Synthesis and Application of Rosin-Based Surfactants

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5.1 Introduction

Surfactants are amphipathic molecules with both hydrophilic and hydrophobic moieties. The amphipathic structure makes them capable of reducing surface and interfacial tension, forming microemulsion and exhibiting some superficial or interfacial activity in solvents [1]. Since the advent of surfactants in the twentieth century, the use of surfactants has matured and there are now thousands of different kinds of surfactant products on the market for use in industry. The quality of our lives is closely related to the safe use of surfactants [2]. Nowadays, surfactants play an important role in almost every chemical industry, including detergents, emulsions, paints, foaming agents, paper products, cosmetics, pharmaceuticals and insecticides [3]. The worldwide production of surfactants was about 12 million tonnes in 2008 and the demand for them is expected to increase at a rate of 3% per year [4]. With the increasing concern for the need to save energy and protect the environment, renewable resources is a crucial area in the search for alternatives to fossil-based raw materials. In the surfactants field, common synthetic products from petrochemicals have often shown good functional properties, but they do not fulfill the requirements for environmental protection and sustainable development. There are millions of naturally occurring compounds which can be used as raw materials for the design of surfactants. They can incorporate special structures in the final products that may lead to surfactants with unexpected properties. The use of naturally occurring raw materials in surfactant synthesis is expected to provide new types of surfactants with better biodegradability. Further, in order to achieve long-term sustainable production, it will become necessary to use renewable sources [5]. The interest in designing highly specialised synthetic surfactants incorporating natural structural moieties has increased remarkably during the last few years [6]. The varieties of naturally occurring structures provide abundant selection for surfactant design. Some natural resources can provide hydrophilic groups, and some can provide a hydrophobic moiety. Renewable sources of hydrophilic groups include carbohydrates, proteins, amino acids and lactic acid, and sources of the hydrophobic moiety are steroids, monoterpenes, rosin acids, fatty
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acids and long chain alkyl groups, as well as aromatic compounds [7]. Rosin acids are a novel source of hydrophobic groups with a tricyclic hydrophenanthrene structure that can be used for the synthesis of surfactants with natural origins.

Since the first rosin-based surfactant (rosin acid sodium salt) was reported, the synthesis and application of rosin-based surfactants have attracted great attention [8]. Scientists from the United States, Japan, Germany and Russia carried out much work from the 1920s to the 1960s. After the 1970s, with the rise in labour costs for tapping in developed countries, the amount of gum rosin reduced greatly in those countries, they mostly focused on the application of rosin surfactants. However, from that time on, Chinese scientists have done much work in this field. In recent years, many new types of surfactants such as gemini and bora surfactants derived from rosin have been synthesised and their applications investigated. Rosin is an important natural resource, whose main components are resin acids, and they have attracted great interest for use in surfactant synthesis and applications because of their special chemical structures and wide range of applications. There are three kinds of rosin: gum rosin, wood rosin and tall oil rosin. Gum rosin occupies about 60% of the industrial market, wood rosin about 5% and tall oil rosin about 35%. The total world annual production volume of rosin has remained at 1.1-1.2 million tons since the 1990s. The most common pine resin acids have the molecular formula \(C_{20}H_{30}O_2\), [9]. Most pine resin acids belong to three basic skeletal classes: abietane, pimarane and isopimarane, and labdane. Rosin or modified rosin are widely used as sizes, adhesives, printing inks, emulsifiers, and these applications account for most of the rosin used in industry. Pine resin acids have been widely investigated, but the industrial use of them is low because of their high cost. With the development of science and technology, pure pine resin acids and their derivatives can be easily separated from commercial products on a large scale. For example, dehydroabiatic acid (DAA) can be isolated by crystallisation of the 2-aminoethanol salt from disproportionate rosin, and dehydroabietylamine can be isolated by crystallisation of the acetic acid salt from commercial disproportionate rosin amine [10]. Rosin and its derivatives are useful building blocks for the hydrophobic moiety of surfactants since they contain the tricyclic hydrophenanthrene structure, and hydrophilic groups can be introduced through reactions of carboxyl groups. The hydrophenanthrene can be obtained in enantiomerically pure form. Chiral surfactants from rosin can be used as chiral phase transfer catalysts and chiral separation agents. Surfactants with structures similar to derivatives of fatty acids, amines and alcohols, can be synthesised from rosin.

5.2 Synthesis of Rosin-based Surfactants

Classification of surfactants based on the charge characteristics of their polar (hydrophilic) head groups is commonly used. Like other surfactants, rosin-based
surfactants can be classified into four groups: cationic, anionic, zwitterionic and nonionic. Cationic surfactants are those that have a positive charge on their polar head group. Anionic surfactants are those that have a negative charge on their polar head group. Zwitterionic surfactants have the potential to have both positive and negative charges, depending on the environment in which they are placed. Nonionic surfactants have no charge on their head group. The methods for the synthesis of different kinds of rosin-based surfactants are summarised below.

5.2.1 Synthesis of Cationic Surfactants

The majority of rosin-based cationic surfactants are quaternary ammonium compounds, in which the nitrogen atom carries a positive charge. The preferred soluble anion is a halide or methyl sulfate ion and they have the structure of $N^+R_1R_2R_3R_4$ ($R_1, R_2, R_3$ and $R_4$ are substituted groups) [11]. There are two kinds of rosin-based cationic surfactants. One is an ester quaternary ammonium surfactant and the other, a dehydroabietylamine-derived quaternary ammonium surfactant. There are two methods to prepare rosin-based quaternary ammonium compounds. One is to quaternise a tertiary amine with a halide and most rosin-based cationic surfactants are synthesised by this method. The other is to graft rosin derivatives with active quaternary ammonium salts.

5.2.1.1 Rosin Acid-based Ester Quaternary Ammonium Salts

Rosin is a diterpenic monoacid with a tricyclic hydrophenanthrene structure. Due to the steric hindrance of the tricyclic hydrophenanthrene structure, the reactions on the carboxylic acid groups occur with some difficulties. Therefore, high temperature, catalyst and high pressure are required in some cases. However, this shortcoming can be overcome by changing the carboxylic acid to a more active acyl chloride intermediate. The acyl chloride reacts with $N,N$-dimethylethanolamine to form the corresponding amino ester using standard reaction conditions and then rosin-based ester quaternary ammonium compounds can be obtained after quaternisation by halide compounds using a standard procedure.

Radbil and co-workers used DAA or a mixture of rosin acids to synthesise quaternary ammonium compounds through chloride intermediates. Chlorides of resin acids prepared by phosphorus trichloride were esterified with $N,N$-dimethanolamine. The corresponding ester quaternary ammonium surfactants (C01-C04) were obtained after quaternisation with halide [12]. Their synthesis route is shown in Scheme 5.1.
Rosin-based surfactants can be designed through modification of the carboxylic acid group or hydrophenanthrene group in the molecule. The tricyclic hydrophenanthrene structure can be modified by an acrylic group through the Diels-Alder addition reaction, which produces dicarboxylic acids of rosin. Wang and co-workers reported that a novel bipyridine quaternary ammonium salt cationic surfactant (C05) was prepared by acrylic-modified rosin (Scheme 5.2). The intermediate reacted with thionyl chloride to form a chloride intermediate, after quaternisation to form rosin-based bora type dicationic compounds [13].

Under classical conditions, the reactions for synthesising cationic surfactants require a long reaction time (from 24 to 48 h) to complete the quaternisation reaction, which results in a lower total yield of the final products and the production of more byproducts. Microwave activation, as a nonconventional energy source, has become a very popular and useful technology in organic chemistry [14]. Chemical reactions brought about by microwave irradiation have gathered momentum in recent years mainly because of their simplicity, high yield, short time span, and ecofriendly conditions [15-16].

 Gemini surfactants have attracted great interest in recent years. They are made up of two amphiphilic moieties connected at the head group by a spacer group [17].
Surfactants have better surface active properties such as remarkably lower critical micelle concentration (CMC) values than corresponding conventional surfactants of equal chain length [18]. Jia and co-workers reported that a gemini surfactant with rosin-based hydrophenanthrene structure (C06) was synthesised by conventional thermal conditions and microwave irradiation, respectively (Scheme 5.3). The method of microwave irradiation greatly reduced the reaction time with better yield compared to the conventional method [19].

Scheme 5.3 Synthesis of gemini surfactant with rosin-based hydrophenanthrene structure (C06)

Rosin acids can react easily with the epoxy group under mild conditions. Epoxy chloropropane is the most widely used reagent to react with rosin and its derivatives, in order to provide a halide or epoxy intermediate to the rosin-based skeleton in an easy way. The intermediate can react with a tertiary amine in a standard procedure to prepare quaternary ammonium compounds. A halide intermediate can be formed from DAA and epoxy chloropropane (Scheme 5.4), after a standard quaternisation procedure to prepare quaternary ammonium compounds (C07) [20]. Wei and co-workers reported bora type bis-quaternary ammonium cationic surfactants (C08-C09) which were synthesised from acrylic-modified rosin as shown in Scheme 5.5 [21]. Chen and co-workers reported the synthesis of a new sulfodehydroabietic acid based on a bis-quaternary ammonium cationic surfactant (C10), which was synthesised by the sulfonation of DAA, followed by reaction with epoxy chloropropane and triethylamine (Scheme 5.6) [22]. Hu and co-workers reported the synthesis of a new gemini surfactant C10H2s-α,ω-Bis (dehydroabietylhydroxypropyltetra- methylethylammonium) chloride (C11) through an epoxy chloropropane intermediate (Scheme 5.7) [23].
Scheme 5.4 Synthesis of ester quaternary ammonium surfactant (C07)

Scheme 5.5 Synthesis of bora type bis-quaternary ammonium cationic surfactants (C08-C09)

Scheme 5.6 Synthesis of a sulfodehydroabietic acid-based surfactant (C10)


**Scheme 5.7** Synthesis of a gemini surfactant (C11) through epoxy chloropropane

Rosin acid reacted with epoxy chloropropane in alkaline conditions to form the corresponding ester with an epoxy group, which reacted with amine to form a tertiary amine, and then reacted with halide to form quaternary ammonium salt cationic surfactants (C12-C13, **Scheme 5.8**). Rosin acid reacted with an epoxy group quaternary ammonium salt to form cationic surfactants directly (C14) (**Scheme 5.9**) [20].

**Scheme 5.8** Synthesis of cationic surfactants (C12-C13) through epoxy chloropropane

**Scheme 5.9** Synthesis of a cationic surfactant (C14) directly
5.2.1.2 Dehydroabietylamine Derived Quaternary Ammonium Salts

The most widely used starting materials for the synthesis of rosin-based quaternary ammonium compounds are rosin amine or dehydroabietylamine [24]. Rosin amine or dehydroabietylamine can be used as starting materials to prepare tertiary amine in the presence of formaldehyde and formic acid, and then the rosin based quaternary ammonium salts can be prepared in a standard procedure called quaternisation. N,N-Dimethyldehydroabietylamine (DMDHA) is a very important intermediate for the synthesis of rosin-based cationic surfactants. There are two methods to synthesise DMDHA. It can be synthesised under mild conditions, in which dehydroabietylamine, formic acid and formaldehyde solution are refluxed together at a temperature of 65 °C for about 5-7 h, which gives a yield of 70-80%. The other method is hydrogenation by formaldehyde under pressure, which gives a yield of 89-94%. Ordinarily the first method is widely used because of the mild reaction conditions [25-27].

Wang and co-workers reported a series of quaternary ammonium salts (C15-C20) which were synthesised from dehydroabietylamine by the formic acid and formaldehyde method (Scheme 5.10) at atmospheric pressure [28]. Pan and co-workers reported four novel chiral quaternary ammonium salts (C21-C24) which were synthesised from dehydroabietylamine by the method shown in Scheme 5.11 [29]. Jia and co-workers reported the rosin-based quaternary ammonium gemini surfactants (C25-C28) which were synthesised from dehydroabietylamine by reaction with DMDHA and α, ω- bisbromoalkanes (Scheme 5.12) [30].

Scheme 5.10 Synthesis of cationic surfactants (C15-C20)
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Scheme 5.11 Synthesis of cationic surfactants (C21-C24) through DMDHA

Scheme 5.12 Synthesis of cationic gemini surfactants (C25-C28) through DMDHA

Rosin-based cationic surfactants can also be modified by incorporating polyethylene oxide chains. Dehydroabietylamine reacted with epoxy under pressure with a catalyst to form a tertiary amine, then the tertiary amine was quaternised with halide to form ethylene oxide quaternary ammonium salts (C29-C31) [31]. Their synthesis route is shown in Scheme 5.13.

Scheme 5.13 Synthesis of polyethylene oxide cationic surfactants (C29-C31)
Quaternary ammonium salts can also be introduced into the rosin skeleton directly. Cai and co-workers reported the direct synthesis of 3-dehydroabietylamino-2-hydroxypropyl trimethyl ammonium chloride (C32) from dehydroabietylamine and 3-chloro-2-hydroxypropyl trimethyl ammonium chloride in the presence of an acid-binding agent loaded on to alumina (Scheme 5.14) [32].

Scheme 5.14 Synthesis of cationic surfactant (C32) directly

5.2.2 Synthesis of Anionic Surfactants

Anionic surfactants are the most widely used class of surfactants in industry. There are four kinds of hydrophilic groups (carboxylates, sulfates, sulfonates and phosphates) for rosin-based anionic surfactants, with the tricyclic hydrophenanthrene structure as the hydrophobic group. A general formula may be ascribed to rosin based anionic surfactants: Carboxylate: RCOO-X; Sulfate: ROO-SO3-X; Sulfonate: RSO3-X; Phosphate: ROPO(OH)O-X; R is the rosin-based tricyclic hydrophenanthrene group and X is Na or K.

Carboxylates were the earliest rosin-based surfactants. They consist of rosin soaps, e.g., sodium, potassium or calcium rosin soaps (A01) (Scheme 5.15). The rosin is saponified by addition of a base so that it becomes soluble in water. Since the first report of rosin soap as an anionic surfactant by Strassbury in 1919, these compounds have been widely used as paper sizing agents and in rubber production [20]. Rosin acids can be modified into multicarboxylic acids by the Diels-Alder addition reaction. Wang and co-workers reported that a new type of chiral surfactant, sodium maleopimaric acid (SMA) (A02), was synthesised from rosin and maleic anhydride adduct compounds and then reacted with sodium hydroxide solution by the method shown in Scheme 5.16 [33]. Compared with rosin soap, SMA has three carboxylates in the tricyclic structure.
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Scheme 5.15 Synthesis of rosin soaps (A01)

Scheme 5.16 Synthesis of sodium maleopimaric acid (A02)

Sulfate surfactants (A03-A05) are often prepared by the esterification of hydroxyl derivatives of rosin by sulfonate reagents. Chlorosulfonic acid was chosen as a sulfonating reagent to react with rosin-based alcohol. After neutralisation by an alkali or tertiary amine, rosin-based anionic surfactants were obtained (Scheme 5.17). Concentrated sulfuric acid was also chosen as a sulfonating reagent to react with rosin-based alcohol [34].

Scheme 5.17 Synthesis of sulfate surfactants (A03-A05)
Sulfonate surfactants contain a sulfur atom which is directly attached to the carbon atom of the alkyl group, giving the molecule stability against hydrolysis compared with the sulfate surfactants. There are three methods to introduce the sulfonate group into rosin and its derivatives: the first one is to sulfonate the hydroxyl groups directly with sulfonating agent such as concentrated sulfuric acid, the second is to add sulfate salt to the double bonds of rosin derivatives and the third one is to react the rosin derivative with a functional group containing a sulfonate group. DAA has an aromatic ring, which provides another group for preparing sulfonate anionic surfactants. Chen and co-workers reported a new unsymmetrical bora form surfactant, (disodium sulfodehydroabietate [A06]) which was synthesised by sulfonation of dehydroabietic acid followed by neutralisation (Scheme 5.18) [35].

**Scheme 5.18** Synthesis of bora form sulfonate surfactant (A06)

The most widely studied of rosin-based anionic surfactants are sulfonate salts, which are usually prepared by reacting rosin acid or rosin amine with alcohol. The terminal hydroxyl group is then esterified with maleic anhydride (MA), followed by the addition of sulfate to the double bond to form the corresponding sulfonate anionic surfactants (Scheme 5.19). Rosin, rosin amine or dehydroabietylamine, rosin hydroxyl ethyl amide and acrylic rosin can be ethoxylated by epoxy and the terminal hydroxyl group can be esterified by MA, after addition of sulfate to the double bond to form corresponding sulfonate anionic surfactants (A07-A11) [36, 37].
Scheme 5.19 Synthesis of sulfonate anionic surfactants (A07-A11)
The mono- or diester of MA can be obtained by controlling the ratio of polyoxyethylene and MA during the reaction. Anionic surfactants of rosin alcohol polyoxyethylene monoether sodium monosulfosuccinates (A12) can be synthesised by two steps of reactions (Scheme 5.20). The influence of the degree of polymerisation of ethylene oxide on the physical and chemical properties of the products was also studied [38]. The sodium sulfosuccinate diester of disproportionated rosin alcohol polyoxyethylene ether (A13) can be synthesised from disproportionated rosin alcohol polyoxyethylene ether by changing the molar ratio of the two reaction components (Scheme 5.21) [39].

Rosin acids can be changed into acid chlorides, salts and amines, which greatly improve the reactivity. The chlorides, salts and amines can be reacted with a sulphonate-containing alcohol (Scheme 5.22) to form sulfonate surfactants under ambient conditions (A14-A16). Jia and co-workers reported using dehydroabietylamine, α, ω-dibromoalkane and sodium 2-bromoethylsulfonate as raw materials (Scheme 5.23) for synthesising new gemini anionic surfactants (N, N′-Sodium-2-diethylsulfonate-N, N′-didehydroabietate- α ω-diamines [A17]). [40]
Alkyl phosphates are made by treating the ester ethoxylates of rosin with a phosphorylating agent, usually phosphorous pentoxide. The reaction yields a mixture of mono- and diesters of phosphoric acid. Wang and co-workers reported (Scheme 5.24) that a phosphate anionic surfactant was synthesised by phosphorylating polyoxyethylene abietate (A18) using phosphorus pentoxide as the phosphorylating. Polyoxyethylene abietate was prepared from disproportionated rosin and ethylene oxide [41].
5.2.3 Synthesis of Zwitterionic Surfactants

When a single surfactant molecule exhibits both anionic and cationic dissociations it is called zwitterionic [42]. The main characteristic of zwitterionic surfactants is their dependence on the pH value of the solution in which they are dissolved. In acid solutions, the molecule acquires a positive charge and behaves like a cationic surfactant, whereas in alkaline solutions it becomes negatively-charged and behaves like an anionic one [43].

The majority of rosin-based zwitterionic surfactants are amino acids, including amino carboxylic acids, amino sulfonatic acids and amino phosphonic acids. Cui and co-workers reported three new betaine-type amphoteric surfactants, N-(2-dehydroabietyloxy)ethyl-N,N-dimethyl carboxymethyl betaine, N-(2-dehydroabietyloxy)ethyl-N,N-dimethyl sulfoxpropyl betaine and N-(2-dehydroabietyloxy)ethyl-N,N-dimethyl phosphate betaine (Z01-Z03), which were synthesised using DAA as starting material (Scheme 5.25) [44].

![Scheme 5.25 Synthesis of betaine-type amphoteric surfactants (Z01-Z03)](image)

Rosin-based amino acids are widely investigated zwitterionic surfactants. Rosin acid and dehydroabietylamine can be used as raw materials for the synthesis (Scheme 5.26) of this kind of surfactant (Z04-Z08). Rosin acid chloride can react with an amino acid to form zwitterionic surfactants. This reaction can take place with different kind of amino acids to form different kinds of zwitterionic surfactants. Liu and co-workers reported that abietinylglycine was synthesised by the reaction of glycine and abietic chloride in a water/aceton system and the reaction was accelerated by a phase transfer catalyst. Benzyl trimethylammonium bromide was a good catalyst and pyridine was a good base for the reaction [45]. Fang and co-workers reported using disproportionated rosin and sarcosine as the main starting materials to prepare disproportionated rosinoyl sarcosine through a chloride intermediate in the same way [46, 47].
Rosin-based aminosulfonic acids are the other important zwitterionic surfactants. A quaternary ammonium salt derived from DAA, epichlorohydrin and trimethylamine can be reacted with concentrated sulfuric acid to form (Scheme 5.27) a zwitterionic surfactant (Z09) [48]. Zhao and co-workers reported (Scheme 5.28) the synthesis of 3-[(3-dehydroabietamidopropyl)dimethylammonio]-1-propanesulfonate (DHAMAP) (Z10), a new type of chiral surfactant, from DAA. The ability of this compound to perform chiral separation of amino acids has been investigated by capillary electrophoresis (CE) [49]. Wang and co-workers reported a new chiral derivatising
reagent (Scheme 5.29), dehydroabietylisothiocyanate (DHAIC), which can be used for the enantiomeric separation of chiral compounds in capillary electrophoresis (CE) (Z11) [50].

Scheme 5.27 Synthesis of a zwitterionic surfactant (Z09)

Scheme 5.28 Synthesis of DHAMAP (Z10)

Scheme 5.29 Synthesis of DHAIC (Z11)
5.2.4 Synthesis of Nonionic Surfactants

A nonionic surfactant has no charge groups on its head. As a consequence, these surfactants are much less sensitive to electrolytes, and can be used in high salinity conditions or hard water [11]. The most common nonionic surfactants are those based on ethylene oxide and are referred to as ethoxylated surfactants. Several classes can be distinguished: rosin acid ethoxylates, rosin alcohol ethoxylates, monoalkanolamides ethoxylates and rosin amine ethoxylates. The other kind of rosin-based nonionic surfactant is a sugar-based surfactant; in which glucose and sucrose were introduced to the basic skeleton of rosin. Another important class of nonionic surfactant comprises multihydroxyl products such as glycol esters and poly glycerol esters. Specialty surfactants such as silicone and ether crown surfactants have also been reported.

The most common nonionic surfactants are those based on ethylene oxide and are prepared by the addition of ethylene oxide to carboxylic acid, primary or secondary amines, alcohol or monoalkanolamide, or by the reaction of rosin acid with polyethylene glycol (PEG) (Scheme 5.30) with different molecular weights to form surfactants (N01-N06) [20].
Scheme 5.30 Synthesis of nonionic surfactants based on ethylene oxide (N01-N06)
The hydroxyl group of rosin ester can also be esterified. Wei and co-workers reported the synthesis of hydrogenated rosin-polyethylene glycol ester (N07) under microwave irradiation (Scheme 5.31). The reaction time using microwave irradiation was shorter than when the conventional heating method was used [51]. Then, the target product hydrogenated rosin-polyethylene glycol-citric acid ester (N08) (Scheme 5.32) was prepared by further esterification of the intermediate with citric acid. Wei and co-workers reported the preparation of disproportionated rosin-polyethylene glycol ester using the same method [52].

Sugar is a green, natural hydrophilic building block for surfactants and for this reason, surfactants based on sugar are attracting a great deal of attention. Glucose and sucrose were introduced into the skeleton of rosin by different kinds of reaction. Xu and co-workers reported that glucose dehydroabietate (N09) was synthesised by O-acylation of dehydroabietyl chloride with glucose in the presence of an ionic liquid 1-butyl-3-methylimidazolium bromide as a green reaction solvent (Scheme 5.33). The catalyst could be recycled and used for three times [53]. Cen and co-workers reported
that the acid chloride of rosin reacted with sucrose to form the corresponding ester (N10) (Scheme 5.34) [54]. They also reported using rosin as the raw material for the synthesis of rosin glycid diethanolamine propenoic acid sucrose ester (N11) (Scheme 5.35) [55]. Mehltretter and co-workers reported that rosin amine reacted with gluconolactone to form the corresponding glucose rosin nonionic surfactant (N12) (Scheme 5.36) [56].
The hydrophilicity of glycerol is weak but it can be improved by polymerisation reactions. Rosin-based polyglycerol (N13) nonionic surfactants with different degrees of polymerisation of polyglycerol were obtained (Scheme 5.37) by an esterification reaction [57]. Wang and co-workers reported that the nonionic surfactant polyglycerol maleated rosin ester (N14) was synthesised by the reaction of maleated rosin and polyglycerol (Scheme 5.38). The relationships between the surface physicochemical properties of the product and the degree of polymerisation of polyglycerol were studied systematically [58].
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Specialty surfactants such as silicone surfactants can lower the surface tension of water to below 20 mN/m. Silicone surfactants are sometimes referred to as ‘superwetters’ as they cause enhanced wetting and spreading in aqueous solution [59]. However, they are much more expensive than conventional surfactants and are only used for specific applications for which low surface tension is a desirable property. Silicone-modified rosin-based surfactants (N15) can be synthesised from rosin acid chloride (Scheme 5.39) [20].

\[
\text{Scheme 5.39 Synthesis of silicone modified rosin (N15)}
\]

Azacrown ethers are new functional compounds. They have specific surface activities, catalytic activities, complex selectivity and good adsorption properties for many heavy or precious metal ions. Yang and co-workers [60] reported the synthesis of three chiral azacrown ethers from rosin: N-dehydroabietyl monoaza-15-crown-5 (N16), N-dehydroabietyl monoaza-18-crown-6 (N17) and N-nor-dehydroabietyl monoaza-12-crown-4 (N18) (Scheme 5.40). Dehydroabietylamine and nor-dehydroabietylamine can react with ether diiodide to form the corresponding azacrown ethers. Hydroxyl derivatives of rosin reacted with tosylate to form the corresponding azacrown ethers. The azacrown ethers can be employed as phase transfer catalysts in the asymmetric Michael addition of 2-nitropropane to chalcone.
5.3 Physicochemical Properties

5.3.1 Physical Properties

The physical properties of rosin-based surfactants change significantly when different hydrophilic groups are attached to the rosin skeleton [1]. The most important change is their critical micelle concentration (CMC) and surface tension at critical micelle concentration ($\delta_{\text{CMC}}$) values. Each surfactant molecule has a characteristic CMC at a given temperature and electrolyte concentration. The most common technique for measuring the CMC is by determining the surface tension.
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Table 5.1 lists some of the physical properties of cationic rosin-based surfactants. Their surface activities were compared with that of the widely used cationic surfactant, benzalkonium bromide. The CMC values of most cationic quaternary ammonium compounds such as C01-C04 are between $10^{-4}$-$10^{-3}$ mol/L with $\delta_{\text{CMC}}$ values between 32-50 mN/m. However, the rosin-based cationic gemini surfactants, such as C06, C25-C28, exhibited lower CMC values, which were near $10^{-5}$ mol/L with $\delta_{\text{CMC}}$ values between 23-31 mN/m. Gemini surfactants had a low $\delta_{\text{CMC}}$ and CMC value, and the CMC of these was about two orders of magnitude lower than the corresponding conventional surfactants with the same alkyl chain length.

![Table 5.1 Physical properties of rosin based cationic surfactants](image)

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>$\delta_{\text{CMC}}(25^\circ\text{C})(\text{mN/m})$</th>
<th>CMC (mol/L)</th>
<th>FP(0/5min) (mm)</th>
<th>EP (Benzene) (°C)</th>
<th>KP (°C)</th>
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</thead>
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<td>—</td>
</tr>
<tr>
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<td>—</td>
<td>—</td>
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</tr>
<tr>
<td>C05</td>
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<td>45/40</td>
<td>5 d</td>
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<td>89/54</td>
<td>30 s</td>
<td>60-65</td>
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<tr>
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<td>$1.0\times10^{-4}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>C11</td>
<td>37.5</td>
<td>$5.3\times10^{-4}$</td>
<td>85/65</td>
<td>2480 s</td>
<td>90</td>
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<td>—</td>
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<tr>
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<td>140/90</td>
<td>20 m</td>
<td>&lt;0</td>
</tr>
</tbody>
</table>
Table 5.2 shows the physical properties of some rosin-based anionic surfactants, and their surface activities were compared with that of widely used anionic surfactant of sodium dodecyl sulfate (K12) and alcohol ether sulfate (AES). The $\delta_{\text{CMC}}$ of most anionic surfactants were between 24 and 40, and their CMC values were between $10^{-4}$-$10^{-3}$ mol/L. Rosin-based anionic gemini surfactants also showed better CMC and $\delta_{\text{CMC}}$ values than conventional ones.
### Table 5.2 Physical properties of rosin based anionic surfactants

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>$\delta_{\text{CMC}}$ (25 °C) (mN/m)</th>
<th>CMC (mol/L)</th>
<th>FP (0/5min)/mm</th>
<th>EP min</th>
<th>KP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A06</td>
<td>50.63</td>
<td>24.5×10^{-3}</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>A07(n=5)</td>
<td>36.5</td>
<td>6.1×10^{-3}</td>
<td>130/90</td>
<td>14</td>
<td>&lt;0</td>
</tr>
<tr>
<td>A07(n=10)</td>
<td>37.5</td>
<td>3.3×10^{-3}</td>
<td>130/90</td>
<td>17</td>
<td>&lt;0</td>
</tr>
<tr>
<td>A07(n=19)</td>
<td>41.0</td>
<td>1.4×10^{-3}</td>
<td>115/20</td>
<td>21</td>
<td>&lt;0</td>
</tr>
<tr>
<td>A08(n=6)</td>
<td>33.1</td>
<td>6.2×10^{-3}</td>
<td>138/135</td>
<td>10</td>
<td>&lt;0</td>
</tr>
<tr>
<td>A08(n=10)</td>
<td>34.2</td>
<td>4.4×10^{-3}</td>
<td>132/129</td>
<td>89</td>
<td>&lt;0</td>
</tr>
<tr>
<td>A08(n=20)</td>
<td>37.0</td>
<td>2.1×10^{-3}</td>
<td>129/124</td>
<td>85</td>
<td>&lt;0</td>
</tr>
<tr>
<td>A09(n=9)</td>
<td>38.2</td>
<td>5.3×10^{-3}</td>
<td>112/109</td>
<td>17</td>
<td>&lt;0</td>
</tr>
<tr>
<td>A10(n=10)</td>
<td>39.7</td>
<td>—</td>
<td>120/10</td>
<td>10</td>
<td>&lt;0</td>
</tr>
<tr>
<td>A11</td>
<td>24.74</td>
<td>0.8×10^{-3}</td>
<td>145/145</td>
<td>9</td>
<td>—</td>
</tr>
<tr>
<td>A15</td>
<td>—</td>
<td>1.1×10^{-4}</td>
<td>—</td>
<td>—</td>
<td>&lt;0</td>
</tr>
<tr>
<td>A16</td>
<td>—</td>
<td>1.6×10^{-4}</td>
<td>—</td>
<td>—</td>
<td>&lt;0</td>
</tr>
<tr>
<td>A17(n=2)</td>
<td>31.0</td>
<td>3.2×10^{-4}</td>
<td>2/0</td>
<td>20</td>
<td>&lt;0</td>
</tr>
<tr>
<td>A17(n=4)</td>
<td>28.6</td>
<td>2.9×10^{-4}</td>
<td>2/0</td>
<td>30</td>
<td>&lt;0</td>
</tr>
<tr>
<td>A17(n=6)</td>
<td>29.4</td>
<td>1.8×10^{-4}</td>
<td>60/40</td>
<td>60</td>
<td>&lt;0</td>
</tr>
<tr>
<td>A17(n=8)</td>
<td>28.1</td>
<td>1.3×10^{-4}</td>
<td>2/0</td>
<td>20</td>
<td>&lt;0</td>
</tr>
<tr>
<td>K_{12}</td>
<td>33</td>
<td>8.1×10^{-3}</td>
<td>175/170</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>AES</td>
<td>28</td>
<td>3.7×10^{-3}</td>
<td>175/168</td>
<td>13</td>
<td>&lt;0</td>
</tr>
</tbody>
</table>

K_{12} - sodium dodecyl sulfate
AES - alcohol ether sulfate

Data adapted from references [20, 35-37, 40]

Table 5.3 shows the physical properties of some rosin based zwitterionic surfactants. The $\delta_{\text{CMC}}$ of most zwitterionic surfactants were between 24 and 40, and their CMC values were near $10^{-3}$ mol/L.
<table>
<thead>
<tr>
<th>Surfactants</th>
<th>$\delta_{\text{CMC}}$(25 °C) (mN/m)</th>
<th>CMC (mol/L)</th>
<th>FP(0/5 min) mm</th>
<th>EP min</th>
<th>KP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z01</td>
<td>21.3</td>
<td>$1.39\times10^{-3}$</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Z02</td>
<td>31.91</td>
<td>$3.16\times10^{-3}$</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Z03</td>
<td>33.20</td>
<td>$3.01\times10^{-3}$</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Z04</td>
<td>25.79</td>
<td>$2.56\times10^{-3}$</td>
<td>88/81</td>
<td>13</td>
<td>--</td>
</tr>
<tr>
<td>Z06</td>
<td>--</td>
<td>$5.16\times10^{-3}$</td>
<td>88/81</td>
<td>13</td>
<td>--</td>
</tr>
<tr>
<td>Z07</td>
<td>53.25</td>
<td>$9\times10^{-1}$</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Z09</td>
<td>35.0</td>
<td>$2.0\times10^{-3}$</td>
<td>150/90</td>
<td>1.5</td>
<td>&lt;0</td>
</tr>
<tr>
<td>Z10</td>
<td>36.5</td>
<td>$1.3\times10^{-3}$</td>
<td>130/60</td>
<td>2.0</td>
<td>&lt;0</td>
</tr>
</tbody>
</table>

Data adapted from references [20, 35-37, 40]

Table 5.4 shows the physical properties of some rosin based nonionic surfactants. The $\delta_{\text{CMC}}$ of most anionic surfactants are near 40, and their CMC values are near $10^{-3}$ mol/L. Rosin-based nonionic surfactants with different degree of polymerisation were investigated in detail and the results showed that their CMC values were near $10^{-4}$ mol/L and the $\delta_{\text{CMC}}$ values were between 32-40 mN/m.

### 5.3.2 Phase Behaviour

The theoretical study of rosin-based surfactants has attracted little attention in recent years. Compared with fatty acid as a hydrophobic group, the tricyclic hydrophenanthrene structure may show different phase behaviour.

Persson and co-workers investigated [61] the phase behaviour of two rosin-based nonionic surfactants, polyoxyethylene dehydroabietates (DeHAb(EtO)) with polyoxyethylene chains of 11 and 22, in water and decanol system (Figure 5.1). DeHAb(EtO)$_{11}$ is completely miscible with water but has a low capacity for solubilisation of decanol. However, at DeHAb(EtO)$_{22}$ surfactant concentrations of 0-25%, the maximum solubilisation capacity for decanol represents a nearly constant ratio between the amount of solubilise and surfactant. The results showed that the two rosin-based surfactants behave similarly to nonionic surfactants with a hydrophobic aliphatic carbon chain and a polyethylene oxide chain as the hydrophilic group. However, the acyclic surfactant has a good solubilising capacity for most
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compounds. In both systems, a lamellar liquid crystalline phase is formed, indicating that the surfactants have lamellar structures in the system.

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>$\delta_{\text{CMC}}$</th>
<th>CMC (mol/L)</th>
<th>FP(0/5min)</th>
<th>EP (min)</th>
<th>TP (°C)</th>
<th>HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td>N01(n=10)</td>
<td>34.6</td>
<td>2.9×10^{-4}</td>
<td>45/39</td>
<td>4.8</td>
<td>59</td>
<td>11.0</td>
</tr>
<tr>
<td>N01(n=19)</td>
<td>36.4</td>
<td>4.5×10^{-4}</td>
<td>82/76</td>
<td>4.6</td>
<td>77</td>
<td>14.9</td>
</tr>
<tr>
<td>N02(n=10)</td>
<td>32.7</td>
<td>1.0×10^{-4}</td>
<td>80/77</td>
<td>5.3</td>
<td>&gt;10</td>
<td>—</td>
</tr>
<tr>
<td>N02(n=20)</td>
<td>35.1</td>
<td>2.4×10^{-4}</td>
<td>80/76</td>
<td>5.3</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>N03(n=9)</td>
<td>35.0</td>
<td>2.3×10^{-4}</td>
<td>78/76</td>
<td>4.8</td>
<td>71</td>
<td>—</td>
</tr>
<tr>
<td>N04(n=10)</td>
<td>36.8</td>
<td>—</td>
<td>80/74</td>
<td>4.9</td>
<td>46</td>
<td>—</td>
</tr>
<tr>
<td>N05-200</td>
<td>37.7</td>
<td>—</td>
<td>&gt;150</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>N05-1000</td>
<td>37.6</td>
<td>—</td>
<td>25.8</td>
<td>80</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>N07</td>
<td>42.0</td>
<td>—</td>
<td>18.5/—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>N08</td>
<td>41.5</td>
<td>—</td>
<td>17/—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>N10</td>
<td>50.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>N11</td>
<td>22.9</td>
<td>9×10^{-3}</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>N13</td>
<td>44.2-49.6</td>
<td>8.4×10^{-4}</td>
<td>6-46/</td>
<td>44-85</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>N14</td>
<td>39.9-46</td>
<td>9.4×10^{-4}</td>
<td>11-65/</td>
<td>38-100</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>C_{12}EO(n=10)</td>
<td>37.0</td>
<td>—</td>
<td>140/100</td>
<td>—</td>
<td>53</td>
<td>13.9</td>
</tr>
</tbody>
</table>

TP – Cloud point

Data adapted from references [20, 51, 52, 54, 55, 57, 58]
Jiang and co-workers [62] reported that critical aggregation numbers of micelles (N) of rosin-modified quaternary ammonium gemini surfactants (C25-C27) were determined by a steady-state fluorescence probe method. The results showed that N increased linearly with the increase of the surfactant concentration in a range of 5-15 times CMC and critical aggregation numbers of micelle (Nm) can be extrapolated from the N—C curve, which were 10, 19, and 20 for C25, C26 and C27 respectively.

5.4 Applications

5.4.1 Paper Sizing and the Rubber Industry

Rosin acids are tacky solids at room temperature. Saponify the rosin by addition of base so that it becomes soluble in water and it then can be added effectively to a paper machine. Different industries use gum rosin in varying amounts as is indicated in Figure 5.2. Soap production, paper making and the synthetic rubber industry consume large amounts of rosin [63].
Most rosin soaps have water-loving carboxylate groups, and the remainder of the rosin molecule has a water-hating hydrocarbon group. The rosin soap exists as micelles in solution, and the groups of soap molecules associate with each other so that the water-hating parts face each other to avoid contact with water. Aluminum compounds are needed for paper making furnish. Aluminum ions react with the carboxylate groups in the rosin, which causes the rosin to precipitate on to the fibre surface. The recommended pH conditions for rosin soap sizing are dictated by the effect of pH on the predominant species of the aluminum ions. Low pH conditions favour the presence of trivalent aluminum, a hydrated form of Al\(^{3+}\). This is the species that appears to be most useful for the retention and setting of rosin soap size [64].

Rosin soaps are designed for use as an emulsifier in the polymerisation of styrene-butadiene rubber and other synthetic rubbers. It was used for the polymerisation of styrene-butadiene rubber emulsifiers. When dispersed in the aqueous phase of the monomer emulsion they facilitate micelle formation, thereby forming stable monomers. Rosin calcium soap is used in paints. Lead, cobalt and manganese have been used traditionally as driers in these paints.

### 5.4.2 Antibacterial Activity

The antibacterial activity of rosin-based surfactants has been mostly focused on cationic surfactants (quaternary ammonium salts). Quaternary ammonium salts are frequently used as antibacterial agents because they can disrupt cell membranes.
through the binding of their ammonium cationic groups to anionic sites in the outer tissue layers of bacteria [65]. As a result of the combination of their tricyclic hydrophenanthrene structure and quaternary ammonium group, rosin-based cationic surfactants exhibit good antibacterial activity.

Quaternary ammonium salts (C01-C04) were tested by the standard procedures of measuring the zone of microorganism growth suppression. Their activities were similar to widely used biocides, such as triclosan, aseptodin and biopag-2. They exhibited strong antibacterial and antifungal activities [12].

Wang and co-workers reported that six dehydroabietylamine-based cationic surfactants exhibited antibacterial activity against Staphylococcus aureus (S. aureus) and Escherichia coli. The activity of C16 against S. aureus is similar to that of benzalkonium bromide; the minimum inhibitory concentration (MIC) reached 7.81 μg/mL [28].

Jia and co-workers reported that N,N,N′,N′-tetramethyl N,N′-diethanolamine dehydroabietate diamine dibromide and N,N,N′,N′-tetramethyl N,N′-didehydroabietate diamine dibromide had antibacterial activity against E. coli, Klebsiella pneumoniae (K. pneumoniae), Enterobacter aerogenes (E. aerogenes), S. aureus, Staphylococcus epidermidis (S. epidermidis), Pseudomonas aeruginosa (P. aeruginosa), and Salmonella typhi (S. typhi). In particular, N,N,N′,N′-tetramethyl N,N′-diethanolamine dehydroabietate diamine dibromide showed marked antibacterial activities against E. aerogenes, S. aureus, S. epidermidis and P. aeruginosa; the minimum inhibitory concentrations were 16-64 μg/mL [66].

Cai and co-workers reported that antibacterial activity of 3-dehydroabietylamo-2-hydroxypropyl trimethylammonium chloride (DHAHPTMA) (C32) was evaluated according to its minimum inhibitory concentrations against S. aureus, S. epidermidis, Clostridium perfringens, K. pneumoniae, E. coli, P. aeruginosa and Salmonella. The results (Figure 5.3) indicated that DHAHPTMA exhibited good antibacterial activity; the minimum inhibitory concentrations of DHAHPTMA against S. aureus, S. epidermidis and E. coli were lower than that of bromo-geranium and higher than ofloxacin against theses bacteria [32].
Rosin-based Chemicals and Polymers

![Antibacterial Activity Graph](image)

**Figure 5.3** Antibacterial activity of (C32) compared with bromo-geranium and ofloxacin, the data adapted from reference [32]

### 5.4.3 Corrosion Inhibition

Inhibition of metal corrosion by organic compounds is a result of the adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer reduces or prevents corrosion of the metal. The extent of adsorption depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor, and the type of corrosion medium [67].

Rosin-based cationic surfactants exhibited corrosion inhibition activity. Wang and co-workers reported [28] their corrosion inhibition activities against steel, which were investigated in hydrochloric acid solution by the weight loss method. Six kinds of cationic surfactants which acted as corrosion inhibitors are listed in Table 5.5. Most of them exhibited higher activity than benzalkonium bromide. The inhibition ratio reached 99.1% for C20 compared with 93.0% for benzalkonium bromide.

Rosin-based nonionic surfactants also exhibited anticorrosion activity. A series of $N,N$-polyoxyethylene dehydroabietylamines (N02) with different numbers of oxyethylene units (n) were used as corrosion inhibitors for metals (Table 5.5) [20]. The relationships between performance and chemical structure of the products were investigated. The corrosion inhibition activities of the rosin-based nonionic surfactants with fewer than 20 ethylene oxide units were higher than that of benzalkonium bromide. The inhibition rate reached 95.1% for surfactants with 15 ethylene oxide units. However the hydroxyl amides of rosin acids (N03) had a little lower activity than the above products, and their inhibition activity was equal to that of benzalkonium bromide.
Table 5.5 Corrosion inhibition of some rosin-based cationic surfactants

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>Corrosion rate (mm/year)</th>
<th>Corrosion inhibition rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>17.83</td>
<td>—</td>
</tr>
<tr>
<td>C15</td>
<td>0.25</td>
<td>98.6</td>
</tr>
<tr>
<td>C16</td>
<td>1.57</td>
<td>91.2</td>
</tr>
<tr>
<td>C17</td>
<td>0.30</td>
<td>98.3</td>
</tr>
<tr>
<td>C18</td>
<td>1.07</td>
<td>94.0</td>
</tr>
<tr>
<td>C19</td>
<td>0.48</td>
<td>97.5</td>
</tr>
<tr>
<td>C20</td>
<td>0.16</td>
<td>99.1</td>
</tr>
<tr>
<td>N02(p+q=6)</td>
<td>1.212</td>
<td>93.2</td>
</tr>
<tr>
<td>N02(p+q=10)</td>
<td>0.945</td>
<td>94.7</td>
</tr>
<tr>
<td>N02(p+q=15)</td>
<td>0.874</td>
<td>95.1</td>
</tr>
<tr>
<td>N02(p+q=20)</td>
<td>1.337</td>
<td>92.5</td>
</tr>
<tr>
<td>N03(n=4)</td>
<td>1.23</td>
<td>93.1</td>
</tr>
<tr>
<td>N03(n=6)</td>
<td>1.09</td>
<td>93.9</td>
</tr>
<tr>
<td>N03(n=9)</td>
<td>1.28</td>
<td>92.8</td>
</tr>
<tr>
<td>N03(n=14)</td>
<td>1.41</td>
<td>92.1</td>
</tr>
<tr>
<td>N03(n=16)</td>
<td>1.76</td>
<td>90.1</td>
</tr>
<tr>
<td>Benzalkonium bromide</td>
<td>1.25</td>
<td>93.0</td>
</tr>
</tbody>
</table>

n, p and q are degrees of polymerisation

Data adapted from references [20, 28]

5.4.4 Chiral Catalyst

The majority of uses of rosin-based surfactants are in paper sizing agent, as a rubber emulsifier and as antibacterial agents. The uses of diterpene resin acids as convenient chiral pools for the synthesis of chiral ligands suitable for metallocomplex catalysts of asymmetric reactions have been studied [68] but, so far, there have been few applications in this field. The use of pine resin acids as chiral pools would also be useful for the preparation of chiral surfactants.
Pan and co-workers reported [29] using four novel chiral quaternary ammonium salts (C21-C24) synthesised from dehydroabietylamine as phase transfer catalysts in asymmetric epoxidation reactions of chalcone (Scheme 5.41). The results indicated that chalcone cannot be oxidised by sodium chlorate or hydrogen peroxide without catalysts in several days. However the reaction could occur in the presence of a rosin-based chiral catalyst. The structure and amount of catalyst affected the reaction greatly. The catalyst that contained benzene groups at the head greatly accelerated the reaction procedure, with higher selectivity compared to a catalyst with an alkyl group. They afforded the corresponding epoxides in high yields and up to 20% enantiomeric excess (ee) [69].

![Scheme 5.41 Rosin based cationic surfactant as phase transfer catalyst](image)

Yang and co-workers used [60] three chiral azacrown ethers, i.e., N-dehydroabietyl monoaza-1,5-crown-5, N-dehydroabietyl monoaza-1,8-crown-6 and N-degrading-dehydroabietyl monoaza-12-crown-4 [N16-N18] synthesised from rosin as phase transfer catalysts in the asymmetric Michael addition of 2-nitropropane to chalcone (Scheme 5.42). This afforded the corresponding Michael addition products with up to 35% ee value. Three kinds of rosin-based chiral azacrown ethers can catalyse chalcone Michael addition reactions. The yield is about 43-51% and the ee value reached 35% with the best catalyst activity. The structure of the azacrown ether greatly affected the selectivity of the catalyst reactions. These chiral azacrown ethers can also catalyse epoxidation reactions of chalcone, and the yield of products reached 47-69%. However, these catalysts almost have no selectivity to form enantiomeric products.

![Scheme 5.42 Chiral azacrown ethers as phase transfer catalysts in asymmetric Michael addition](image)
### 5.4.5 Chiral Separation

Because there are many chiral carbon atoms in the pine resin acids and their derivatives, they have been widely used in the separation technology. Pine resin acids and amines are used as chiral reagents for the resolution of isomers of biological compounds. For example, dehydroabietic acid is used as a reagent for separating chiral amines and dehydroabietylamine is used as a reagent to separate chiral acids. These separation reactions usually depend on salt formation reactions, and according to their solubility in organic solvents, resolution of the biological isomers can be obtained by recrystallisation. With the development of separation technology, micellar electrokinetic chromatography (MEKC), as an electrokinetic separation technique [70], has become one of the most popular techniques in the field of separation science due to its high resolving power and capability of separating both ionic and neutral compounds. One of the attractive applications of MEKC is enantiomer separation [71]. In MEKC, chiral surfactants have been used as a pseudostationary phase for chiral separation. Rosin is a naturally occurring enantiomeric diterpenic acid, which is an excellent starting material for preparing chiral surfactants because of its wide availability and special stereostructure.

Wang and co-workers reported [33] a new type of anionic chiral surfactant (SMA, [A02, see Scheme 5.16]), which was used for the enantioselective MEKC separation of amino acid enantiomers derivatised with naphthalene-2,3- dicarboxaldehyde (NDA-d/l-AA). Under the conditions selected, two pairs of tested amino acid enantiomers, including NDA-d/l-trypotphan and NDA-d/l-kynurenine were resolved. On the other hand, SMA showed high aqueous solubility and low CMC, which simplified the MEKC methodology, and avoided the use of a comicellar phase system and organic solvents for chiral separation [33].

Zhao and co-workers reported [49] a new type of zwitterionic chiral surfactant, DHAMAP, (Z10, see Scheme 5.28) which was used to perform chiral separation of d/l-amino acids by capillary electrophoresis (CE). Six pairs of tested amino acids enantiomers including NDA-d/l-tryptophan (NDA-d/l-Trp), NDA-d/l-phenylalanine (NDA-d/l-Phen), NDA-d/l-kynurenine (NDA-d/l-Kyn), NDA-d/l-β-phenylalanine (NDA-d/l-β-Phen), NDA-d/l-4-methylphenylalanine (NDA-d/l-4-M-Phe) and NDA-d/l-arginine were well-resolved (Figure 5.4). All compounds were fully separated by using a chiral running buffer consisting of a rosin-based surfactant DHAMAP. However, separation was not obtained if the running buffer did not contain DHAMAP. DHAMAP is an amphoteric chiral surfactant; alterations of buffer pH can affect the charge on the analyte and the chiral pseudophase, thus influencing the chiral separation.
The advantages of rosin-based surfactants as a chiral surfactant for the separation of amino acids are that the tricyclic hydrophenanthrene structure contains many chiral centres, the synthetic procedure for the surfactants is relatively simple and the starting material is a natural product which easily available.

\section*{5.4.6 Material Synthesis}

The ability of surfactants to self-assemble into well-defined structures has been taken advantage of for the design and synthesis of inorganic materials with nanosized dimensions \cite{72}. This approach to nanomaterials preparation has triggered substantial interest both in the surface chemistry and the materials chemistry community. In the previous research, surfactants have been used as templates in the synthesis of nanoinorganic powder materials, nanostructured materials, nanocomposite materials and Langmuir-Blodgett films. The size, charge, and shape of the surfactant are important structure-determining parameters in the synthesis of the materials.

As special structure surfactants, rosin-based surfactants may be used to synthesise inorganic materials. Han and co-workers reported \cite{73} that nickel hydroxide materials were prepared by a microwave solvothermal method with a rosin-based surfactant.
(referred to as S1 but no structure was given [73]). Nickel hydroxide coral-like microspheres with a diameter of 2 μm were synthesised by using S1 surfactant. It was shown that these microspheres were assembled from nanosheets with a thickness of 30 nm and a width of 2 μm. The homogeneous size and uniform appearance of the nickel hydroxide materials could be controlled through the addition of S1. The micelles of surfactant made the foam stable, which was better for the formation of nuclei for the nickel hydroxide particles and, at the same time, the micelles of surfactant ensured that the nickel hydroxide particles were well-dispersed in the reaction system. Due to the special stereostructures and easily availability of rosin-based surfactants their use for the synthesis of, and applications for, nanomaterials may attract more and more attention, because those surfactants can act as templates for nanostructured materials.

5.5 Development Trends of Rosin-Based Surfactants

The surfactant industry is facing an important challenge, with growing environmental concerns over the issues of biodegradability, pollution control in manufacturing processes, and consumer desire for ‘green’ ingredients and products. The development of ‘green’ surfactants based on natural renewable resources is a concept that is gaining recognition in fundamental research and applications. There are many advantages of using natural-based products as raw materials for surfactant applications compared to petroleum-based raw materials. With the increasing amount of pine forestry that can be tapped, the output of rosin will increase more and more. Natural products offer unique special structural elements in the surfactant molecule, which make the surfactants exhibit unique chemical physical properties. Surfactants based on natural starting materials can often be made more biodegradable, less toxic and less allergenic. As natural-based fine chemicals, rosin-based surfactants will attract more and more attention, not only because of the large quantity of product of raw material which is available, but also because of the special stereostructures which they contain. Traditional rosin-based surfactants have been investigated and applied widely in past years. However, as we know, no single kind of surfactant can be used in industry. It is often necessary to use several kinds of surfactants together, so the usage of rosin-based surfactants with other surfactants, or different kinds of rosin-based surfactants used together, should be paid more and more attention. Traditional rosin-based surfactants are commonly used for industrial applications, such as paper sizing, in the rubber industry, as antibacterial and antifungal agents, and as corrosion inhibitors. New application fields of rosin-based surfactants need to be researched. Focusing on the special structure of rosin-based surfactants, their uses as chiral catalysts, for chiral separation and for the synthesis of nanomaterials will represent a new trend in future research because little work has been done in these fields.
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