# CHAPTER I

INTRODUCTION

Surfactants properties play important roles in performance of a wide array of industrial and consumer products, including detergents, paints, paper products, pharmaceuticals and cosmetics. Surfactants are also used in diverse exotic roles as emulsifiers during enhanced oil recovery from deeply located oil wells. The last few years showed an increased interest in work involving the preparation and study of surfactants based on natural products. Examples are surfactants based on sugars [1-7]. Such surfactants are interesting because they are generally easily biodegraded [8]. In industry there is a desire to find new surfactants with improved properties, in comparison to conventional surfactants. Additionally, there is a trend to move towards a more sustainable production, using renewable natural products instead of petrochemical ones.

Surfactants are made from petrochemicals (derived from crude oil or natural gas) or oleochemicals (derived from fats and oils). Some types of surfactants can be made from either raw material source (**Figure 1.1**). Petrochemicals are often termed "synthetic" materials, while oleochemicals are sometimes called "natural." Both have "natural" sources, since crude oil is extracted from the earth and oleochemicals come from plants or animals [9].
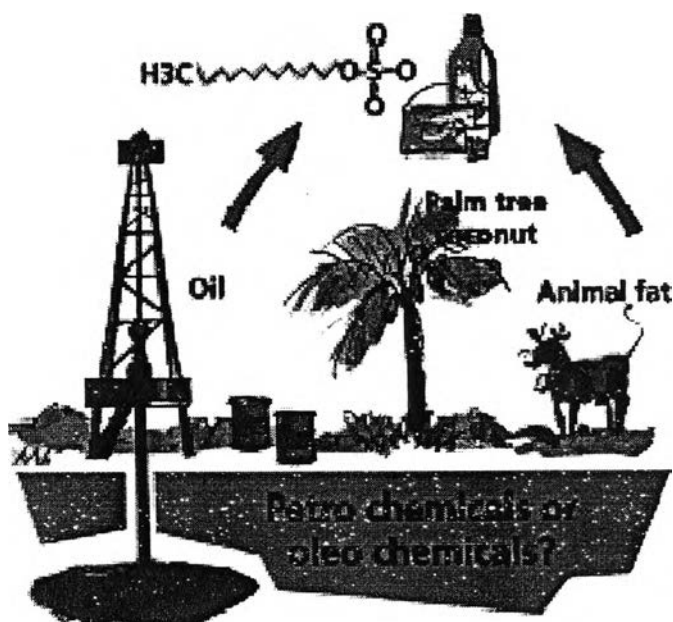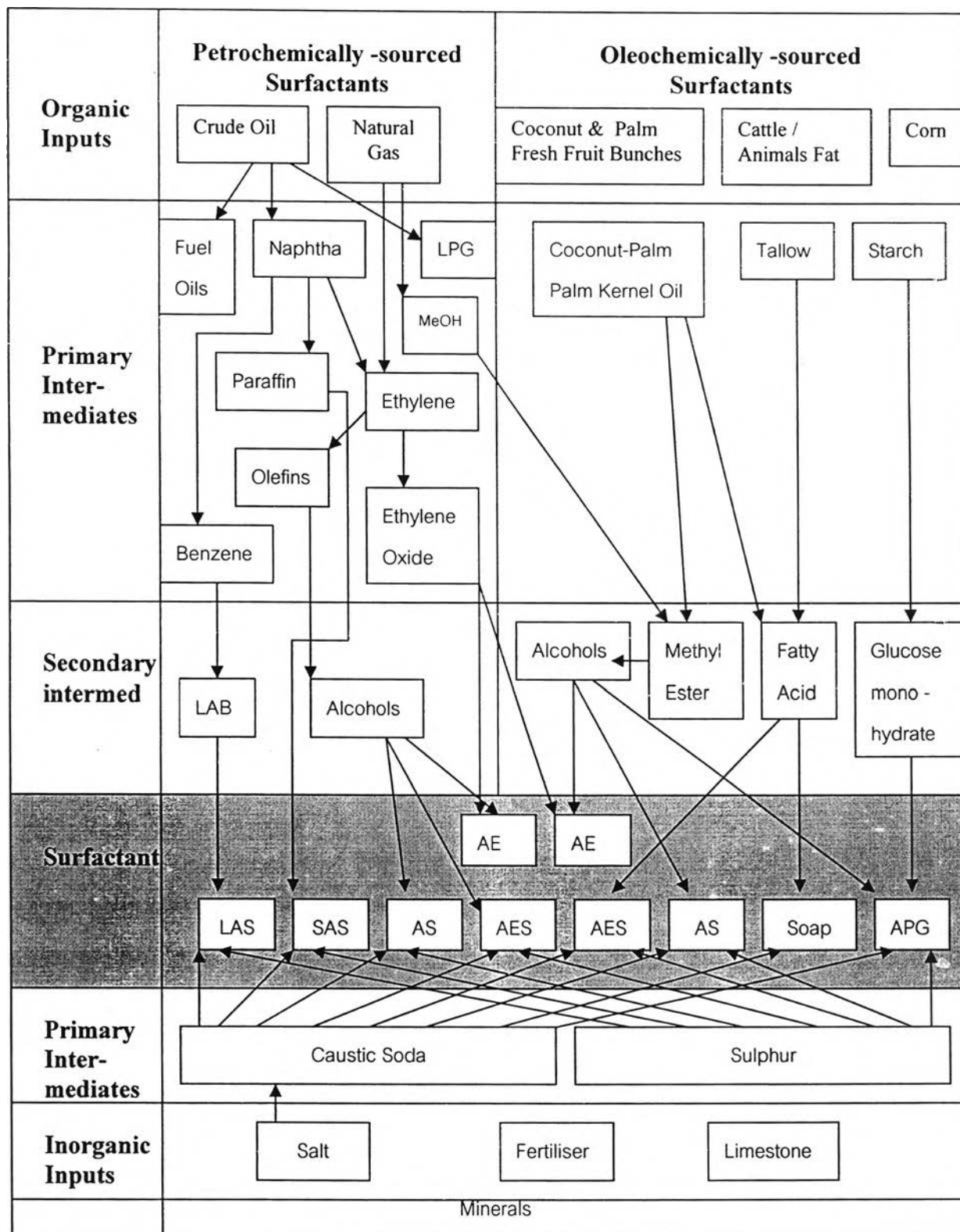
Figure 1.1 Sourcing diagram for surfactant [9]

AE : Alcohol ethoxylates ; AES : Alcohol ethoxy sulphates ; APG : Alkyl polyglucosides ; AS : Alcohol sulphates ; LAS : Linear alkyl benzene sulphonates ; LAB : Linear alkyl benzene; LPG : Liquid petroleum gas ; SAS: Secondary alkane sulphonate

1.1 Surfactant

Surfactants, defined as surface-active agents, consist of a hydrophobic and a hydrophilic moiety that are clearly separated in the molecular structure. The polar part engages in electrostatic interactions (hydrogen bonding, dipolar interactions, ionic bonding *etc.*) with surrounding molecules, *e.g.* water and ions. The non-polar part, on the other hand, associates with neighbouring non-polar structures *via* hydrophobic and van der Waals interactions. The associated structures first formed when the surfactant concentration in an aqueous solution is increased are typically closed structures that are relatively small. Such structures are called micelles and they can exist in various sizes and shapes depending on surfactant concentration, surfactant structure, pH, ionic strength and temperature *etc*. The self-association process starts at a well-defined concentration, the micelle concentration, *CMC*. Thus, surfactants associate with both polar and non-polar compounds, but different parts of the surfactant are involved in the association with molecules of different polarity. Surfactants are usually classified according to their polar head group as anionic, cationic, nonionic or zwitterionic.

1.1.1 Surfactant properties

In this thesis some major properties of surfactants are briefly discussed. The presentation is based on a recent comprehensive description of surfactant and polymer properties [10] as well as on information provided elsewhere [11-12].

1.1.1.1 Surface tension

Surfactants have the property to aggregate in solution or at interfaces forming micelles in aqueous solutions and structured films at the liquid-gas interface. This property is known as adsorption and results in an increase in the surfactant concentration at the solid-liquid or liquid-gas interface in comparison to the bulk concentration. Soluble surfactants adsorb to interfaces in equilibrium with their bulk. The study of such adsorption permits to determine the energy changes (ΔG), (ΔH) and (ΔS) in the system. These properties provide information on the type and mechanism of any interaction between the surfactant and the interface. The amount of adsorbed surfactant is determined as a function of solution concentration. It can give information to deduce the mechanism from the adsorption isotherm. Increment of bulk concentration rises the surface adsorption. The region approaching the CMC is the zone in which increasing bulk surfactant concentration yields increasing surface

excess concentration. At the liquid-water interface the surface excess surfactant concentration (Γ) can be calculated using the Gibbs adsorption equation.

$$\left(\frac{\partial \gamma}{\partial \ln(c)} \right)_T = -RT\Gamma$$

The surface excess surfactant concentration (Γ), can be graphically calculated from the variation of surface tension (Γ) with the logarithmic change in bulk concentration (C). The molecules of a liquid attract each other due to dispersion, dipole-dipole and dipole-induced-dipole forces, as well as hydrogen bonding. In the bulk liquid a molecule senses the same attractive and repellent forces in all directions, while for a molecule at the surface those forces are lacking in one direction. This asymmetry of forces is the origin of the surface energy or equivalent the surface tension. For example, there is a surface tension between water and air of the order of 73 dynes/cm. For the reasons mentioned above, a compound will possess higher surface tension, the more polar it is. Likewise, two liquids are immiscible if the surface tension between them is large, but for entropic reasons they are miscible if that tension is low enough. Then practically, what a surfactant does, is to lower the surface tension. This leads to increase solubility of non-polar molecules in aqueous solutions (*e.g.* solubilization of micelles). Surfactants can also improve the stability of dispersions, emulsions and foams. There is, of course, a practical limit to how low the surface tension can be. With special formulations, so-called ultra low interfacial tension, values in the range of 10^{-3} mN/m or lower can be reached. Such microemulsion systems are of interest for the purpose of enhanced oil recovery.

1.1.1.2 CMC and micellar growth

When added to an aqueous solution, surfactant molecules minimize their energy by creating a monolayer on the air-water surface. This is a slow process with large molecules, for example polymers (equilibrium times can vary from seconds to days), but considerably faster for surfactants (ms to s). In order to minimize their free energy, the hydrophobic parts of the surfactants are directed towards the less polar air, while the hydrophilic groups are directed towards the polar water molecules. Upon increased surfactant concentration, the surface becomes increasingly saturated by

surfactant molecules, which decrease the surface tension of the solution. In other words, the surface tension will decrease upon the addition of surfactants.

The minimum surface tension reachable is determined by how effective the packing of the surfactants is at the surface and on the interactions between the surfactants at the interface; different hydrophobic and hydrophilic groups thus create different minimum surface tensions. With concentrations above the saturation point, called the critical micellization concentration, the CMC, the freely dissociated surfactant molecules in the water bulk phase start to form closed micellar structures, that can be spherical, tablet shaped or rod-like, with a hydrophilic surface and a hydrophobic interior (**Figure 1.2**). Such micelles usually have *hydrodynamic radii*, RH, ranging from 20 to 400 Å.
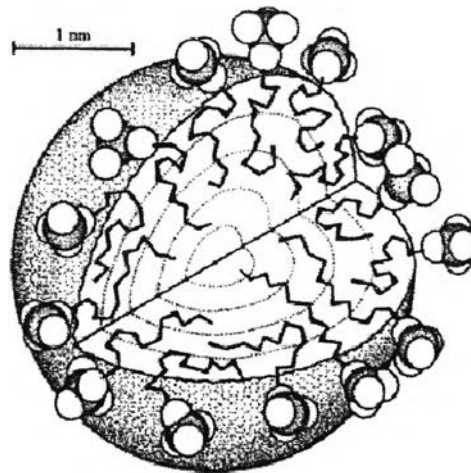

Figure 1.2 An illustration of a spherical micelle (of dodecyl sulfate) emphasizing the liquid-like character with a disordered hydrocarbon core and a rough surface [13]

The surfactant's amphiphilic natures allow for self-aggregation into small vesicles termed micelles. In polar solvents, such as water, monomers assemble to form a micelle in such a way that the polar head groups project outwards into the polar bulk solvent and their hydrocarbon tails buddle in the core of the micelle. This way, the hydrophobic tails are shielded from water (**Figure 1.3**).
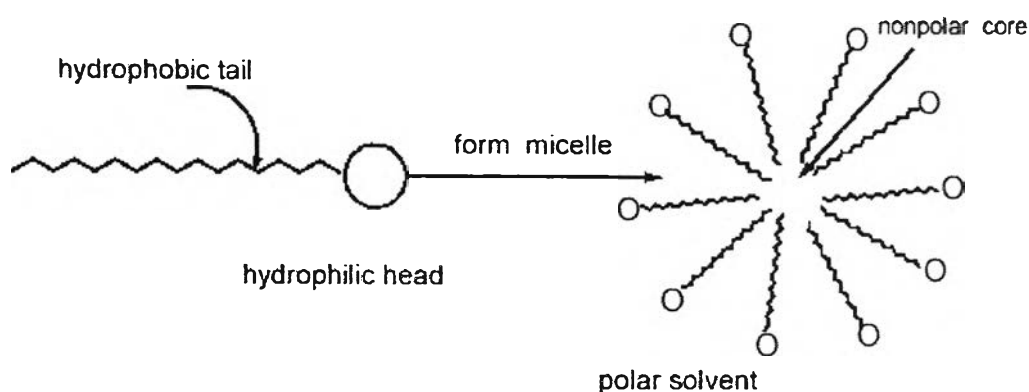
Figure 1.3 Formation of micelle w/o [14]

Aggregates can also occur in nonpolar solvents. These systems are called reverse micelles or inverted micelles (**Figure 1.4**). Head groups of surfactant monomers are located inside to form a polar core and hydrocarbon tails are projected toward the bulk solution to form the outside shell of the micelle. If there is any water in the solution, it will be entrapped in the core. Reverse micelles are able to solubilize a relatively large amount of water in their cores, and this capacity can allow them to solubilize water-soluble substances in a nonpolar solvent. For example, it has been reported that water can be solubilized in carbon dioxide, a non-polar solvent, when the appropriate surfactant is chosen [14]. The surface activity of the surfactant is determined by the nature and ratio of lipophilic and hydrophilic groups and by the spatial arrangement. This dual nature of the surfactant is responsible for the properties of micellization, surface activity, and solubilization. When the surfactant concentration is close to CMC, micelles are small. As the surfactant concentration increases they become larger, and after a certain concentration they elongate and convert into rodlike micelles. The presence of salt or organic additives can also lead to this conversion or affect the conversion concentration.
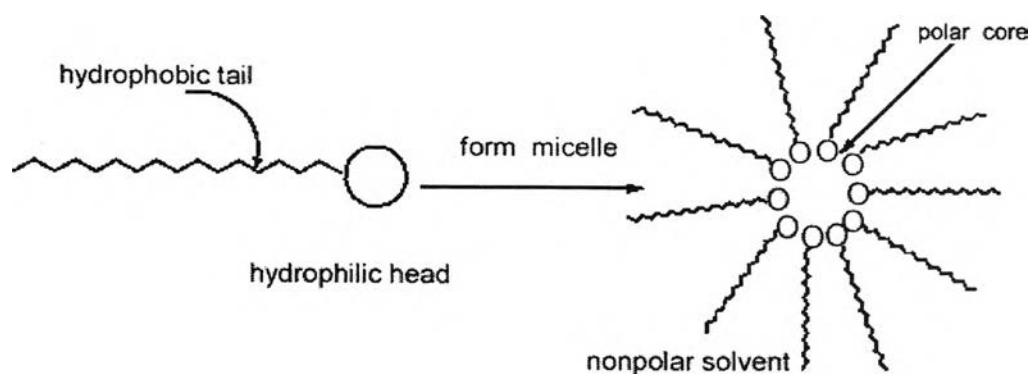
Figure 1.4 Formation of reverse micelle o/w [14]

1.1.1.3 Solubility and krafft point

Since surfactants are designed as amphiphilic molecules, which interact with both hydrophobic and hydrophilic interfaces. They have limited solubility in all types of solvents. Surfactants have limited aqueous solubility, which needs to reach the level of the CMC of the surfactant to allow maximum performance. The point, at which the temperature-solubility curve of the surfactant crosses the temperature-CMC curve, is called the Krafft point. The Krafft point increases irregularly with increased alkyl chain length. The Krafft point can also be increased by added salt or decreased by other cosolutes. Some surfactants are not soluble enough ever to reach a critical micellization concentration. Certain surfactants, depending on the balance between hydrophilic and hydrophobic moieties, named the hydrophilic-lipophilic balance (HLB) The hydrophilic lipophilic balance (HLB) number was introduced by Griffin [15]. The HLB number provides a semiquantitative description of the efficacy of surfactants with respect to emulsification of water and oil systems. This scale was introduced to characterize nonionic surfactants using oxyethylene oligomer as hydrophilic group. The HLB number for nonionic surfactants can be calculated through the following equation [15].

$$HLB = 20 \left(\frac{M_H}{M_H + M_L} \right)$$

where M_L is the formula weight of the hydrophobic portion of the molecule and M_H is the formula weight of the hydrophilic portion of the molecule. Table 1.1 lists HLB values along with typical performance.

Table 1.1 Hydrophile lipophile balance (HLB) and their typical properties [15]

HLB	Property
3-6	w/o emulsifier
7-9	wetting agent
8-18	o/w emulsifier
13-15	detergent
15-18	solubilizer

A low value indicates a hydrophobic surfactant, while a high number indicates a hydrophilic surfactant. Naturally, many surfactants with low aqueous solubility can be found to be more soluble in solvents such as methanol or ethanol. Excessively fat surfactants, those with a low HLB, are thus soluble only in nonpolar solvents. For practical purposes, it is in most applications necessary that surfactants be designed to be soluble up to their CMC values.

1.1.1.4 Foaming

Foaming depends on the stability of liquid-gas interfaces. Foaming studies are often performed according to the Ross-Miles method [16], in which a surfactant solution is poured onto an identical surfactant solution, after which the height of the foam produced is measured (often during some minutes). The initial foam height is a measure of foamability and the decay of the foam with time is a measure of foam stability. Another common method is the Bikermann method [17], in which a stream of air is bubbled through a surfactant solution at increasing speed until the rate of foam breakdown is equal to the rate of foam production. Both foamability and foam stability are of interest in different applications. It is important to realize that when foamability is measured, new interfaces are continuously being created. Thus, the rate at which the surfactant adsorbs to interfaces and creates a monolayer that facilitates stabilization of the foam, compared with the rate at which new interfaces are created, is crucial. A high foamability is facilitated by rapid adsorption, high surface elasticity, and high surface viscosity at low nonequilibrium surfactant coverage and by strongly repulsive forces between the air and water interfaces. In foam-stability measurements, on the other hand, the (nearly) equilibrium properties of the adsorbed surfactant monolayer are important. The breakdown of foam lamellae first involves the drainage

of the liquid film and then, once the film has become sufficiently thin, a rupture of the film. The drainage rate is slow by a high bulk viscosity, surface viscosity, surface elasticity and long-range repulsive forces between the interfaces. The final rupture is a stochastic process promoted by thermal and mechanical fluctuations as well as the liquid film counteracts it. This energy barrier increases when the repulsive forces between the interfaces increase and when the cohesive energy of the monolayer is increased. The cohesive energy in the monolayer is strongly influenced by the packing of the surfactant at the interface. A simplified way of describing the packing is by means of the critical packing parameter (CPP) can be calculated through the following equation:

$$\textbf{CPP} \quad = \quad \frac{V}{al}$$

where V is the volume of the hydrophobic group, a is the optimal area per surfactant, and is l the length of the nonpolar group.

1.1.1.5 Adsorption and wetting

Surfactants become adsorbed on surfaces, often forming complete bilayers or bilayers aggregates on hydrophilic surfaces (examples: glass, silica) and monolayers on hydrophobic surfaces (example: mica clay). To describe the adsorption process on solid surfaces is rather complex since one has to take into account interactions between surfactant and surface as well as between adsorbed surfactants. Common, but highly simplified approaches, are to use the regular solution theory and the Langmuir equation.

Surfactant adsorption at the liquid-solid interfaces may be driven by various combinations of the above forces. In the limit of noninteracting adsorption (*i.e*, where adsorbed surfactant molecules do not interact with each other), the adsorption may be modelled by the Langmuir adsorption isotherm as follows.

$$\Gamma \quad = \quad \frac{b\,c\,\Gamma_s}{b\,c + 1}$$

Where Γ is the adsorbed amount (typically μ mol/m^2), Γ_s represents the saturation monolayer coverage, c is the equilibrium surfactant concentration in the solution phase, and the equilibrium constant b, which describes the adsorption process.

$$b = exp\left(-\frac{\Delta G_{ads}}{R\,T}\right)$$

The free energy of adsorption is assigned to ΔG_{ads}, R is the gas constant, and T is the temperature. In addition, an alternative representation of the Langmuir adsorption isotherm is given by the following equation:

$$\frac{c}{\Gamma} = \frac{1}{b\Gamma_s} + \frac{c}{\Gamma_s}$$

In this case, a plot of c/Γ as function of c yields a straight line, in which the slope represents the saturation coverage. Afterwards, the equilibrium constant can be calculated from the interception between this line and the X axis C.

Adsorption studies are often performed using reflectometry or null ellipsometry, a polarometric method. The methods require that complete saturation of the surfactant and the surface occurs, but this is a rare case with large, bulky and kinetically slow molecules. Cationic surfactants, of course, interact more strongly with anionic surfaces than with non-ionic ones. Since the total amount adsorbed can be determined by these methods, it is easy to calculate the total area that each molecule occupies on the surface, the area per molecule.

A small droplet of pure water, unaffected by gravitational forces, will, due to the balance of three interfacial tensions (between liquid and air, liquid and solid and air and solid), have an inner angle (the angle between the surface and the droplet surface) of $110°$ on hydrophobic surfaces, such as hydrocarbon, and $98\,°$ on parafilm. This angle will decrease with added surfactant, down to an optimum minimum of $0\,°$, which means complete droplet spreading. The process itself is called wetting and is

useful, for example, in detergency, in commercial painting products and in mineral flotation. In the latter application a high contact angle is required in order to allow the air bubbles to attach to the mineral particle and lift them to the top of the flotation chamber where they can be collected. It is known that adsorption increases as the CPP increases, although that is not always the case. Generally, an increase in the hydrophobicity of a surfactant will increase the wetting function of the surfactant towards a hydrophobic surface. The advancing and receding wetting angles can be measured using a Wilhelmy plate wetting tensiometer.

1.2 Surfactants derived from natural products

The existing commercial surfactants are mostly based on slowly degradable compounds or at some point during their degradation they become harmful to the environment or to human beings. The reasons for choosing natural raw materials are as follows:

- Renewable starting materials

Natural raw materials are renewable. They can be produced in nature.

- Cheap starting materials

Materials produced in nature are generally easy to obtain and purify, which results in low prices. Examples are sucrose, lactose, D-fructose, D-glucose, fatty acids and terpenoids.

- Lower toxicity, less environmental impact and commercially feasible

Since nature provides the starting materials, there are microorganisms that are adapted to the degradation of the products. When the surfactants are degraded into their nature as smaller components (*i.e.* hydrophobic and hydrophilic ones), it is assumed that they are included into the natural ecological cycles, without any significant toxicological impact. Most natural product based surfactants are also believed to be degraded fast and should, therefore, pass the eco-tests for toxicity, bio-degradability and bioaccumulation, necessary for commercial products. Thus, they will, hopefully, not put a burden on the natural balances as many of the nonnatural products based surfactants do. For example, sugar-based surfactants show good skin compatibility [18] and are widely used in a range of cleaning formulations, from all-purposed cleaners to laundry detergents.

1.3 Sugar based surfactants

In recent years there has been a focus on three classes of surfactants with sugar or a polyol derived from sugar as the polar head group: alkyl polyglucosides (APGs), alkyl glucamides and sugar esters. Representative structures of the three surfactant types are shown in **Figure 1.5**. There is currently a very strong interest in exploring alkyl polyglucosides (APGs) as surfactants for several types of applications. APGs are synthesized by the direct reaction of glucose with fatty alcohol, using a large excess of alcohol in order to minimize sugar oligomerization. Alternatively, they are made by transacetalization of a short-chain alkyl glucoside, such as ethyl or butyl glucoside, with a long-chain alcohol. An acid catalyst is used in both processes. Either glucose or a degraded starch fraction is used as the starting material (**Figure 1.6**) illustrates the synthesis. Alkyl glucosides can also be made by enzymatic synthesis, using β-glucosidase as the catalyst, which yields only the β-anomer (low yield). The corresponding α-anomer can more readily be obtained by β-glucosidase catalysed hydrolysis of the racemate. There are considerable diffierences between the α and β mixture obtained by organic synthesis and the pure enantiomers obtained by the bio-organic route.
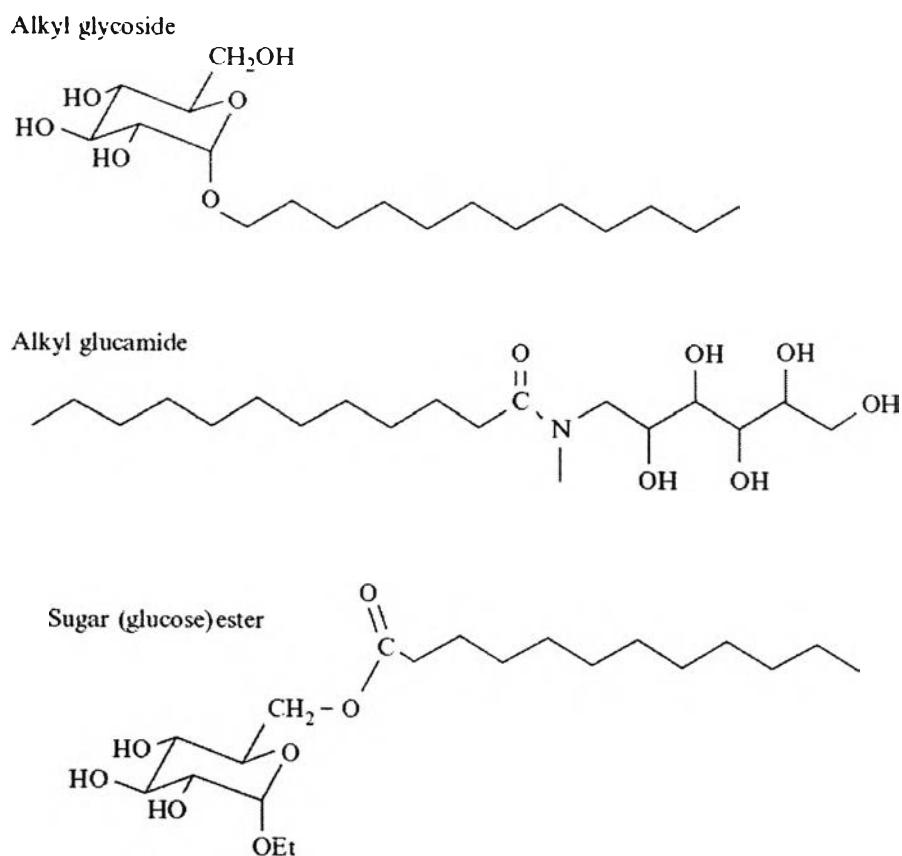
Alkyl glycoside

Alkyl glucamide

Sugar (glucose) ester

Figure 1.5 Structures of some representative polyol surfactants [19]
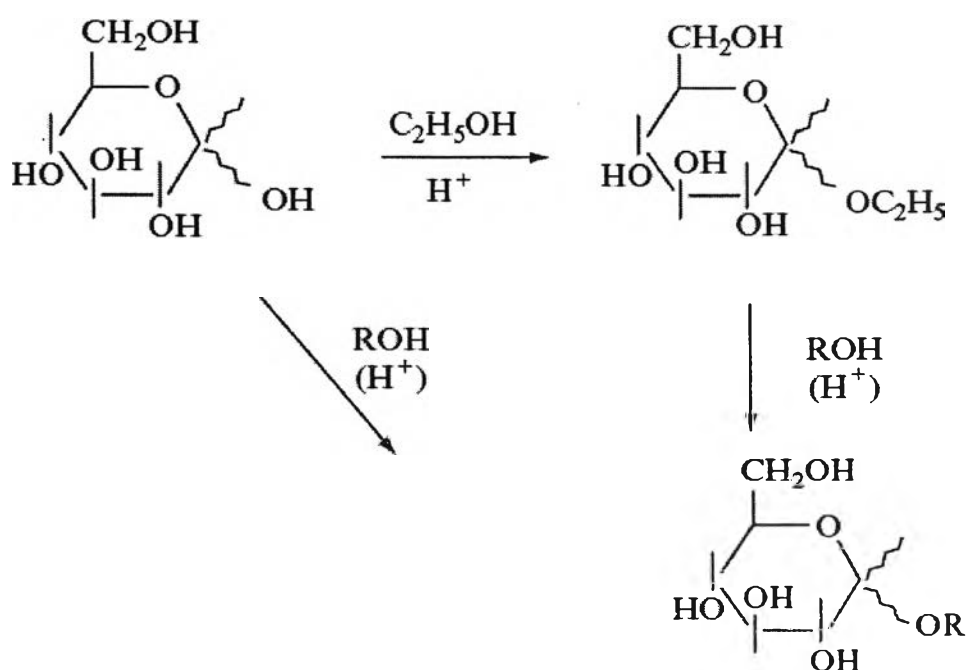

Figure 1.6 Route of preparation of alkyl glucoside surfactants [19]

The β-anomer of *n*-octyl glucoside has been found to use as a surfactant in biochemical work. Alkyl glucosides are stable at high pH and sensitive to low pH where they hydrolyse to sugar and fatty alcohol. A sugar unit is more water-soluble and less soluble in hydrocarbons than the corresponding polyoxyethylene unit; hence, APGs and other polyol-based surfactants are more lipophobic than their polyoxyethylene-based surfactant counterparts. This makes the physico-chemical behavior of APG surfactants in oil-water systems distinctly different from that of conventional non-ionics. Furthermore, APGs do not show the pronounced inverse solubility *vs.* temperature relationship that normal non-ionics do. This makes an important diffierence in solution behaviour between APGs and polyoxyethylene-based surfactants. The main attractiveness of APGs lies in their favourable environmental profile: the rate of biodegradation is usually high and the aquatic toxicity is low. In addition, APGs exhibit favourable dermatological properties, being very mild to the skin and eye. This mildness makes this surfactant class attractive for personal care products, although APGs have also found a wide range of technical applications. Alkyl glucamides (**Figure 1.5**), more strictly named as *N*-alkanoyl-*N*-methylglucamines, are commercially important products. The product sold in large quantities for the detergent sector is *N*-dodecanoyl-*N*-methylglucamine, *i.e.* the C_{12}-derivative. This product is prepared from glucose, methyl amine, hydrogen and methyl laurate by a two-step reaction. The physicochemical properties and many other characteristics of this surfactant class are similar to those of APGs. However, whereas alkyl glucosides are very stable to alkali and labile to acids, alkyl glucamides are stable to alkali and also relatively stable to acids.

Esters of glucose (**Figure 1.5**) can be made either by enzymatic synthesis, using a lipase catalyst, or by an organic chemical route. Using the right enzyme the bio-organic route can give esterification almost exclusively at the 6-position of the sugar moiety. The organic synthesis requires extensive use of protecting groups to obtain high selectivity. The selective enzymatic synthesis of sugar esters other than glucose has been difficult to achieve without the use of protective groups. Starting from sugar acetals and fatty acids, monoesters of sugars can be obtained in good yield, after a deprotection step, from several starting materials, both mono-and disaccharides. All sugar esters are very labile on the alkaline side and fairly stable to acid. Their degradation products, *i.e.* sugar and fatty acids, are both very natural products thus, sugar esters are ideal candidates as food surfactants. Sugar esters seem

to undergo rapid biodegradation regardless of the sugar head group size or the acyl chain length. Sulfonated sugar esters have also been prepared. These anionic surfactants were found to undergo less rapid biodegradation. Polyol surfactants have many attractive properties: they are mild to the skin, they exhibit a low aquatic toxicity and a high rate of biodegradation, and they are easy to work with in that they show good tolerance to high electrolyte concentrations.

1.4 Properties of sugar surfactants

Sugar-based surfactants are compounds of a very broad range of structural diversities. Sugars (monosaccharides, disaccharides etc.) may be connected to the hydrophobe at any of its hydroxyl groups and by different types of connecting linkages. Secondly, the hydrophilicity of sugar can be changed by oxidation, reduction or addition of hydrophilic groups, such as a sulfonic acid residue or a polyoxyethylene chain. Thirdly, the hydrophobic moiety or moieties can also be subjected to a wide array of changes.

Sugar surfactants have several rather flexible properties. Furthermore, sugar esters and sugar glycosides are generally non-toxic and non-cumulative. They are temperature insensitive as to their properties, in contrast to the like-wise non-ionic alkyl-PEG surfactants [20]. This means that sugar surfactants and other non-ionic surfactants complement each other in different applications. Non-ionic surfactants are not sensitive to the hardness of water [21]. The understanding of the surfactant properties of aqueous systems containing sugar surfactants is reasonably good and data about surface tensions, theoretical packing and CMCs exist for both the pure glycosides and mixtures with other surfactants or other compounds that affect the packing (often referred to as hydrotropes). The effects of structural elements on the CMC are known for non-ionics, the addition of two carbon atoms to the hydrocarbon chain of the surfactant decreases the CMC by a factor of 10, the addition of an ethylene oxide unit to PEG-based surfactants increases the CMC by a few percent and the addition of additional sugar head groups to sugar surfactants has only minor increasing or decreasing effects [22-23]. There are several indications that the

complex isomerism of the sugar head group determines the physico-chemical properties of alkyl polyglucosides [24-25]. Sugar surfactants are generally known to be good foaming agents [26]. Although equilibrium surface tensions are well-known for several sugar surfactants, little is known of their dynamic surface tensions. The mechanisms of adsorption of sugar surfactants, which are the forces responsible for detergency processes, wetting and dispersion, are also not fully understood, since only one dialkyl chain gluconamide has been studied so far [27]. It is known that the best detergent properties are found in branched hydrophobe surfactants, while they are also the least biodegradable ones [28]. Sugar surfactants with small hydrophobic moieties are known to be good hydrotropes [29-30]. For example, gluconamides are traditional hydrotropes, but are no longer used. Sugar surfactants with block co-polymers are good for the formation of emulsions and these are non-toxic, efficient and cheap [31].

Sugar surfactants are also known to be more lipophobic and hydrophilic than polyethylene oxide surfactants [32]. They have low organic solubilities and have low capacity of solubilizing the surfactant in oil media [33]. Sugar surfactants are known to be mild towards the skin [34] and possess lower hemolytic activity than other types of surfactants [35]. The structure-activity relationships of various glycosides are reasonably well understood and the differences in properties of α and β-glycosides and the effect of hydrophobe branching are explained [36]. Technical and biotechnological applications are expected to be of increasing importance [37].

1.5 Gluconamide (GA)

Several papers have been addressed upon the synthesis of sugar-based surfactants. The saccharide derivatives with amide linking groups are mostly prepared by reaction of aldonic acid or aldonolactone with amine or amino derivatives. The surfactants with two long-chain alkyl residues, also denoted as glycolipids [38], can be applied as cell or membrane units and modifiers [39]. Surprisingly such saccharide surfactants possess better solubility than the related compounds with one alkyl chain. It is assumed that this geometry destroys the hydrogen-bond network between the hydrophilic head groups. The better solubility of aldonamides containing an additional residue at the nitrogen atom in the amide group was previously reported by Pfannemüller and Welte and Syper et al [40].

Gluconamides have long been known and used in consumer products, were two methods of preparation are commonly used, differing in the solvents and temperatures only. The starting material is the commercially available D-(+)-glucono-1,5-lactone (or the aqueous equilibrium form D -gluconic acid). The lactone is aminolysed into a D-gluconamide by an amine in MeOH or DMSO [41]. Many gluconamides, including the *N*-octyl and *N*-decyl derivatives, have been used commercially as surfactants. Gluconamides with a fatty acid chain containing a heteroatom have been used as the surface active agents in certain shampoos, since they have good foaming properties [42]. The properties of primary gluconamides are quite well understood, while there is a notable lack of data on secondary gluconamide. D-gluconamides are generally prepared from D-glucose according to Figure 1.7.

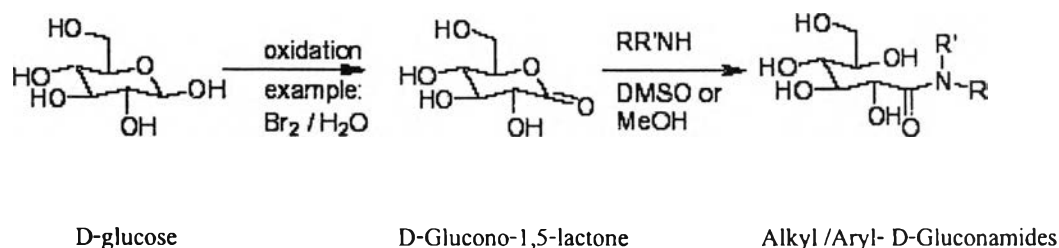| D-glucose | D-Glucono-1,5-lactone | Alkyl /Aryl- D-Gluconamides |

Figure 1.7 D-gluconamides prepared from D-glucose [41]

A large number of D-gluconamides were prepared and their surface properties were characterized. Most often, DMSO was used as solvent, although certain compounds required the use of MeOH for successful syntheses. Purification often consisted of evaporation of the solvent and recrystallization of the compound one to three times. A few compounds had to be purified chromatographically, *e.g. N,N*-diethyl-D-gluconamide. Secondary gluconamides required more purification work than primary ones. It was found that many of secondary D-gluconamides were not stable in aerobic environments and oxidized gradually.

1.6 Literature reviews

Gluconamide is sugar surfactant which isolated from D-(+)-glucono- 1,5-lactone prepared by reaction of aldonic acid or aldonlactone with amine. D-(+)-glucono- 1,5-lactone is prepared by direct crystallization from the aqueous solution of

gluconic acid, which generally prepared from D-glucose such as from oxidation of D-glucose with bromide water.

The synthesis and isolation of gluconic acid and surfactants from sugar have been reported in 1931 Isbell and Flush [43] isolated aldonic acid and bromide ion from the oxidation of bromide by oxidizing aldose by hypobromide as shown in scheme 1.1.
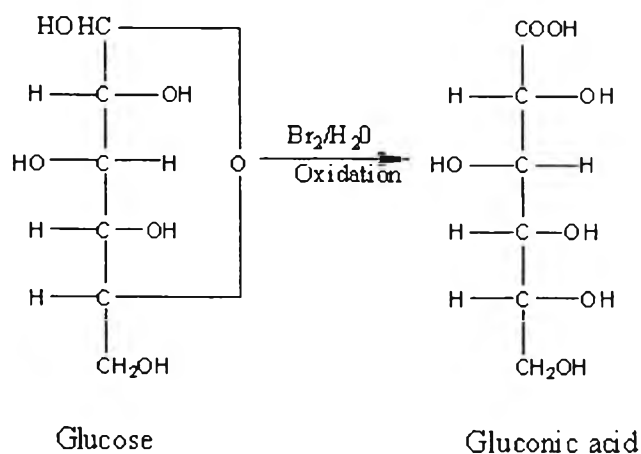

Scheme 1.1 Oxidation of glucose by hypobromite

In 1994 Choaksomboonkul and Aunsomboon [44] isolated gluconic acid which was synthesized from glucose by using electrolytic oxidation process synthesis of sodium gluconate for preparing gluconic acid.

In 1994 Roswitha and coworkers [45] synthesized N-(n-octyl)-6-deoxy-D-gluconamide and studied its crystal and molecular structure. N-(n-Octyl)-6-deoxy-D-gluconamide crystallizes in the orthorhombic space group with a = 5.4524(5), b = 16.662(3), and c = 36.897(5)A°. The structure was determined by X-ray diffraction and refined to R = 9.2%. The asymmetric crystal unit contains two molecules (A,B) with significantly different conformations. In contrast to the crystal structures of the N-(n-alkyl)-D-gluconamide family, in which the molecules were found arranged in head-to-tail monolayers, molecules A and B form a complex motif with pairwise alternating orientations and interdigitating antiparallel aliphatic chains. The two symmetry independent molecules form considerably different hydrogen bond patterns. Investigations with mannose exhibit different thermal behaviour of the C-6-OH and the C-6-deoxy form, and a comparison of 6-deoxy-L-mannose-S,S-diacyl-acetal with the stereoisomeric o-mannose form also shows a different thermic

behaviour. Deletion of the terminal hydroxyl group of mannose causes absence of a mesophase in a crystal-crystal transition.

In 1999 Bogdan and coworkers [46] synthesized and characterized surface properties of N-alkyl-N-methylgluconamides(MGA) and N-alkyl-N methyllactobionamides(MLA). The presence of a methyl group attached to the amide nitrogen in N-alkyl-N-methyl-gluconamide and lactobionamides increases the surfactants solubility in water. The determined 0.1% Krafft points, which are lower for the Cn-MLA than for the Cn-MGA series, show the latter to be less water soluble than the former at concentrations much higher than CMC. The presence of one double bond in the alkyl chain as in the oleyl-amides results in lower Krafft points than those containing the saturated C18 hydrocarbon chain and gluconic moiety was more surface active than the respective ones containing a disaccharide, i.e., a lactobionic group.
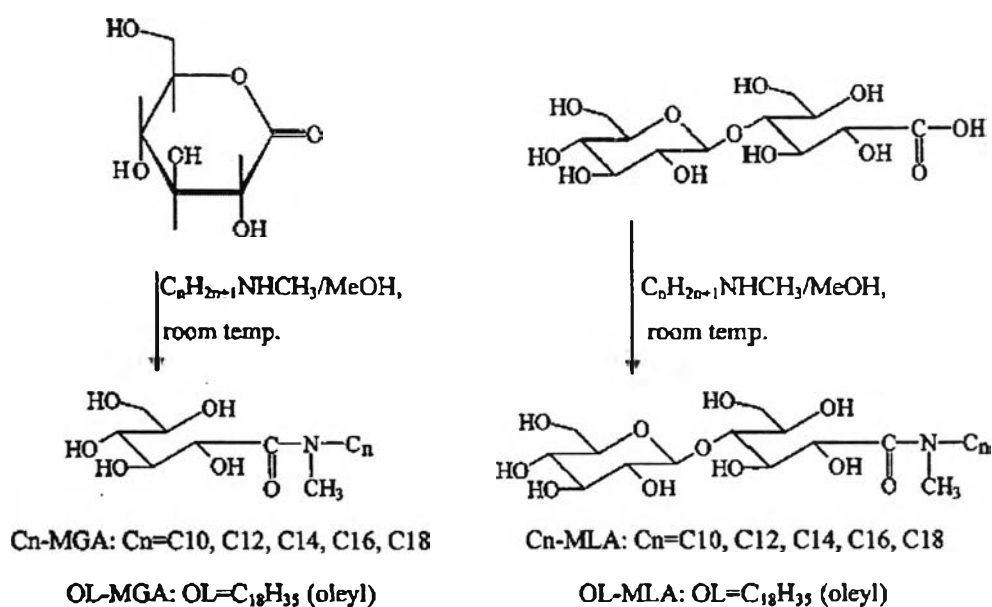

Scheme 1.2 Synthesized and characterized examined surface properties of N-alkyl-N-methylgluconamides and N-alkyl-N methyllactobionamides

In 2000, Baker and coworkers [47] demonstrated that sugar fatty acid esters could be used as a nonionic surfactant by varying the different-sized sugar head groups (glucose, sucrose, or raffinose) and different lengths and numbers of alkyl chains lauric (C12) or palmitic (C16) acid.

In 2001, Holmberg's [48] review, which has an emphasis on work published since1998, covers three categories of natural surfactants: amphiphiles produced by

yeast or bacteria, amphiphiles containing a natural polar headgroup and amphiphiles containing a natural hydrophobic tail. Microorganisms produce both high molecular weight and low molecular weight surfactants. Only the low molecular weight compounds are included in the review. Sugars and amino acids are the two most important examples of surfactant polar headgroups of natural origin. The research is particularly intense in the area of sugar surfactants and the review covers three types: alkylglucosides, alkylglucamides and sugar esters. Surfactants based on two types of natural hydrophobic tails are included: fatty acid monoethanolamides and sterol ethoxylates. Routes of preparation as well as physico-chemical properties are discussed for the surfactants prepared by organic synthesis. The surfactants based on either a natural polar headgroup or a natural hydrophobic tail show great promise for the future.

In the same year, Soultani and coworkers [49] synthesized *via* lipase-catalyzed synthesis of fatty acid sugar esters through direct esterification in 2-methyl-2-butanol. Fructose and saturated fatty acids were used as substrates and the reaction was catalyzed by immobilized *Cavdida antarctica* lipase.
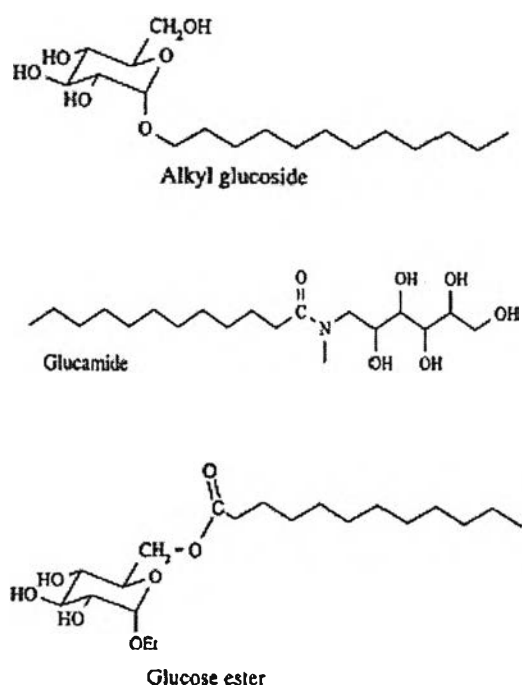
Scheme 1.3 Natural surfactants.

In 2002, Maruyama and coworkers [50] enzymatically synthesized sugar amino acid esters in polar organic solvents using surfactant-enzyme complexes, which were previously developed as a highly active biocatalyst in organic solvents. In the same year, Dofour and coworkers [51] reported three tests of increasing complexity to assess the antioxidant activity of five synthetic gallic esters of sucrose bearing 3, 6, 7, or 8 galloyl units. In the same year, Khanbabaee and Grober [52] reported the synthesis of natural 1,3-di-O-galloyl-4,6-O-(S)-hexahydroxydiphenoyl-β-D-glucopyranoside.

In 2004, Dorota and coworkers [53] studied the efficiency of surface-active N,N-di-n-alkyl-substituted amides derived from δ-D-gluconolactone and α-D-glucoheptonic-γ-lactone. The new synthesized N,N-di-n-alkylaldonamides showed a good ability to lower surface tension, despite their limited solubility in water. They do not form micelles in aqueous solutions. Their aqueous solutions reveal medium foamability. The N,N-di-n-alkylglucoheptonamide adsorption properties differ only slightly from those of the related N,N-di-n-alkylgluconamides. The surface performance of this group of saccharide surfactants seems to be improved with respect to the related aldonamides with one alkyl chain. The adsorption properties of the nonionic N,N-di-n-alkylaldonamides are quite different from those known for common single chain surfactants. The most remarkable feature of the former is the occurrence of a pronounced optimum in the surface parameters of cross-sectional area and surface interaction at chain lengths between $nC = 4$ and $nC = 6$. This feature not only is of considerable interest from the theoretical point of view but also suggests some special possibilities for practical application. Thus, for example, it is imaginable that foamability of surfactant solutions being mainly determined by the surfactants' adsorption properties could be monitored more precisely because the N,N-di-n-alkylaldonamides' surface properties change so dramatically by altering the alkyl chain by one methylene group only. The processes of foam stabilization and/or defoaming or any other process of application might then decisively be controlled by minor changes in the amphiphiles chain length.
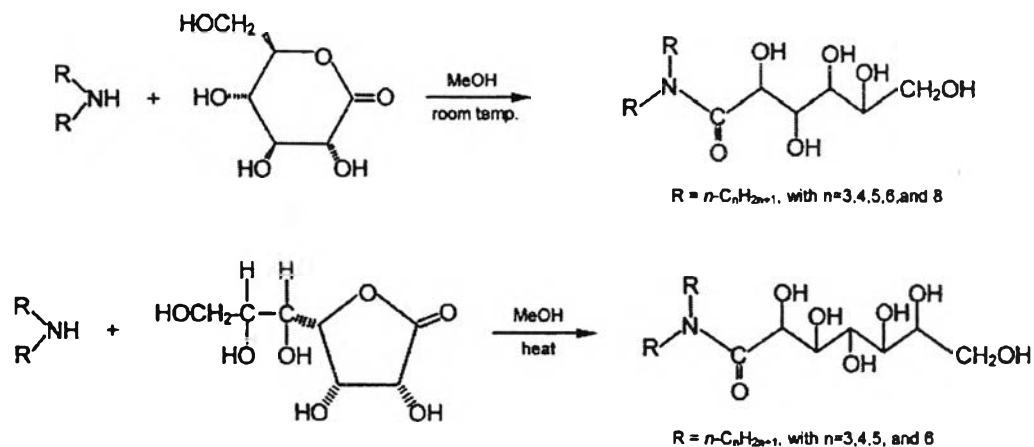
Scheme 1.4 The general synthetic routes for *N*,*N*-di-*n*-alkylaldonamides

1.7 Goal of this research

The aim of this research is to synthesize and investigate the properties of sugar-based surfactants. The approach involves the synthesis of derivatives containing amide linking groups mostly prepared by the reaction of aldonic acid or aldonolactone with selected amines. The goal of this research can therefore be summarized as follows:

1. To synthesize sugar-based surfactants with two symmetric *n*-alkyl chains as the hydrophobic group.

2. To study structure-activity relationships for the surfactants derived based on the structural elements of the hydrophobe.

3. To study the physical characteristics and surface properties based on the structural elements of the hydrophobe.