REVIEW ARTICLE

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Surfactant: Properties and applications

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ABSTRACT: Surfactants are surface-active compounds capable of reducing surface and interfacial tension at the interfaces between liquids, solids and gases, thereby allowing them to mix or disperse readily as emulsions in water or other liquids; therefore it forms a distinctive class of chemical compounds in pharmaceutical world. Surfactants are unique due to its nature and physical properties and their ability to drastically modify surface and interfacial properties. They self-associate and solubilize themselves in form of micelles and also associate as mixtures of oppositely charged surfactants, so called catanionic mixtures to form several different types of surfactant aggregates of various forms and sizes such as lamellar structures, or as vesicles. This article reviews about the surfactants, their basics explaining the mechanism to form micelles and its applications related to various site of action.

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INTRODUCTIONS:

Surface chemistry deals with the behavior of matter where such behavior is determined largely by forces acting on the surfaces. When phases exist together, the boundary between two of them is termed as interface. Several types of interface can exist depending on whether the adjacent phases are in the solid, liquid or gaseous state. The term surface is customarily used when referring to either a gas-solid or a gas-liquid interface. Every surface is an interface. Interfacial phenomena in pharmacy and medicine are significant factors that affect absorption of drugs onto solid adjuncts in dosage forms, penetration of molecules through biologic membranes, emulsion formation and stability, and the dispersion of insoluble particles in liquid media

to form suspensions. When a water droplet is in the air, surface tension, a force to reduce the surface area acts on the surface of the water, resulting in spherical water droplets or when water and oil are present in a container, they do not mix together even after stirring and separate into two layers [1]. When two immiscible substances are in contact, the contact surface is called interface. Interfacial tension, a kind of surface tension acts on the interface so that the two substances separate from each other. As interfacial tension increases, the force to separate two substances becomes stronger. Surfactant weakens interfacial tension and changes the properties of an interface.

Surfactants are compounds that lower the surface tension of a liquid, the interfacial tension between two liquids, or that between a liquid and a solid. They are wetting agents that lower the surface tension of a liquid, allowing easier spreading, and can also lower the interfacial tension between two liquids. The term surfactant was coined by Antara Products in 1950. Surfactants are usually organic compounds that are amphipathic, as they contain both hydrophobic groups ("tails") and hydrophilic groups ("heads"). Therefore, they are soluble in both organic solvents and water. Surfactants are indicated by the presence of both polar and non polar region. Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Therefore, a surfactant molecule contains both a water insoluble and a water soluble component (Fig 1).

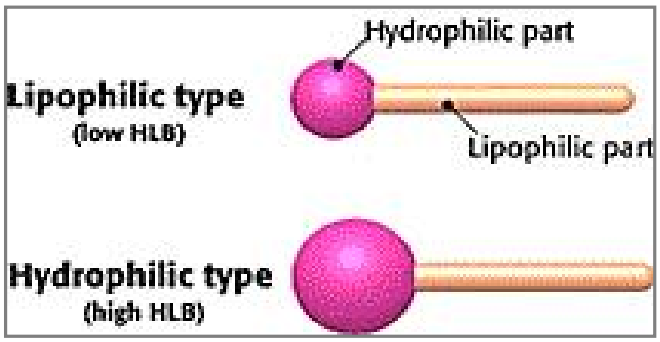

Fig 1. Hydrophilic and lipophilic part of a surfactant molecule.

When a surfactant is added to a mixture of water and oil, it is arranged on the interface, anchoring its hydrophilic part into water and its lipophilic part into oil. On the interface surface of water and air and of oil and air, the hydrophilic part and the lipophilic part are adsorbed and arranged around the interface. The interfacial tension is reduced by the emulsifier. That is, the force to separate the oil and water is thus weakened, resulting in the easily mixing of oil and water [2]. The interfacial properties of a surface active agent can also be seen in human body e.g. surfactants are found in the lining of alveoli of the lung and are responsible for the efficient operation of the organ. This surface tension in the surface is defined as the force per unit length that must be applied parallel to the surface so as to counterbalance the net inward pull. This surface tension has units of dyne/cm in the cgs system. Interfacial tension is the force per unit length existing at the interface between two immiscible liquid phases and, like surface tension, the units are dyne/cm. Interfacial tensions are less than surface tensions because the adhesive forces between two liquid phases forming an interface are greater than when a liquid and gas phase exist together. It follows that if two liquids are completely miscible; no interfacial tension exists between them. The formation of a liquid surface involves a surface free energy change. The surface free energy, which is defined as the work or energy required to increase the surface area by one unit. The units for surface free energy are milli joules/ m^2.

Micelle:

Surfactants adsorb preferably at interfaces where they find the energetically most favorable conditions due to their two-part structure. At a water surface, for example, the surfactants orient themselves in such a way that the head group resides in the water and the hydrocarbon chain points to the gaseous phase (see figure 2). Thus surfactants can "mediate" between two phases as they can form strong interactions with both of them. Because a surfactant has opposite properties; hydrophilic and lipophilic, its solution does not become a simple aqueous solution but a colloidal solution, of which properties greatly vary depending on its concentration.

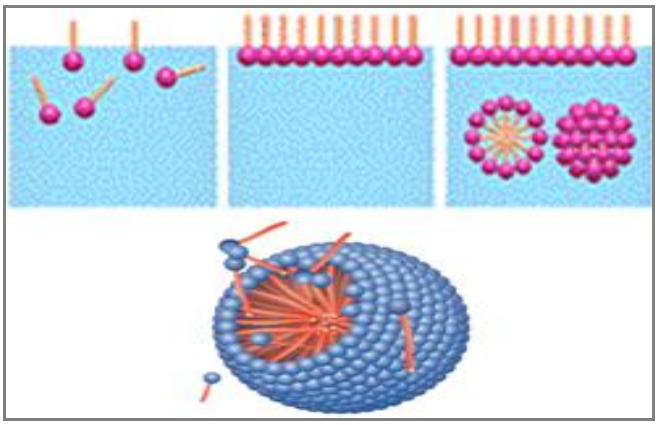

Fig 2. Micelle formation.

Mechanism of Micelle formation [3]***:***

- In an extremely-diluted solution, there is no special change, but the emulsifier gathers on the interface and the surface tension is reduced as an increase of its concentration.
- As further increase of the concentration, a uniform mono molecular layer is made on the surface and the surface tension drops to the minimum.
- A further increase of the concentration causes micelle formation, micelles formation occurs when the excess molecules, in which the lipophilic groups are positioned face to face, gather and there is no change in the surface tension.
- The concentration to start micelle formation is called critical micelle concentration (CMC) and the properties of the solution change greatly with a change of this concentration.
- When the concentration exceeds CMC (Fig 3), spherical micelles appear at first and disperse into water.
- A further increase in the concentration causes rod-shape micelles. Finally, lamellar micelles with higher structures called liquid crystal are produced.

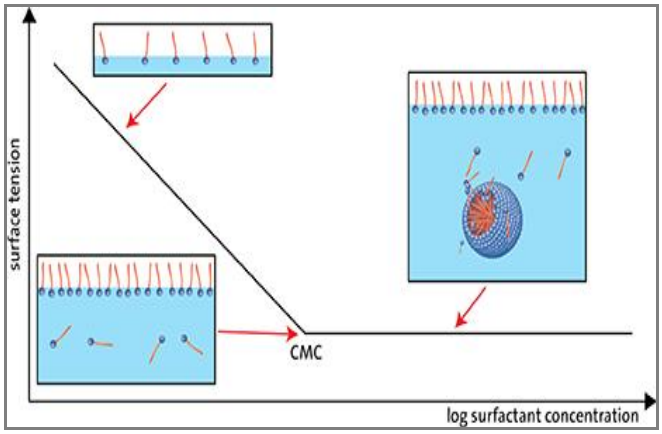

Fig 3. Critical micelle concentration graph.

Solubilization:

Solubilisation is the process of preparation of thermodynamically stable isotropic solution of a substance (normally insoluble or sparingly soluble in a given solvent) by incorporation of an additional amphiphilic component(s). It is the incorporation of the compound (referred to as solubilisate or substrate) within micellar or reverse micellar system. Lipophilic (water insoluble) substances become incorporated in the normal micelle phase. The site of incorporation of the solubilisate is closely related to its structure, as illustrated in Fig 4.

Process of solubilization can be divided into following steps such are a) Breaking of inter-ionic or inter–molecular bonds in the solute, b) Separation of solute molecules to provide space for the solute and c) Interaction between the solvent and solute molecule or ion - i) Molecules of solids break away from bulk, ii) Separation of solvent molecules and iii) Freed solid molecules is integrated into the holes of solvent molecule.

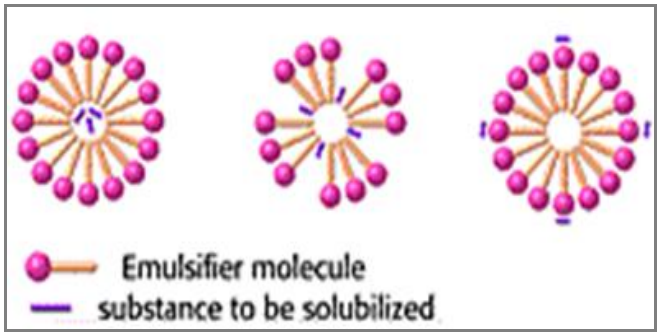

Fig 4. Solubilization Model.

Solid monoglyceride has a large capacity of crystallization which affects its performance. It also makes a liquid crystal which has intermediate characteristics between solid crystal and liquid. The form varies with the kind of emulsifier, temperature and its concentration. In practical use, it is necessary to select a suitable surfactant with consideration to conditions, including temperature and present constituents. The point is how surfactant binds with water and disperses in it, but it is difficult to predict the results based on an equation. In actual use, to predict the results based on the empirical rule is most desirable as well as information on the surfactant [4].

Manufacturer:

The glycerides used to make surfactants contain saturated and unsaturated carboxylic acids which have an even number of carbon atoms, generally within the range 12-20, for example, octadecanoic acid (stearic acid), $CH_3(CH_2)_{16}CO_2H$. Synthetic surfactants have one very important advantage over soaps. Because soaps form insoluble calcium and magnesium salts with the calcium and magnesium ions in hard water and in the clays which are present in dirt, much of the soap is wasted forming an insoluble scum. However, this is avoided when using a synthetic surfactant. For example, in the anionic surfactants, the carboxylate group in soap is replaced by a sulfonate or sulfate group as the hydrophilic component. The corresponding calcium and magnesium salts of carboxylic acids [5].

Classification of Surfactants [5]:

Ionic surfactant:

I. Anionic: based on permanent anions;

a. Sulfates: Alkyl sulfates: ammonium lauryl sulfate, sodium lauryl sulfate (SDS, sodium dodecyl sulfate, another name for the compound).

b. Sulfonates: Docusates: dioctyl sodium sulfosuccinate.

c. Phosphates: Alkyl aryl ether phosphate.

d. Carboxylates: Alkyl carboxylates: Fatty acid salts (soaps): sodium stearate.

II. Cationic: based on:

a. pH-dependent primary, secondary or tertiary amines: primary amines become positively charged at pH < 10, secondary amines become charged at pH < 4. E.g. Octenidine dihydrochloride.

b. Permanently charged quaternary ammonium cation;

i. Alkyltrimethylammonium salts: cetyl trimethylammonium bromide (CTAB).

ii. Benzalkonium chloride (BAC).

III. Zwitterionic (amphoteric): based on primary, secondary or tertiary amines or quaternary ammonium cation with:

a. Sulfonates: CHAPS (3-[(3-Cholamidopropyl) dimethylammonio]-1-propanesulfonate).

b. Carboxylates: Amino acids.

c. Phosphates: lecithin.

Non Ionic surfactant:

I. Polyoxyethylene glycol alkyl ethers (Brij).

II. Glucoside alkyl ethers.

a. Lauryl glucoside.

III. Sorbitan alkyl esters: Span.

IV. Glycerol alkyl esters - Glyceryl laurate.

V. Polyoxyethylene glycol sorbitan alkyl esters: Polysorbates (Tween).

VI. Octylphenoxypolyethoxyethanol (Igepal).

VII. Fatty alcohol

a. Cetyl alcohol.

b. Stearyl alcohol.

HLB (HYDROPHILIC-LIPOPHILIC BALANCE):

The Hydrophilic-lipophilic balance of a surfactant is a measure of the degree to which it is hydrophilic or lipophilic, determined by calculating values for the different regions of the molecule (Fig 5). There are various methods to calculate HLB value of a surfactant, some are as follows:

Griffin's method: Griffin's method for non-ionic surfactants as described in 1954 works as follows:

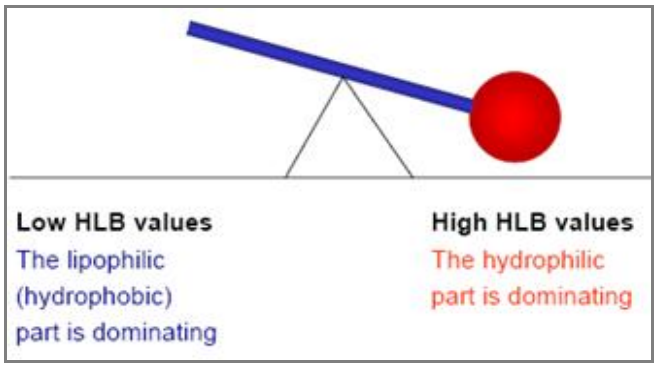

Fig 5. HLB value of surfactants.

$HLB = (20 \times M_h)/M$ …… (1)

Where, M_h is the molecular mass of the hydrophilic portion of the Molecule, and M is the molecular mass of the whole molecule, giving a result on an arbitrary scale of 0 to 20. An HLB value of 0 corresponds to a completely hydrophobic molecule, and a value of 20 would correspond to a molecule made up completely of hydrophilic components [6].

Davies'method: In 1957, Davies suggested a method based on calculating a value based on the chemical groups of the molecule. The advantage of this method is that it takes into account the effect of strongly and less strongly hydrophilic groups [7]. The method works as follows:

$HLB = 7 + m \times H_h - n \times H_l$ …….(2)

Where, m is the number of hydrophilic groups in the molecule, H_h is the value of the hydrophilic groups, n is the number of lipophilic groups in the molecule and H_l is the value of the lipophilic groups.

A surfactant with higher lipophilicity shows a lower HLB whereas higher hydrophilicity has high HLB, and the behaviors and functions to water depend on this HLB [6]. The value ranges from 0 to 20 as shown in Table 1.

PROPERTIES OF SURFACTANT:

Emulsification:

Oil and water produce emulsion by stirring; however, the emulsion starts to break down immediately after stirring is stopped. The aim of emulsification is to stabilize emulsion by preventing break down. The breakdown of emulsion occurs due to creaming, aggregation and coalescence. To solve this, several measures have been taken, to decrease the size of dispersed particles, to reduce the density difference of dispersion and to protect the surface of oil droplets [8]. There are two types of emulsion, O/W emulsion or oil droplets in water and W/O emulsion or water droplets in oil.

Table 1. HLB scale of various surfectants.

Characteristic behaviors related to water	HLB	Ratio		Functions	
		Hydrophilic part	Lipophilic part		
Not dispersing	0	0	100	Anti-foaming agent	
	2	10	90		
Slightly dispersing	4	20	80	Wetting agent	W/O emulsification
	6	30	70		
Milky dispersion	8	40	60		
Stable milky dispersion	10	50	50		
Transparent dispersion	12	60	40		O/W emulsification
	14	70	30	Cleaning agent	
	16	80	20	Solubilizing agent	
Colloidal solution	18	90	10		
	20	100	0		

For production of both types of emulsions surfactants are necessarily included in their formulas.

Recently, developments of W/O/W type emulsion within oil droplets of O/W type emulsion and O/W/O type, an opposite type emulsion have been progressing [9].

Dispersion:

Water-insoluble fine powder like cocoa is difficult to disperse as small lumps tends form on the surface interface. Powders gradually aggregate and precipitate even if dispersed by shaking. Maintaing suspension of such water insoluble fine powder is called dispersion. (When the dispersing material is liquid, we call it emulsion). Surfactant adsorbed on the surface of insoluble fine powder changes the particle surface to be hydrophilic or lipophilic. The results of which produce stable water or fats and oils at the outer layer and stabilize suspension, by increasing the affinity to water or oil in the outer phase [10].

Foaming:

Foaming ability is one of the major characteristics of surfactants. When a solution containing a surfactant is stirred, the surfactant is adsorbed on the surface of the produced foam to make a mono-molecular layer and the foam outside of the solution makes a bimolecular layer of the surfactant. The film surrounding a soap bubble is about 100 times thicker than a bimolecular layer, but a bubble breaks as soon as the migration of the liquid trapped between bimolecular films occurs. The foaming effects are utilized for the production of such items as cream. Thus, smooth texture can be obtained as well as expanded volume[11].

Defoaming:

Surfactant also has form extinguishers; one is called anti-foaming and the other de-foaming. A surfactant with foam extinguishing action is used. Foam extinguish have the following properties; that are water insoluble, floatable on the surface because of its small specific gravity and small surface tension and easy spreading on liquid surface. These properties easy lower the surface tension and so, the foam becomes thinner. As these agents spread easily on the liquid surface, all foam can be diminished. These are used in the fermentation industry [12].

Wetting:

Wetting agents means spreading of a liquid over a solid surface. (Solid material is mixed with a surfactant is spread with it, the surface then becomes hydrophilic). Wetting is expressed as contact angle between the tangent to the surface of a drop and the solid surface [13]. For example, if a drop of water placed on a clean glass surface it covers the surface as a thin film, it indicates complete wetting. On the other hand if a drop of mercury is placed on a glass surface it tends to remain as a drop without any wetting of the glass surface (Fig 6).

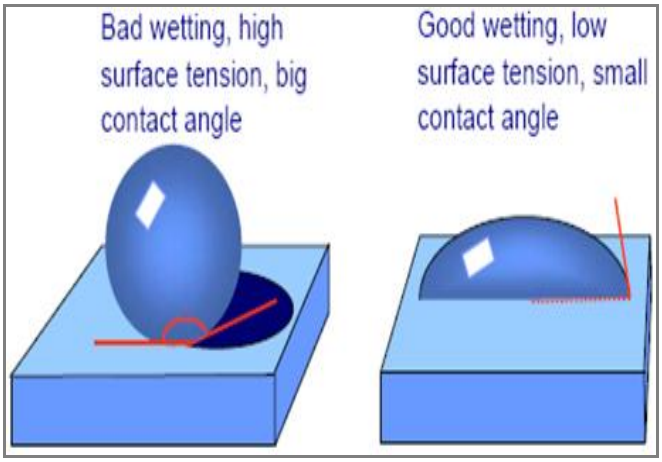

Fig 6. Contact angle showing good and bad wetting.

Chewing gum is apt to stick to teeth - Adhesion to natural teeth does not occur easily because the enamel is hydrophilic and always wet, whereas the adhesion to artificial teeth, occurs easily. We can prevent adhesion by wetting the surface of chewing gum by adding emulsifier [14].

Bacteriostatic effects:

Ionic surfactants are adsorbed on the cell surface by electrostatic interaction. As a result the cell surface loses its integrity and the essential materials are lost through the leaks. Thus antibacterial action is produced. Examples are quaternary ammonium compounds. Monoglycerides, polyglycerol esters of low molecular fatty acid have specific bacteriostatic effects, which can be use as a bacteriostatic agent [15].

APPLICATIONS OF SURFACTANTS:

Emulsifiers, wetting agents, foaming agents, collecting agents - there are a vast number of names for surfactants depending on the areas in which they are used. Surfactants reduce the surface tension or interfacial tension with respect to an adjacent phase and therefore lie at the heart of interfacial chemistry.

With decades of experience in tensiometry, contact angle measurement and foam analysis, we make an important contribution to surfactant research and development. Our measuring methods reflect process conditions such as temperature, pressure and speed or the type of wetting process. Our products enable the use of surfactants to be optimized for the particular application [16].

Formulation of Suspension (Dispersants):

If the suspension is to be produced by a dispersion technique (as opposed to precipitation techniques), surfactants may be used in the formulation to aid dispersion of the solid particles in the liquid. This is particularly important if the powder is not readily wetted by the liquid vehicle. Surfactants can reduce the interfacial tension between the solid particles and the liquid vehicle. The advancing contact angle is reduced, and wetting of the solid particles promoted. Such a system is said to be deflocculated. The inclusion of a surface-active agent to improve powder wettability can often improve the bioavailability of the formulation. The forces at the surface of a particle affect the degree of flocculation and agglomeration in a suspension. Particles dispersed in a liquid medium may become charged in one of two main ways. Ionic species present in solution may be adsorbed at the surface or, alternatively charges on the surface may arise due to ionization of groups (such as carboxyl groups for example) which may be located at the surface. The surface charge will influence the distribution of ions in the aqueous medium surrounding the solid particles [17].

The result is the formation of what is known as an ‘‘electric double layer.’’ If the surface charge is positive, immediately adjacent to the surface will be a region of tightly bound solvent molecules and negative counter ions. Thus, the first layer is tightly bound, while the second layer (which still contains an excess of negative ions) is more diffuse. As two particles approach each other in aqueous medium, a weak attractive force exists just beyond the range of the double layer- repulsive forces. This region is responsible for the particle interaction termed ‘‘flocculation’’ [18].

Formulation of Emulsions:

In surfactants, the lipophilic protein of the molecule generally accounting for the surface activity of the molecule. Owing to their opposing ionic charges, anionic and cationic agents tend to neutralize each other if present in the same system and are thus considered incompatible with one another.

Depending upon their individual nature certain members of these groups form o/w emulsions and others w/o emulsions. Anionic emulsifiers include various monovalent, poplyvalent, and organic soaps such as triethanolamine oleate and sulfonate such as sodium lauryl sulfate, benzalkonium type of emulsifier. Agents of the nonionic type include sorbiton esters and the polyoxtetylene derivatives. The ionic nature of the surfactant is of prime consideration in the selection of a surfactant to utilize in forming an emulsion. Non ionic surfactants are effective over pH range 3 to 10, cationic surfactants are effective over pH range 3 to 7, and anionic surfactants require a pH of greater than 8. A hydrophilic Tween can be combined with a lipophilic Span surfactant at varying proportions so as to produce the desired o/w or w/o emulsion .Boyd et al discussed the molecular association of Tween 40 and Span 80 in stabilizing the emulsions. If the hydrocarbon portion of the Span 80 (sorbiton mono oleate) molecule lies in the oil globule, the sorbiton radical lies in the aqueous phase. The bulky sorbiton heads of the Span molecule prevent the hydrocarbon tails from associating closely in the oil phase. When Tween 40 (polyoxyethylene sorbiton monopalmitate) is added, it orients at the interface such that part of its hydrocarbon tail is in the oil phase, and the reminder of the chain, together with the sorbiton ring and the polyoxyethylene chains, is located in the water phase. It is observed that the hydrocarbon chain of the Tween 40 molecule is situated in the oil globule between the Span 80 chains, and this orientation results in effective van der waals attraction. In this manner the interfacial film is strengthened and the stability of the o/w emulsion is increased against particle coalescence [19].

Formulation of Aerosols:

Surfactants are found in both solution and suspension formulations of metered dose inhalers (MDIs). The most common surfactants found in pressurized aerosol preparations include sorbitan trioleate (Span 85), oleic acid, and lecithins at concentrations of 0.1–2.0% (w/w). These agents are non-volatile liquids which dissolve in

the propellant blend. Their function in the formulation is to provide lubrication for the metering valves and, in the case of suspension formulations, to maintain the disperse nature of the drug.

The three surfactants commonly used in chlorofluorocarbon (CFC)-based MDI formulations are insoluble in the CFC-replacement propellants, hydrofluoroalkane (HFA) 134a and HFA 227. Possible formulation alternatives involve the use of an adjuvant such as ethanol to aid dissolution of the surfactant or a novel surfactant. Several companies have investigated novel materials among which are fluorosurfactants, polyoxyethylenes and drugs coated with surfactant [20].

Formulation of Ointments:

Ointments are semisolid preparation meant for external application to skin or mucous membrane; they usually contain medicaments or medicaments in dissolved, suspended or emulsified in an ointment base. Sometimes in the ointment preparation surfactants are useful for the easy removal from the skin by washing with water & also for the consistency by reduction of surface tension. Surfactants are also used in formulation of cold cream, cleansing cream, vanishing cream, shaving cream or any media [21].

Formulation of Shampoo:

Shampoo is a hair care product used for the removal of oils, dirt, skin particles, dandruff, environmental pollutants and other contaminant particles that gradually build up in hair. The goal is to remove the unwanted build-up without stripping out so much as to make hair unmanageable. Shampoo, when lathered with water, is a surfactant, which, while cleaning the hair and scalp, can remove the natural oils (sebum) which lubricate the hair shaft [22].

Hard Gelatin Capsules and Tablets Wetting agents:

Surfactants are used in capsule and tablet formulations as wetting agents to aid dissolution.

Lubricants, anti-adherents, and glidants:

The primary function of tablet lubricants is to reduce the friction arising at the interface of tablet and die walls during compression and ejection. Lubricants also possess antiadherent (prevention of sticking to the punch and, to a lesser extent, to the die wall) and glidant (improvement of flow characteristics of powders or granulates) characteristics and are useful in the processing of hard gelatin capsules. Magnesium stearate is used extensively as a lubricant in tablet manufacture. It is an example of a ‘‘boundary lubricant,’’ that is, the polar regions of the molecule adhere to the metal surface of the die wall (in tablet manufacture). Adsorption of magnesium stearate to the powder or granule surfaces also prevents agglomeration of the feed material and aids flow. Lubricants may be classified as water-soluble or water-insoluble. The latter are generally more effective than water-soluble lubricants and can be used at a lower concentration. Common water-insoluble lubricants (which are surfactants) include magnesium stearate, calcium stearate, sodium stearate, and stearic acid; water-soluble lubricants include sodium lauryl sulphate and magnesium lauryl sulphate. Sodium lauryl sulphate is used in the production of hard gelatin capsules where it is added to the gelatin solution during the preparation stage. The stainless steel molds are lubricated prior to dipping into the gelatin solution and sodium lauryl sulphate is added to reduce the surface tension of the mix and cause the mold pins to wet more uniformly [23].

Suppositories:

Several non-ionic surface-active materials have been developed as suppositories vehicles. Many of these bases, known as water-dispersible bases, can be used for the formulation of both water-soluble and oilsoluble drugs. The surfactants most commonly used are thepolyoxyethylene sorbitan fatty acid esters (Tweens), the polyoxyethylene stearates, and the sorbitan fatty acidesters (Spans). These surfactants may be used alone, blended, or with other suppository base materials to yield a wide range of melting points and consistencies [24].

Surfactants as Laxatives and Spermicides:

Disodium octyl sulfosuccinate the long term use is laxative. The mechanism of this action has not been fully explained. Certain non-ionic ethers or nonyl- and octyl phenol are widely used as spermicides in concentration. ranging as high as about 5 %. The spermicidal action of these non-ionic ethers probably by their ability to distrup vible membranes or ability to dissociate lipids from lipoproteins. Since mucous membrane of vaginal membrane are not damaged by presence of nonoxynols or octoxynols [25].

Surfactants as enhancers for percutaneous absorption:

The transport of molecules through the skin can be increased by the use of certain adjuvant known as enhancers. Ionic surfactants enhance transdermal absorption by disordering the lipid layer of the stratum corneum and by denaturation of keratin. Enhancers may

increase drug penetration by causing the stratum corneum to swell and/or leach out some of the structural components, thus reducing the diffusional resistance and increasing the permeability of the skin . The poor permeability of the skin is due to the ordered layer of intercellular lipids and to low water content. Proteins in keratinized tissue are rich in cysteine residues, and the strong disulfide bonds may be the reason for the insoluble nature of this protein. The reducing agents cause a decrease in the number of disulfide bridges, thus increasing the hydration of the proteins, which results in increased skin permeability [25].

Surfactants used in transdermal penetration of drugs:

The permeability of a drug depends on the hydration of the stratum corneum. The higher the hydration, greater the permeability. The dermal tissue is fully hydrated, while the concentration of water in the stratum corneum is much lower, depending on ambient conditions. Hydration may promote the passage of drugs in the following way. Water associate through hydrogen bonding with the polar head groups of the lipid bilayers present in the intercellular spaces. The formation of a hydrogen shell loosens the lipid packing so that the bilayer region becomes more fluid. This facilitates the migration of drugs across the stratum corneum. From the rate of transpiration (passage of water from inner layers to the stratum corneum) and diffusivity of water in the stratum corneum, the amount of water in the tissue can be obtained. Surfactants help in increasing the hydration of the skin and thus increase the penetration of the drug through skin layers [25].

CONCLUSION:

Surfactants are smart chemicals that may be completely invisible to us most of the time but which benefit our lives in many different ways. They can be produced from either synthetic or natural raw materials and their versatility makes them key to both the quality of modern life and pharmaceutical industries. Surfactants are special is their ability to mobilize and combine materials - typically water, oils, fats and solvents - that otherwise would not mix due to their incompatible molecular properties.

They are also used to formulate compounds sparingly soluble in water. Polymeric micelles made by surfactants have a whole set of unique characteristics, which make them a very promising drug carriers for a wide range of drugs.

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