more eco-friendly.
- Perceived as safer and gentler by consumers, aligning with trends like "clean beauty."

Disadvantages

- It may have limited thickening efficiency compared to synthetic options.
- It can be less stable in extreme pH or temperature conditions.

Synthetic Rheology Modifiers

Advantages

- Highly effective in small quantities, offering superior thickening and stabilization.
- Greater compatibility with a wide range of actives and formulation conditions.

Disadvantages

- Typically derived from petroleum-based resources.
- It may not align with consumer demand for natural or sustainable ingredients.

6. SHEAR THINNING[30]

Non- Newtonian fluids are classified as shear-thinning, shear-thickening, thixotropic and rheopectic fluids. Shear thinning is the property of fluids where an increase in shear rate causes decrease in viscosity, thus making the fluid easy to flow. This property makes thick substances to become thin. Shear thinning is the non-Newtonian or pseudo plastic behavior of fluids. By applying a shear strain the viscosity of fluid decreases. It is sometime considered synonymous with pseudo plastic behaviour and is usually defined as excluding time- dependent effect such as thixotropy. Although shear thinning is generally not observed in pure liquid with low molecular mass or ideal solution of small molecules like sucrose or sodium chloride, it is often observed in polymer solution and molten polymer solution as well as complex fluids and suspension like ketchup, whipped cream, blood, paint and nail polish.

Example for shear thinning fluid: Shampoo, ketchup.

7. RHEOLOGY IN FACE CLEANSER[31,32]

Face cleansers that contain surfactants and rheology modifiers, polymer chain and micellar network exhibit shear-thinning behavior meaning their viscosity decreases by increasing shear rate. This property resists flow under static condition and reorganizes under application of shear stress. There will be a decrease in viscosity as shear rate increases. Face cleansers responds dynamically to mechanical forces like pouring, squeezing and rubbing etc. At rest face cleanser will have a high viscosity. This increase in viscosity helps in enhancing the physical stability of the face cleanser by reducing the separation of the phases and prevents formation of sedimentation of suspended particles. This property also helps in maintaining uniform appearance and consistency during storage and improves product retention on skin while applying.

Upon application of shear during dispensing the product or topical application the internal structure of the cleanser undergoes a reversible breakdown, that helps in transforming the cleanser into a fluid state. Alignment and disentanglement of polymer chains, reorientation of micellar networks formed by surfactants undergoes this reversible breakdown. This results in decrease of viscosity that helps in easy spreading and better skin coverage.

Choosing correct rheological modifiers is very critical in formulating face cleansers as they control flow behavior, viscosity and texture of the product. They influence in the thickness of the face cleanser and also impart non Newtonian behavior.

Choosing right rheology modifier[33]

- **Product type:** A lightweight serum requires a thickener different from that of rich body butter.
- **Formulation stability:** Consider the pH, ionic strength, and interactions with other ingredients.
- **Desired sensory experience:** For example, Carbomer 940 creates a light, non-greasy feel, while PEG-120 Methyl Glucose Dioleate adds a silky, luxurious texture.
- **Regulatory requirements:** Ensure compliance with local and international regulations, especially for natural and "clean beauty" products.

Sensory evaluation like visual and tactile cues, cleansing performance and skin perception indicates that rheology modifiers plays an important role in defining the textural attributes of facial cleansers, particularly influencing viscosity, spreadability, and residual skin feel after application. These all are critical factors governing consumer acceptance.[34]

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