**Chapter 1**

**Introduction**

*Sustainable development is the ongoing trend in all the fields for the better life of the human being through the safe environmental aspects. The industrial development will get stuck up in one phase if it fails to have the eco-friendliness considerations.*

The surfactant industry has broadened its horizon as its day to day applications have increased inevitably. At present “eco - friendly green surfactants” is the driving force for the ongoing developments and researches in the surfactant kingdom. The alkyl polyglucosides which are shortly known as APGs are the one among the best known eco - friendly green surfactants. Even though APGs originated in the eighteenth century, their industrial utilization has attained a new stage only about 20 years ago [Geetha and Tyagi (2012)]. The APGs have been first synthesized and introduced in the literature in the year 1893 by the German scientist Emil Fischer. After 40 years, the first patent application was filed in Germany [Balzer (1993)].

**1.1 Surfactants the amphiphiles**

The term surfactant was framed by Antara Products in 1950. Surfactants are one of the most pervasive and important family of organic compounds. Surfactants in different formulations are being used in almost all industries like cosmetic, personal care, household, painting, coating, textile, polymer, dyes, foodstuff, agrochemical, oils and also in bioremediation [Santonicola et al. (2008)]. The surfactants - the surface active agents are not only concerned with cleaning operations, but also extended their applications to other technological areas such as pharmaceuticals, petroleum recovery processes, and food industries. Surfactant compounds attain their uniqueness due to its amphipathicity: having water-loving hydrophilic head as well as oil-
loving hydrophobic tail. Consequently, the surfactant can be dissolved either in water or oil and have the capacity to solubilize water-in-oil or vice-versa [Rosen (2004)].

1.1.1 A brief history of surfactants

A brief summary of the surfactants development started with soap, whose manufacture was delineated by the Sumerians as long ago as 2500 B.C (an early Mediterranean civilization) [Cirelli et al. (2008)]. Soaps remained an expensive luxury until French Chemist Nicolas Leblanc (1742-1806) found a cheaper way of making them using salt. In 1916, German Chemist Franz Gunther developed the first surfactant for detergents from coal tar. The detergent based surfactants were introduced in the United States during 1930s. Thereafter, synthetic detergents (alkyl sulfates & alkyl benzene sulfonates) were developed to counter soap shortages caused by World War II and soon surpassed traditional soap. The increased concern about water pollution in the early 1960’s and environmental protection laws to forbid the use of propylene-based alkylate in USA and Europe resulted in the development of the biodegradable surfactants.

Global trend in surfactants

Now, the global surfactants market strategies are estimated to register a compound annual growth rate (CAGR) of 5.40% by volume, and 5.80% by value from 2014 to 2019. The global surfactants market is projected to reach 22,802 kilotons by volume and $40,286 million by 2019. Asia-Pacific is estimated to be the largest consumer of surfactants, followed by North America and Europe. Global demand for anionic surfactants was approximately 6.5 million tons in 2010. Anionic and non-ionic surfactants combined account for roughly 85% of global demand for surfactants [Ceresana (2014)]. The non-ionic surfactants are expected to see the strongest growth between 2010 and 2018. Despite this global trend towards nonionic surfactants, anionic
surfactants will remain the second largest product group, especially in Africa, the Middle East, and Asian countries, with the exception of Japan and South Korea. The volatile petroleum prices and environmental concerns are restraints for the synthetic surfactants. On the other hand, the bio-based surfactant market is in its initial stages of growth with the technical constraints such as their higher prices when compared to synthetic surfactants and unskilled workforce. The overall surfactants market has been fragmented and no clear global market leader has emerged. However, few top players include Akzo Nobel N.V. (The Netherlands), BASF SE (Germany), Henkel (Germany), and The Dow Chemical Company (U.S.). BASF, the world’s largest manufacturer of APG surfactants, currently uses a one-step process for making APGs by reacting fatty alcohol directly with glucose. BASF markets their APGs for personal care under the Plantaren name and produces them at plants in Dusseldorf, Germany, Cincinnati, USA and Jinshan, China. Europe dominates the global APGs market and the trend is expected to continue during the forecast period. North America is the second largest market for APGs and it is expected to be the fastest growing region for alkyl polyglucosides market for the next six years. Despite the skin and environmental benefits of APGs, it remains a challenge to convince some formulators to replace the conventional petroleum based surfactants as a low cost material. India and China are the fastest growing economies in Asia pacific in terms of GDP growth and purchase power parity. Increasing awareness of hazards associated with the conventional non-biodegradable surfactants coupled with increasing disposable income in Asia Pacific is expected to offer huge growth opportunity for APGs market in the near future [Ceresana (2014)].

1.1.2 Working mechanism of surfactants
The working of the surfactants can be covered by three steps, viz. surface tension reduction by adsorption at the surface, formation of micelles by surface saturation and micelle growth at equilibrium. As the nature favor the reduction of free energy, surfactant works to reduce the free energy of the surface or interface (interfacial free energy) by adsorbing themselves on the surface or interface. The surface tension of water is equivalent to the interfacial free energy per unit area of the boundary between water and the air above it [Hill (2000)]. When the surfactant is dissolved in water, the surfactant molecule orient themselves as the polar hydrophilic head, keep a contact with water and the non-polar tail form a core with oil [Rosen (2004) and Holmberg (2003)]. The head group repulsion is responsible for minimizing the unfavorable water/hydrophobic tail contact and thus bringing the head group into close proximity. The strength of head group repulsion depends on the nature of the surfactant. In the case of an ionic surfactants, each of the droplets will be charged (-ve for anionic; +ve for cationic). The droplet coalescence is restricted by the electrostatic stabilization (like charges repel). In the case of nonionic surfactants, the polymeric head chains act as little springs that push off other droplets, stopping them from coalescing by steric stabilization [Mishra et al. (2009)].

The non-polar hydrophobic tail interacts with water molecule by weak van der Waals force of attraction whereas, the polar hydrophilic head group is attracted by dipole-dipole or ion-dipole interactions. Moreover, the much weaker Vander Waals force of attraction breaks the much stronger hydrogen bonds between water molecules. Thus, the surfactants are forced to the interfaces of the system, where the hydrophobic tails get oriented in a way to keep minimum contact with water (hydrophobic effect) [Rosen (2004)]. All the four types of surfactants viz. anionic, nonionic, cationic and amphoteric have been evaluated primarily on the basis of their ability to reduce surface tension with minimum critical micelle concentration i.e., the
concentration at which surfactant aggregation occur. The degree of surfactant concentration at a boundary that is the strength of the adsorption depends upon the surfactant structure and other factors as follows: [Myers (2006)]

i. The chemical nature of the species being adsorbed, including the nature of the head group *viz.* anionic, cationic, nonionic and zwitterionic, the length, nature of the chain and the degree of branching of the hydrophobic chain.

ii. The nature of the solid surface onto which the surfactant is being adsorbed (highly charged, non-polar, etc.).

iii. The nature of the liquid environment (in water, the pH, electrolyte content, temperature, additives, *etc.*).

All the efficient functions of surfactants start with the micelles. During micellization, there is a gain in entropy ($\Delta S = \text{positive}$) by the release of structured water molecules which are surrounding the monomeric surfactant molecule (hydrophobic hydration) [Rosen (2004)]. Surfactants have the remarkable ability to radically alter surface and interfacial properties and to self-associate and solubilize themselves as micelles[Rosen (2004)]. Moreover, all the characteristic functions of surfactants such as detergency have been covered by the following three different mechanisms [Mishra et al. (2009)]:

i. Roll-up mechanism: The surfactant lowers the interfacial tension of oil/solution and fabric/solution interfaces and lifts the stain or oil as ball.

ii. Emulsification: The surfactant lowers the interfacial tension of the oil solution and makes easy emulsification of the oil.
iii. Solubilization: The surfactant interacts with the oil substance with the micelles, dissolve the substance and form a stable and clear solution.

Among these three mechanisms, the solubilization and emulsification are major factors in removal of oily soils from hydrophobic, synthetic fabrics. Unlike roll-up, in which the interaction of the fabric with the oily soil and water is most critical, the solubilization-emulsification mechanism occurs primarily at the soil-detergent solution interface and is therefore directly influenced by the phase behavior of the corresponding oil-water surfactant system.

1.1.3 Types of surfactants

The surfactants are mainly classified into four categories on the basis of the charge of the polar head group and based on their dissociation in water as follows [Rosen (2004)]:

i. Anionic Surfactants e.g., Sodium dodecyl sulfate

\[
\text{Na}^+ \text{S} \text{O}_3^- \text{O} \text{C} \text{H}_{2} \text{C} = \text{C} \text{H} \text{C} \text{H} \text{C} \text{H} \text{C} \text{H} \text{C} \text{H} \text{C} \text{H} \text{C} \text{H}_2 \text{OH}
\]

ii. Nonionic Surfactants e.g., Alkyl polyglucosides
iii. Cationic Surfactants e.g., Cetyl trimethylammonium bromide

iv. Zwitterionic Surfactants e.g., SulfoBetaine

1.1.4 Carbohydrate based surfactants

The awareness in environmental conservation and demand of natural products is increasing day by day. The postulated sustainable development of our civilization requires that the rate of depletion of non-renewable resources, such as fossil fuels and minerals should be slowed down. This means that humanity’s resource base must be conserved and enhanced [Holmberg (2003)].
In this context, biomass seems to be of great value as a feedstock for the chemical industry. The main constituents are mono and polysaccharides, which together make up three-fourths of the world’s biomass. Thus, the carbohydrate based surfactants have invoked increased interest over the last decades for several reasons viz. fundamental, practical, economical and environmental orders due to the following reasons [Hill (2000)]:

i. They can be prepared from the most abundant renewable vegetable biomass (cellulose, pectin, hemicelluloses, starch etc.) in a wide range of structure and geometry.

ii. The structural diversity (multi-functionality) makes them as an excellent model for getting insight into the surfactant mechanism in modifying interfacial properties.

iii. Their bio-compatibility to the environment makes them a valuable alternative to the petroleum based surfactants.

The carbohydrate based surfactants equivalently known as glycolipids [Hato et al. (2004)] are constituted by a saccharide unit (mono-, di-, oligo- or polysaccharide) linked to a hydrophobic part of one, two or multi hydrocarbon chains by a single or several bonds. These may be an ester, thio-ester, ether, amine or amide group [Stubenrauch (2001)]. Moreover, the carbohydrate moiety can be attached to a hydrophobic fragment, either by the oxygen atom (alkyl polyglucosides) or by nitrogen atom (N-alkylaldosyl-amines). It is estimated that about 400 billion tons of sugar is produced annually through natural photosynthesis, among them, cellulose takes first place (about 50 billion tons), and starch second [Razafindralambo et al. (2011)]. Their major advantage over petrochemical feedstock is that they do not pose significant hazards in terms of acute or chronic toxicity to human health and the environment. This is why glucose based alkyl polyglucosides seem to be novel, valuable, and gaining attention now-a-days by fulfilling the principles of green chemistry [Hill (2000)]. Also, it has recently been reported that
among 63 major classes of surfactants that are commercially available, 14 are based entirely on renewable materials and 21 are made from petrochemical and natural feedstock [Hill (2000)]. Furthermore, that report indicated that the growth of carbohydrate surfactant consumption in western Europe increased from about 20,000 tons in the early 1990s to 60,000 tons in 1997 [Ruiz (2011)]. Sorbien esters, sucrose esters, fatty acyl glucamides and alkyl polyglucosides are some of the carbohydrate based surfactants produced and used on an industrial scale.

1.1.5 Overview of alkyl polyglucosides

Alkyl polyglucosides (APGs), the polymeric acetals of glucose and fatty alcohols with structural formula \( H-(C_6H_{10})_m-O-C_{n+1}H_{2n+1}(n=10-16) \) are a non-ionic, highly effective carbohydrate–derived surfactants. The nomenclature used to describe the APGs is \( C_nDP_m \) where, \( n \)- number of carbon atoms in the alkyl chain and \( m \)- average number of glucoside units in the polar head group. Although APGs are undoubtedly a group of non-ionic surfactant, some authors claim that some electric charge remains on the APG molecule, due to the considerable hydration capacity of the cumulative OH group [He et al. (2007)]. Taking into account of their carbohydrate origin and other interesting interfacial properties, APGs have been gaining attention from research groups and in cross - category applications used primarily in the pharmaceutical, detergent, food, cosmetic industries and nano- sized delivery systems.
In practical applications, instead of the pure alkyl mono glycosides, a complex mixture of alkyl mono-, di-, tri- and oligo-glucosides have been used [Holmberg (2003)]. The products are characterized by alkyl chain length and the degree of polymerization (DP). Moreover, the APG products have a very complex spectrum, due to the presence of isomerism: stereoisomerism with α– and β- anomers (when the hydroxyl group on the glucose ring is axially oriented at carbon 1 an α– linkage will occur, linkage is formed when the hydroxyl group is equatorially oriented); linkage isomerism, where 1, 6- and 1, 4- inter glucoside linkages; and ring isomerism with pyranoside and furanoside forms. When the alkyl mono glucoside is considered, they have four isomeric forms, the di glucosides have about 30 isomeric forms and the tri glucosides have 64 isomeric forms. The isomeric forms will be extended even more if the glucoside is synthesized with branched oligo-saccharides [Balzer (1993)]. These structural variances increase the research possibility to invent the surfactant with desired properties. Interestingly, the anomers exhibit significant difference in their physical properties. For instance, the β-anomer is highly soluble in water than α–anomer due to the lower crystal energy of the α- form. Also, β-anomer generates larger foam volume and more stable foam compared to the α- anomer due to the slightly higher surface excess of the former one. APGs constitute a broad class of bio-surfactant and are categorized based on the chain length of fatty alcohol in their structure. Generally, the APGs are
classified as: small chain (C_4-C_8), medium chain (C_{10}-C_{12}) and long chain (C_{14}-C_{22}) [Holmberg (2003)].

Moreover, in the Asia Pacific, the naturally derived surfactants sectors currently make up approximately 10% of the total $600 million (Euro 413 million) worth world market of surfactants and is expected to increase by 4% each year, with the group of APG surfactants registering the strongest growth [Ceresana (2014)].

1.2 Synthesis of APGs

APGs have been synthesized by several laboratory methods such as the Koenigs-Knorr method [Bocker et al. (1989), DeGrip et al. (1979) and Vill et al. (1989)], the Lewis-acid method [Vill et al. (1989)] the Schmidt method, base catalyzed alkylation [Klotz et al. (2006)], enzymatically catalyzed synthesis [Vulfson et al. (1990)]. Fischer syntheses have been widely adopted even for industrial production of APGs, because of their ability to control the degree of polymerization of the product over a wide range and their emission free technology [Homberg (2003), Geetha and Tyagi (2012)]. Fischer proposed two important methods for APGs preparation viz. direct and indirect (transacetalization) synthesis which is given in Figure 1.2. These two methods can be conducted either in batches or continuously by using acid catalyst. In both the processes, stoichiometrically excess fatty alcohol has been used as the raw material in order to minimize the self- polymerization of sugar. As seen in Scheme 1.1 & Figure 1.3 the final product obtained is the mixture of glucoside and residual alcohol. Thus, it can create high pressures that impose more stringent demand on equipment and in turn it leads to higher plant cost. Figure 1.4 illustrates the APGs synthetic routes both from equipment as well as economic point of view. In the glucoside synthesis, a poly- functional sugar component is combined with a nucleophile i.e.,
alcohol. If a selective reaction with one of the hydroxyl groups of the carbohydrate is required, all other functional groups have to be protected in a first step. The necessary complicated chemical protection and de-protection steps for the region-selective synthesis of glucosides can be replaced by the use of suitable enzymes. But, the enzymatic synthesis of APGs on the industrial scale is still under process, due to the problem of availability of suitable catalyst to synthesize APGs in a cost-effective manner. Anyhow, β-glucosidase have been used as a catalyst in the synthesis of β-anomer, but only a low amount of product is obtained, the racemization yield relatively higher amount of α–glucoside product [Homberg (2001)]. Although synthetic routes of glucoside began in 1870, the researches related to the glucoside synthesis are still ongoing and several interesting routes have been developed in the recent past [El-Sukkary et al. (2008), Li et al. (2011), Geetha and Tyagi (2014) and Wang et al. (2012)].

1.2.1 Raw materials for the synthesis of APGs

The hydrophilic part of the APGs is derived from monomeric or polymeric carbohydrates and the hydrophobic part is derived either from natural or synthetic or blends of fatty alcohols [Geetha and Tyagi (2014)]. Carbohydrates can be derived from corn, wheat and potatoes. The alkyl chain length of APGs depends upon the raw material used such as, for C_{12/14} range coconut or palm kernel oils are used and tallow and rapeseed oil are used for the C_{16/18} range fatty alcohols.
Figure 1.2 General synthetic route for alkyl polyglucoside synthesis [Holmberg (2003)]
Scheme 1.1 Synthetic route of glucoside according to Fischer [Holmberg (2003)]

Figure 1.3 Mass balance of the glycosidation process [Hill (2000)]
1.2.2 Role of catalyst in APGs preparation

The acidic catalyst used in the APGs synthesis is to favor the reactions which involve the glucosidic bond [Wang et al. (2015) and Geetha and Tyagi (2014)]. The acids used for this purpose are H$_2$SO$_4$, HCl, H$_3$PO$_4$ or BF$_3$, sulfonic acids or their salts such as sulfonic resins, alkyl sulfates, alkyl benzene sulfates, alkyl sulfonates and sulfosuccinic acid. At the end of the process the acid catalyst is neutralized with a base such as sodium hydroxide (NaOH) [El-Sukkary et al. (2008), Geetha and Tyagi (2012) and Borsotti et al. (1996)]. A serious disadvantage common to all synthesis processes of alkyl polyglucoside is the formation of polyglucoside by-product [Quineau et al. (2008)]. The polyglucose formed leads to the formation of mixture of products and even in small percentage causes an increase in viscosity of the mixture, and in the meantime
it affect the product yield also [Quineau et al. (2008)]. As a result, the separation of the APGs, the recovery and recycling of alkylglucosides and non-reacted alcohols become difficult. The formation of polyglucose side product as well as the degree of polymerization has been controlled by the usage of high alcohol/glucose ratio, but this leads to the problem related to safety and over dimensioning of the APGs production plants. The catalyst usage influences the composition of the reaction product [Boge et al. (1998)]. The percentage of polyglucose obtained is more than 20% in the presence of $\text{H}_2\text{SO}_4$ as catalyst with a molar ratio alcohol / glucose of 2 to 1. In the presence of para-toluene sulfonic acid (PTSA) as catalyst, the percentage is reduced to about 11%. With alkaline alkyl sulfonates (or) aryl sulfonic acid as catalyst, this percentage is further reduced to 9.2% [Boge et al. (1998)]. The new group of sulfonic acid operating with a molar ratio alcohol/glucose of 5 to 1, enables to lower the polyglucose to 2.2% [Borsotti et al. (1996)]. However, this catalyst is very costly. Using a binary catalyst consisting of coupling a weak base and a strong organic acid, operating with a ratio alcohol / glucose of 5 to 1, the percentage of polyglucose becomes 0.7%.

1.2.3 Characterizations of APGs

Physico-chemical properties of APG products strongly depend on the molecular composition. The commercially available APGs are the complex mixtures of species differing in the degree of polymerization (DP) and in the length of alkyl chains [Billian et al. (1998)]. Therefore, detailed analytical investigations of the technical grade APGs are very important. The average number of glucose units linked to an alcohol group is described as the average degree of polymerization (DP). The DP of APG mixtures can be calculated from the mole percent $p_i$ of the respective oligomeric species in the glucoside mixture [Eichorn et al. (1999)].
where, $P_1$ & $P_2$ are the mole fraction of the respective oligomeric species.

The average DP is an important parameter in the determination of physical property like viscosity, polarity, solubility and the applications of APGs. The DP has been greatly controlled by the molecular ratio of glucose to fatty alcohol in the reaction mixture and by the selection of suitable acid catalyst for the APG synthesis. The greater the stoichiometrically excess fatty alcohol employed, the lesser will be the DP.

The commercial APGs generally constitute alkyl mono glucosides (50%), followed by the diglycosides and high oligomers up to heptaglucosides and this composition is mainly determined by the glucose to fatty alcohol ratio in the reaction mixture [Homberg (2003)]. Thus, the complexity of APGs formulations requires efficient analytical techniques for product development, product control, biodegradation, toxicity and environmental studies [Balzer and Luders (2000)]. There are some difficulties that arise while applying few excellent separation methods such as gas chromatography (GC), thin-layer chromatography (TLC) [Klaffke et al. (1998)], and high performance liquid chromatography (HPLC) – mass spectrometry [Kuhn et al. (2004), Svensson et al. (2011) and Billian et al. (1998)]. The gas chromatographic (GC) analysis of APGs can be performed only after their derivatizations (silylation) due to low volatility of these analytes. The derivatizations task is time consuming and complex, so GC is not suitable for rapid routine analysis [Czichocki et al. (2002)]. TLC approaches have been widely used, but problems arise because of incomplete separation of the components and in their quantification [Hubner et al. (2006)]. The use of liquid chromatography with mass spectrometric detection (HPLC – MS) might provide further enhancement. This technique enables not only to perform
analysis without derivatization, but also to obtain high sensitivity and selectivity. Different homologues can be analyzed without complete chromatographic separation and this method is suitable for both quantitative and qualitative determination [Hubner et al. (2006)]. The APGs do not possess either chromophoric or fluorophoric groups, so the application of direct UV or fluorescence detectors is impossible [Buschman et al. (1996)]. Various detectors have been used for the detection of the complex matrix of APGs in shampoo or dishwashing detergents after separation by HPLC. They are UV detector after post-column derivatizations, near infra-red spectrometer, refractive index detector, evaporative light scattering detector (ELSD), electrochemical detector (ED), mass spectrometer (both LC-MS and LC-MS/MS) and nuclear magnetic resonance (NMR) spectrometer [Kim et al. (2001)]. Pulsed amperometric detection (PAD) was used in conjunction with capillary electrophoresis (CE) to analyze APGs in complex matrices without sample preparation [Wallingford et al. (1987) and Svensson et al. (2011)].

1.3 Surface and performance properties of APGs

APGs show peculiar physico-chemical properties [Rybinski et al. (1998)]. They are generally stable at high pH and sensitive to low pH (< 5), at which they dissociate into glucose and fatty alcohol. Due to the presence of sugar hydrophilic part, APGs are more hydrophilic in nature than that of their polyoxyethylene counterpart polysorbate. This property makes the changes in the water-air, water-oil and water-solid interfacial behavior, solution behavior and phase behavior and let them to act distinctly from the conventional nonionic surfactants [Nickel et al. (1992), Rybinski et al. (1998) and Savic et al. (2011)].
1.3.1 Surface and interfacial properties

Interfacial tension

The interfacial tension (IFT) of surfactant at the water/oil interface is of industrial significance for many processes such as emulsification. Temperature invariant, low interfacial tensions seem to be a general characteristic of APGs \textit{i.e.} one to two magnitudes lower when compared with ethoxylated sorbitan mono fatty acid ester or ethoxylated fatty alcohols [Iglauer et al. (2009) and Iglauer et al. (2010)]. Moreover, in contrast to fatty alcohol ethoxylates the IFT values of APGs are largely independent of temperature. IFT of APGs is significantly influenced by various molecular details such as alkyl chain length, sugar head group, stereochemistry, functional groups and addition of salt and co solvent structure. Presence of shorter alkyl chain, two sugar head group (maltosides), β - anomeric form increase the IFT value [Iglauer et al. (2009)]. Alkyl polyglucosides can reach very low interfacial tension (IFT) (0.01mN/m) when formulated with 1- octanol or 1 - hexanol co-surfactants. Instead of alcohol, the addition of other surfactant influences their IFT values much. Blending of ionic surfactant with large head groups such as sodium dodecyl sulphate or tetradecyl trimethyl ammonium bromide increases the interfacial tension. But the addition of nonionic surfactant with a smaller head group than that of APGs, such as sorbitan monolaurate decrease the IFT to a much extent. The addition of salt and integration of functional groups (such as aldehyde, amide-methoxy) into the molecular architecture of the APG skeleton were efficient in reducing IFT. For surfactant-water-oil systems, the long alkyl chain, have a strong influence on interfacial behavior. The increase of alkyl chain length, increase the solubility of the surfactant in the oil phase. The oil polarity has much influence on the interfacial tension against different oils (\textit{viz.}, 2 – octyl dodecanol, isopropyl myristate, n-decane). The IFT value of octyl dodecanol/water is lower than that of
isopropyl myristate/water. IFT (aq-oil) < or = IFT (aq-middle) + IFT (middle-oil) [Iglauer et al. (2010)]. This strategy has been used in improved oil recovery.

**Critical micelle concentration and micelle shape**

The critical micelle concentration (CMC) is the keystone in the research of solution behavior of the surfactants [Myers (2006)]. It is well known that CMC is the concentration above which monomeric surfactant molecules abruptly assemble themselves into aggregates called micelles [Moulik (1996)]. Surface tension is most common tool in the determination of CMC. The other physical methods for CMC determination includes conductivity, solubility, viscosity, light scattering, measuring the surface tension by Wilhelmy plate method or by the method of maximum bubble pressure, measurement of ion activity and by dye incorporation method, gel filtration spectrophotometrically and counter-ion magnetic resonance [Sinha et al.(2002)].

The CMC of APGs is strongly influenced by the alkyl chain length when compared to the number of glucoside groups [Boyd et al. (2000)]. The CMC value of APGs decreases as the number of carbon atoms in the hydrophobic group increases. For given chain length, an increase in the head group size results in a slight increase in the CMC, a significant increase in the surface tension at the CMC, and in a significant decrease of the packing density at the interface.

Depending upon the molecular structure, APGs may form micelles of various shapes [Ruiz et al. (2011)]. The APGs with C₈ – C₁₀ alkyl chains form ball or disc shaped micelles at concentration of above 7 × 10³ wt %. When the concentration increases, the number of aggregates also increases, micelles become deformed and at a concentration of about 5 × 10⁻² wt %, they become cylinder – like. An increase in the chain length to C₁₂ – C₁₄ results in a significant drop in CMC and an increase in the length of cylinder – shaped micelles [Sulek (2006) and Balzer (1993)].
Also, the packing parameters (V/al) determine the shape of the micelles (sphere shape for V/al< 1/3, cylindrical for V/al≤ ½, bilayer shape for V/al≤ 1) [Myers (2003)]. The dimension of a micelle is illustrated in the following Figure 1.5:

![Diagram of micelle dimensions and interactions](image)

Figure 1.5 Dimensions and interactions of a micelle

where, V – Surfactant tail volume; a equilibrium area per molecule at the aggregate interface to tail length l.

**Aggregation number**

A micelle is constructed of a number of surfactant monomers, which is given by aggregation number (N). The value of N depends on the type of surfactant, temperature and electrolyte concentration [Myers (2006)]. If the assumption that surfactant molecules are present as either monomeric units or micelles that have N monomers, there will be a concentration [M] that is expressed as

\[
[M] = \frac{([s]_o - \text{CMC})}{N}
\]

where, N- Mean aggregation number, [M] – average micelle concentration. The micelle shape of nonionic molecules of APG is determined to a large extent
by the aggregation number. A variety of experimental methods such as laser light scattering and fluorescence quenching have been highly used for the determination of aggregation number and the distribution of micelle sizes and their approximate shapes. Due to the higher steric hindrance and repulsive hydration, the APGs with glucoside head groups exhibit larger aggregation number as compared to maltosides for the same chain length. But for a given head group, increase in alkyl chain length favors large aggregation numbers, as the hydrophobic effect from packing the tail groups in the micelle interior becomes stronger (approximately 0.8Kcal/mol per CH₂ group).

**Clouding behavior**

The C₁₂/₁₄ APGs behave similarly to other nonionic surfactants in that it exhibits a concentration and chemical dependent cloud point in distilled water. By changing the degree of glucosidation from 1.75 to 1.85 for C₁₂/₁₄apes, the cloud point increases from 27°C to 87°C. In contrast C₈/₁₀ APGs, form an isotropic liquid phase between 20° and 90°C in distilled water, even at high concentration. When a mixture of Ca and Mg ions is added a narrow liquid / liquid coexistence region appears at low concentration [Nickel et al. (1992)]. The cloud points of APGs are increased by the addition of alkali and anionic surfactants due to the change in the electrical charge of APG micelles [Balzer (1993)]. During the addition of cationic surfactants the cloud point initially decreased, passed through a minimum and then increased due to the charge effect [Iglauer et al. (2009)]. With the exception of NaOH, addition of all electrolytes leads to a distinct reduction in the cloud point of APGs. The distinct effect of electrolytes on APGs may due to the presence of charge at the surface of the alkyl polyglucoside micelles which is absent for alkyl polyglycol ethers [Fukuda et al. (1993)]. Thus, the clouding behavior of APGs is differing from those of alkyl polyglycol ethers due to the difference in the type of hydration of cumulative OH group of glucose unit from those of alkyl polyglycol ethers [Fukuda et al. (2001)].
Phase behavior

The phase diagram of the relatively short chain APGs is considerably simpler [Hill (2000)]. The C_{8/10} APGs present in the isotropic phase at temperature above 20°C up to very high concentration and a birefringent lyotropic phase of nematic texture is formed at around 95% by wt. which changes at around 98% by wt. into a cloudy two-phase region of liquid and solid APGs [Platz et al. (1994)]. At low temperatures, a solid/liquid region below the Kraft point is formed over a wide range of concentration. The system changes to an isotropic liquid phase with an increase in temperature. At low concentration, the isotropic liquid phase changes above 35°C into a two-phase region of two liquid phases and at concentrations above 60% by weight, a sequence of liquid crystalline phases is formed at all temperatures. In the isotropic single-phase region, a distinct streaming birefringence can be observed at concentrations just below the lyotropic phases, disappearing again rapidly on completion of the shearing process. No multiphase regions separate this region from the L_1 phase. In the dilute L_1 phase, there is another region with weaker streaming birefringence that is situated near the minimum of the liquid/liquid miscibility gap. At relatively low temperature, a lamellar liquid crystalline phase is additionally observed between 75% and 85% by wt. The phase behavior of alkyl glucoside surfactant systems and micro-emulsions is heavily influenced by traces of ionic surfactants [Hoffmann et al. (2001)]. The phase behavior of simple APGs – water mixtures differs in certain aspects from other nonionic surfactants [Platz et al. (1994)]. Particularly, temperature is a parameter of minor importance in any comparisons of APGs with fatty alcohol ethoxylates. The phase behavior of simple binary alkyl polyglucosides with water is only slightly influenced by temperature. No temperature-dependent phase inversion is expected to occur in APG containing emulsion,
whereas temperature is the basis of the known phase inversion temperature (PIT) phenomenon for ethoxylated nonionic surfactants.

1.3.2 Performance properties of APGs

**Foaming properties**

The foaming properties of APGs depend upon the alkyl chain length [El-Sukkary et al. (2008)]. APGs are the moderate foamers by themselves and often act as foam boosters for anionic surfactants. APG foam consists of finer bubbles and can be creamier. APGs have been used as a sustainable foaming agent to control the mobility of CO$_2$ in enhanced oil recovery [Rafati et al. (2012)]. The stability of foam increases with the increasing chain length [El-Sukkary et al. (2008) Geetha and Tyagi (2015)]. The foaming capacity of APGs – containing cleaners can readily be reduced by the use of small quantities of soaps or increased by the addition of small quantities of anionic surfactants [Holmberg (2003)].

**Wetting and adsorption**

The wetting power of a surfactant is one of the most important surface properties. The addition of surfactants to water improves the ability of aqueous solutions to wet and spread over solid surfaces. In laundry cleaning of textile processing, the wetting power of a surfactant can accelerate the diffusion or penetration of alkali chemicals and dyes into the fibers thereby improving the detergency or dyeing effect [Engles et al. (1998)]. Moreover, the wettability is very much important for many practical processes such as floating, painting, coating, lubrication and adjuvancy. Understanding the adsorption behavior of surfactant on surfaces is necessary in order to control wetting, dispersion and detergency processes. The wetting ability of APGs decreases with the increase of alkyl chain length. APGs have excellent wetting and penetrating
properties and hence they have been widely used in crop protection formulation [Homberg (2003)]. Traditionally, nonionic surfactant like nonylphenols whose wetting power is high has been used in phytosanitary products are being replaced by APGs, because of the toxicity profile of the biodegradation product of nonylphenol [Engles et al. (1998)]. Recently, it has been observed that the wetting ability of the mixtures of AE : APG show better wettability than the pure surfactant even at low concentration. Also their wettability is not significantly affected by the water hardness and pH. The phosphated APGs exhibit good performance in improving the whiteness and wetting of cotton fabrics in hydrogen peroxide bleaching system [Chen et al. (2010)].

Emulsification

The function of the emulsifying agent (emulsifier) is to stabilize the unstable emulsion system for a sufficient time, so that it can perform some functions. The emulsifier is adsorbed at the liquid/liquid interface of the emulsion and oriented as an interfacial film. The emulsifying power generally depends on the length and nature of the hydrophobic part of the surfactant. The stability of the formed emulsion increases with the increase of alkyl chain length due to the increased solubility of the surfactant in the oil phase [Sukkary et al. (2008)]. The C12/14 APG – mixed emulsifier is declared as a versatile self – emulsifying oil / water base and commonly used as cosmetic active ingredients, including chemical and mineral UV filters [Pantellic et al.(2014)]. The C16/18 APG recently approved by FDA (Food and Drug Administration) has been employed as stabilizer in different types of emulsion vehicle for a number of cosmetic actives and model drugs due to its non-toxicity. APGs form almost temperature invariant micro-emulsion. The micro-emulsion of APGs would appear to be ‘ideal’ vehicle for drug delivery. Long chain APGs show better stability than the medium chain C12/14 APGs in conventional emulsion [Savica et al.
The $C_{18}$ alcohol is being used as co-emulsifier, self-emulsifying o/w basis which is containing 20-60% $C_{16/18}$ APGs are the most suitable in practice for formulating cosmetic creams and lotions. Now-a-days, APGs are excessively investigated as potential stabilizers of diverse nano-systems [Budi et al. (2010)]. The importance of APGs is evident in the case of dispersions of silica nano-spheres in liquid crystals which are alternatively attracting considerable attention due to the frequent use of the combinations of nanoparticles and colloidal systems in cosmetic products [Siddiq et al. (2005)].

1.3.3 Environmental compatibility and toxicological safety of APGs

**Biodegradability**

Rio declaration stipulates that the right to development must be fulfilled by the sustainable development which reflects the close relationship between the protection of the environment and economic, scientific, industrial or any other kind of development [Pantelic (2014)].

Biodegradation is the most important mechanism which is responsible for the irreversible removal of organic compounds such as surfactants from aqueous and soil environments. Biodegradability testing plays a very important role in the assessment of environmental behavior of surfactants. Environmental impact assessment of APGs will need further testing as their use in the chemical, cosmetic, pharmaceutical and agricultural industries are increasing. Yet, currently available studies show that there is no environmental risk even where, APGs are used in large quantities. The prescribed Organization for Economic Co-operation and Development (OECD) method used for detecting the biological primary degradation of non – ionic is not applicable to APGs, because they do not contain any ethylene oxide groups and are thus no BiAS (Bismuth active substance methods) active [Steber et al. (1995)]. It can be extrapolated from the very
favorable ultimate degradation data that the primary degradation step also precedes with ease and this was confirmed in OECD confirmatory test by applying an APG – specific analysis method. Ready ultimate biological degradation was observed with complete mineralization and/or assimilation of APGs under both aerobic and anaerobic conditions. The biodegradability of APGs was determined by shake culture tests, semi-continuous activated sludge test and continuous activated sludge test of surfactants in OECD, American Society for Testing and Materials (ASTM), Japanese Industrial Standards (JIS) and Korean Industrial Standards (KS) [Lee et al. (1995)]. APGs showed 100% foam loss in all tests. In closed bottle test for determining the ultimate biodegradability, APGs exceeded the ready biodegradability limit (60%) of OECD with 75% (Biological oxygen demand) BOD$_{28}$/COD (Chemical oxygen demand). Hence, APGs are considered as readily biodegradable under actual environmental conditions [Grzeskowiak et al. (2008)]. Also, analysis has shown that the APGs with longest alkyl chain and highest number of glucoside units possess little lesser biodegradability (79%) than that of the shorter chain APGs. For lower chain APGs, the screening test results show that the level of biodegradation is higher if the initial concentration is lower.

**Toxicity**

Toxicity studies [Chen et al. (2010)] of APGs based on the OECD guideline NO.401, US toxic substance control act (TOSCA – 40 CFR 798), Federal insecticide, fungicide and Rodenticide Act (FIFRA – 40 CFR 158, 162) show that the glucoside are relatively harmless when ingested and have a very low degree of toxicity (LD$_{50}$ greater than 35 g / kg). APGs did not have any
toxicity on specific strain. Neither of the two strains tested, (Wistar and Sprague Dawley) showed specific sensitivity towards alkyl polyglucoside [Chen et al. (2010)]. On the basis of EU and US classification rules, alkyl polyglucosides do not require hazard classification or labeling. In aquatic organisms showed increasing toxicity in the following order: branched APG < ethyl glucoside mono ester < linear APG < alcohol ethoxylate [Madsen et al. (1996)]. The no observed effect concentration (NOECs) for acute or chronic toxicity, as determined on single species or biocenotic communities of the aquatic and terrestrial environment show that APGs have comparatively low eco – toxicity [Geetha and Tyagi (2012)].

**Skin and eye irritation**

Irritation effect of APGs to rabbit skin and eyes was done by the procedure outlined in “Appraisal of the Safety of Chemicals in Foods, Drug and Cosmetics” showed low skin and eye irritation [Hughes et al. (1970)].

APGs with C₈ – C₁₆ alkyl chains belong to the group of very mild surfactant for body cleansing formulations and it was found that irritation on skin decreases slightly with increasing degree of polymerization (from DP = 1.2 to DP = 1.65) [Holmberg (2003)].

1.4 Derivatives and applications of APGs

1.4.1 Derivatives of APGs

A broad range of alkyl poly glucosides can be prepared by the relatively simple methods such as nucleophilic substitution [Holmberg (2003), Greiner et al. (1988)]. By the presence of their numerous hydroxyl groups, APGs are over functionalized molecules. APGs derivatizations are
carried out by chemical transformation of primary hydroxyl group at the C₆ atom of glucose. In order to avoid the formation of more complex mixture and complicated analysis, it has proven to use APGs with low DP value of 1.1[Holmberg (2003)]. The anionic derivatives of APGs viz, APG citrate, APG tartrate and APG sulfosuccinate have been found to accumulate at the interface to a greater extent than the APGs. Thus they efficiently reduce the interfacial tension and have better wetting and rheological properties [Konya et al. (2004)].

1.4.2 Applications of APGs

**Personal care products**

The development and commercialization of new products with innovative surfactant are more prevalent in the personal care segment which is driven by the interest of consumer. The personal care products include bubble baths, body washes, hand soap cleansers, shaving products, hair shampoos and oral care products. The present cosmetic industry requires the surfactant with all round compatibility with human skin epidermis along with good eco- toxicity profile [Schrader et al. (1996)]. APGs are cosmetic ingredients having a very broad range of applications. In addition to the formulation of shampoos, lotions of APGs have been used in the facial cleansers and eye makeup removers. APGs cosmetic formulations are not only intended to minimize further damage to the skin but also show a better compatibility on pre-damaged skin and sensitive skin. APGs have been used in hair dyes, mild waving lotions, conditioners and bleaching formulations due to their alkalinity tolerance along with the ability to increase the tensile strength of hair strands. Due to the excellent mucosa compatibility, good toxicological values and the good foaming ability, APGs have been started to be used in the dental care products viz. toothpastes and mouthwashes [Schrader (1994)]. APGs have been more intensively
used in the complicated fine hair products. APGs are interesting and promising ingredients whose development potential is far from being exhausted [Savic et al. (2011)].

**Agricultural applications of APGs**

APGs have been known for its agricultural formulations for many years due to their wetting performance, electrolyte tolerance, stability over temperatures and the very good eco-toxicity profile [Hill et al. (2000)]. APGs have been successfully used on the composting of agricultural wastes [Zhang et al. (2011)]. Addition of APGs provides more favorable conditions for micro-organism growth, enhanced organic matter decomposition, accelerating the composting process and improving the compost quality to certain extent [Garst (1997)].

**Detergents and hard surface cleaners**

In the development of laundry detergents, the ecology has been an important factor. Also, the home cleaning requires modern all-purpose cleaners. Today, APGs containing products are found both in all-purpose cleaners and in special cleaners such as bathroom cleaners, toilet cleaners, window cleaners, kitchen cleaners and floor cleaners [Holmberg (2003)]. According to the IPP (Integrated product policy) quality standard, APGs themselves have an excellent cleaning performance and it could be further improved by small addition of anionic surfactant or polymeric boosters. In addition to the removal of bleachable stains, such as tea, coffee, etc., APGs have been used to remove the fat and oil containing soils such as sebum, olive oil, lipstick and facial cream more effectively [Holmberg (2003), Geetha and Tyagi(2012)].

### 1.5 Objectives of the present study

The novel properties associated with alkyl polyglucosides surfactants have motivated efforts to synthesize alkyl polyglucosides in an efficient new way to study their structure-property relationship.
The complexity raised due to the usage of stoichiometrically excess fatty alcohol to glucose raw material has been addressed by the study of catalysts in a simple new cost-effective manner. The following are the main objectives of the study:

i. To synthesize APGs \( i.e. \) APG\textsubscript{12}, APG\textsubscript{14} and APG\textsubscript{16} with optimization of suitable catalyst for better yield and applications.

ii. To characterize all synthesized chemical molecules by instrumental techniques \textit{viz.}, FT-IR, $^1$H-NMR, $^{13}$C-NMR and elemental analysis.

iii. To evaluate the physico-chemical properties of synthesized APGs \textit{viz.}, surface tension, critical micelle concentration, foaming, wetting, emulsification, dispersing ability and biodegradability.

iv. To evaluate their mixed micelles with the various cationic surfactants to know the synergistic effects.

v. To evaluate and compare the oil removal capacity of the middle chain alkyl polyglucosides (APG\textsubscript{12}) in the washing of petroleum contaminated soil.