CHAPTER 9

The chemistry and properties of surfactants

Terence M Baldwinson

9.1 INTRODUCTION

A surfactant was defined in Chapter 8 as: 'an agent, soluble or dispersible in a liquid, which reduces the surface tension of the liquid' [1]. It is helpful to visualise surfactant molecules as being composed of opposing solubility tendencies. Thus, those effective in aqueous media typically contain an oil-soluble hydrocarbon-based chain (the hydrophobe) and a smaller water-solubilising moiety which may or may not confer ionic character (the hydrophile). The limitations of space do not permit a comprehensive detailed treatment of the chemistry of surfactants. The emphasis is therefore on a broad-brush discussion of the principal types of surfactant encountered in textile preparation and coloration processes. Comprehensive accounts of the chemistry and properties of surfactants are available [2–13]. A useful and lucid account of the chemistry and technology of surfactant manufacturing processes is given by Davidsohn and Milwidsky [14].

9.2 HYDROPHILES

The basic purpose of the hydrophile is to confer solubility (aqueous solubility is always to be understood unless otherwise stated). The simple moieties most often employed are as follows:

(a) in anionic surfactants: sodium, potassium or ammonium cations, associated with negatively charged groups on the hydrophobe such as carboxylate, sulphonate, sulphate or phosphate

(b) in cationic surfactants: chloride, bromide or methosulphate ions, juxtaposed with, for example, positively charged quaternary nitrogen atoms

(c) in nonionic surfactants: ethylene oxide or propylene oxide moieties.

More complex hydrophilic moieties are sometimes encountered, however, such as mono-, di- and tri-ethanolamine and the corresponding isopropanolamines in anionic surfactants. Morpholine, once employed, is now obsolete owing to its toxicity.
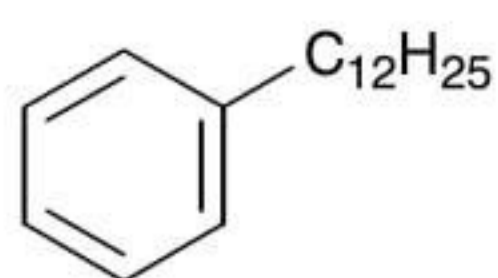
9.3 HYDROPHOBES

There is a much wider choice of hydrophobes. Most are based on substantially linear long-chain alkanes, either saturated or unsaturated. These were originally obtained from naturally occurring fats and oils such as castor, fish, olive, sperm, coconut and tallow oils, but these sources were later superseded by petroleum products which at that time were cheaper. More recently, not only has the price of crude oil escalated, but there has also been a growing

awareness of the finite and diminishing nature of this resource. In 1995, some 75% fossil-sourced raw materials were used in the production of synthetic anionic surfactants (90% if lignosulphonates are excluded) [8], but it is foreseen that more biological materials will be used in the future. It is evident that for some time there has been a systematic and large expansion of vegetable oil production, especially in South East Asia [8]. Typical vegetable oils include: tallow, coconut, palm kernel, palm, soybean, linseed, cotton, rape and sunflower. Most cationic surfactants are still obtained from petrochemical olefins, alcohols, paraffins and aromatics, although some are derived from fatty acids [9].

The most common hydrophobes used as the basis for surfactants are those containing eight to eighteen carbon atoms, such as those listed as carboxylates in Table 9.1. Some hydrophobes are aromatic (benzene or naphthalene) moieties, often containing lower alkyl substituents; dodecylbenzene (9.1) is a common example. Alkyl-substituted toluenes, xylenes and phenols, and mono- and di-alkylated naphthalenes (9.2 and 9.3), are also used.

Table 9.1 Examples of hydrophobes

No. of carbon atoms	Chemical name	Trivial name and formula
8	Octanoate	Caprylate $CH_3(CH_2)_6COO$
10	Decanoate	Caprate $CH_3(CH_2)_8COO$
12	Dodecanoate	Laurate $CH_3(CH_2)_{10}COO$
12	9-Dodecenoate	Lauroleate $CH_3CH_2CH=CH(CH_2)_7COO$
14	Tetradecanoate	Myristate $CH_3(CH_2)_{12}COO$
14	9-Tetradecenoate	Myristoleate $CH_3(CH_2)_3CH=CH(CH_2)_7COO$
15	Pentadecanoate	Isocetate $CH_3(CH_2)_{13}COO$
16	Hexadecanoate	Palmitate $CH_3(CH_2)_{14}COO$
16	9-Hexadecenoate	Palmitoleate $CH_3(CH_2)_5CH=CH(CH_2)_7COO$
17	Heptadecanoate	Margarate $CH_3(CH_2)_{15}COO$
18	Octadecanoate	Stearate $CH_3(CH_2)_{16}COO$
18	9-Octadecenoate	Oleate $CH_3(CH_2)_7CH=CH(CH_2)_7COO$
18	9,12-Octadecadienoate	Linoleate $CH_3(CH_2)_4(CH=CHCH_2)_2(CH_2)_6COO$
18	9,12,15-Octadecatrienoate	Linolenate $CH_3CH_2(CH=CHCH_2)_3(CH_2)_6COO$
18	12-Hydroxy-9-octadecenoate	Ricinoleate $CH_3(CH_2)_5CH(OH)CH_2CH=CH(CH_2)_7COO$

C$_{12}$H$_{25}$

C$_8$H$_{17}$

C$_4$H$_9$

H$_9$C$_4$
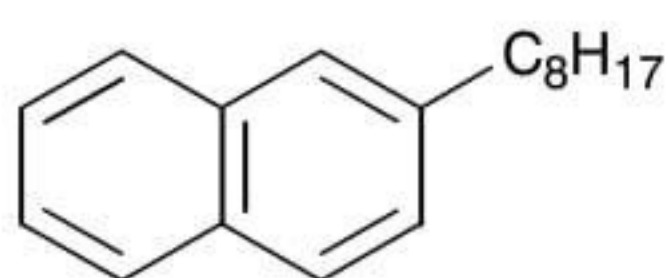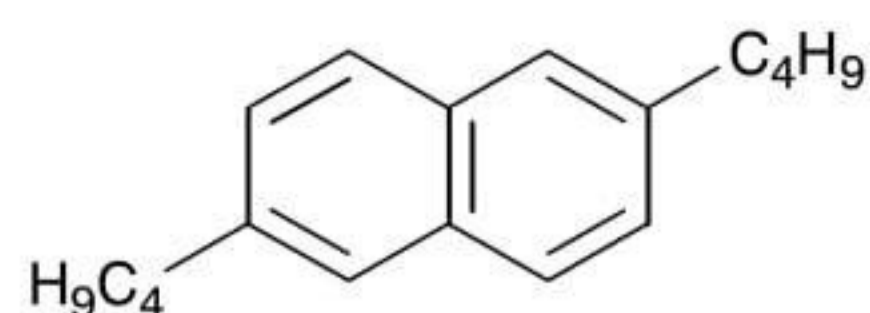
9.1   9.2   9.3

The hydrophobes are usually, though not always, used in the form of acids, alcohols, esters or amines. Commercial products rarely contain a single pure hydrophobe, however; most are mixtures containing a range of hydrophobes, since the raw materials from which they are made are generally themselves mixtures of homologues. For example, a batch of coconut oil, a rich source of the lauric hydrophobe, may have the approximate composition shown in Table 9.2, although the proportions of the individual components may vary by 1–3% between batches. As is the general rule in naturally occurring fats and waxes, only even-numbered carbon compounds are present; odd-numbered ones have to be made by synthesis. Clearly, a surfactant produced from such a mixture will contain a very large, and variable, number of homologues and isomers. Hence two products with the same nominal constitution, but from different manufacturers, often differ in details of composition and properties. This is one fundamental reason why a chemical classification of auxiliaries, analogous to that for dyes in the *Colour Index*, would be extremely difficult to devise.

Table 9.2 Approximate hydrophobe composition of coconut oil

| Trivial name	No. of carbon atoms	Amount (%)
Caproate	6	0.5
Caprylate	8	7.0
Caprate	10	6.5
Laurate	12	49.5
Myristate	14	17.0
Palmitate	16	8.5
Stearate	18	2.5
Oleate	18	6.5
Linoleate	18	2.0

Any hydrophobe can yield each of the main (i.e. anionic, cationic, nonionic or amphoteric) types of surfactant in much the same way as the same chromogenic system can be used in anionic, basic or disperse dyes. This will be demonstrated in the following sections, dealing with each class of surfactant, using the cetyl-containing (C$_{16}$H$_{33}$) hydrophobe.
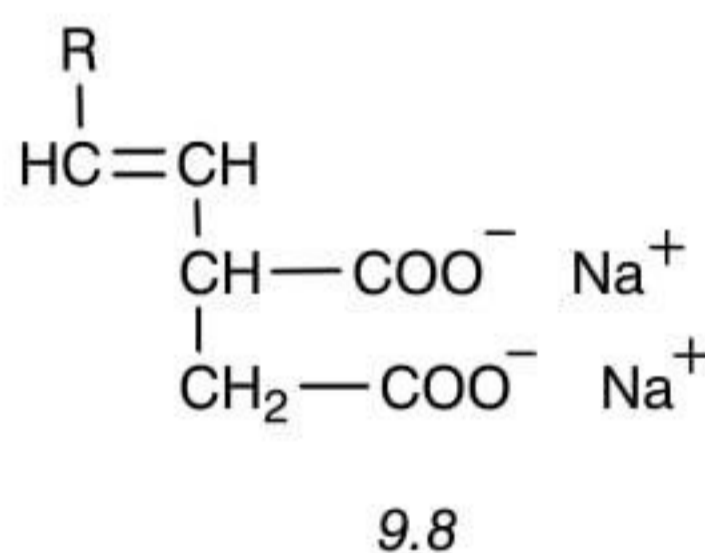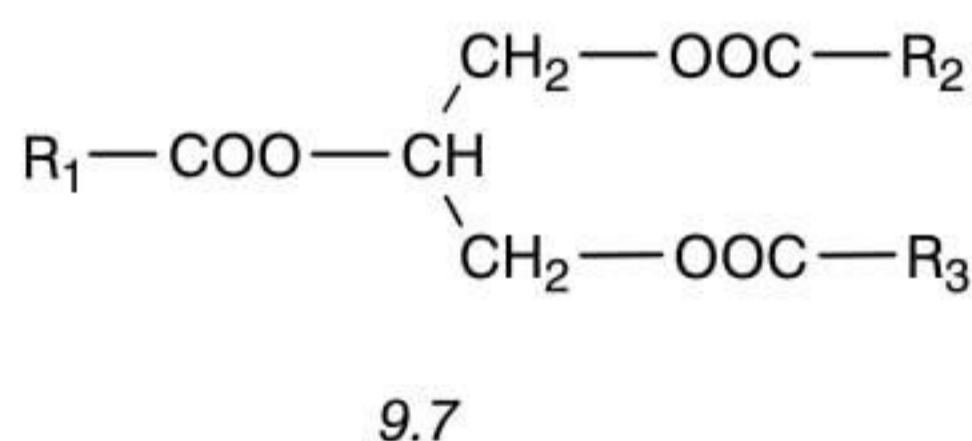
9.4 ANIONIC SURFACTANTS

Until recently this class accounted for by far the largest number of surfactants used in preparation and coloration processes. This dominance is now challenged by the much increased use of nonionic types. The essential feature of the class is a long-chain

hydrophobe linked through an anionic grouping – usually carboxylate, sulphate (sulphuric ester) or sulphonate, but occasionally phosphate, carboxymethyl or other group – to a relatively small cation, generally sodium, although ammonium, potassium and other cations are also used.

Carboxylates (9.4, where R is the long-chain hydrophobe and X the cation) represent the oldest type of surfactants, since they could be obtained from naturally occurring fats and oils long before the advent of the petrochemical industry; sodium heptadecanoate (9.5), for example, incorporates the cetyl group as hydrophobe. Sodium stearate, sodium palmitate and sodium oleate are the simplest carboxylates generally used as surfactants. Alkylaryl compounds (9.6) are also known.

$$R-COO^- \ X^+$$

9.4

$$C_{16}H_{33}COO^- \ Na^+$$

9.5

$$H_{25}C_{12}-\langle\rangle-COO^- \ Na^+$$

9.6
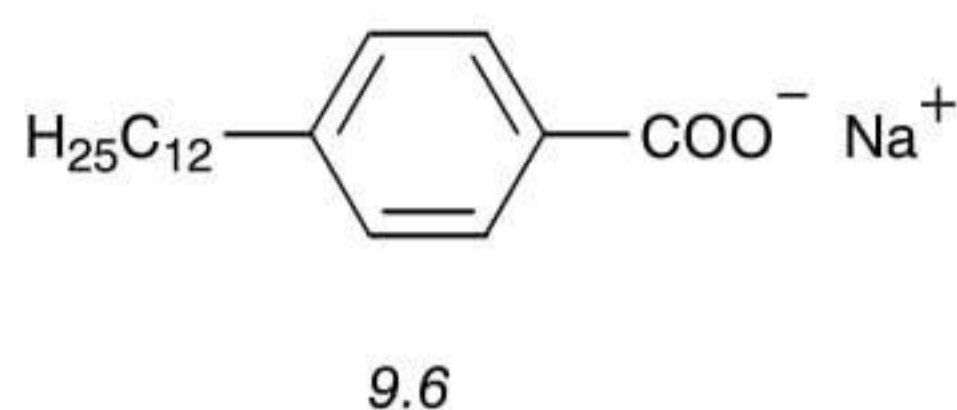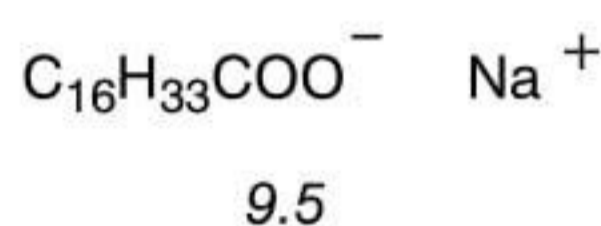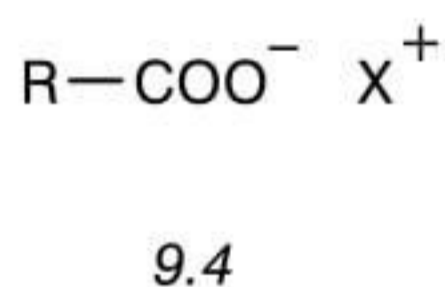
Many carboxylates are used in the form of soaps, obtained by alkaline saponification of triglyceride fats and waxes of general formula 9.7. The three carboxylic ester groups (RCOO) may carry the same or different hydrophobes, generally containing eight to 22 carbon atoms, the most common being laurate, palmitate and stearate among the saturated types, and oleate and linoleate among the unsaturated ones. At ambient temperatures the unsaturated fats tend to be liquids and the saturated ones solids.

$$R_1-COO-CH \begin{smallmatrix} CH_2-OOC-R_2 \\ \\ CH_2-OOC-R_3 \end{smallmatrix}$$

9.7

$$\begin{array}{c} R \\ | \\ HC=CH \\ | \\ CH-COO^- \ Na^+ \\ | \\ CH_2-COO^- \ Na^+ \end{array}$$

9.8

Particularly important as wetting agents are the disodium alkenylsuccinates (9.8), in which the saturated R group may contain from three to fourteen carbon atoms. The surfactant properties of these carboxylates, as with other types of surfactant, are dependent on the number of carbon atoms in the hydrophobe. Significant surfactant properties begin to appear in the C_8 compounds, although the C_8–C_{12} carboxylates are wetting agents rather than detergents. Better detergency and emulsifying properties become evident with C_{12}–C_{18} alkyl groups. Solubility decreases with increasing length of the alkyl group; the solubility of soaps, for example, reaches its useful limit with the C_{22} compounds. The major disadvantage of the carboxylates is that they tend to be precipitated by acids and hard water, since the free acids and the calcium and magnesium salts of the carboxylates are insoluble. This disadvantage provided the main technical reason for finding alternative products that showed tolerance to a wider range of processing conditions.

Modified carboxylates, in which the carboxylate moiety forms part of a carboxymethoxy group, are also available. These are made by reaction of selected nonionic surfactants with chloroacetic acid. The result is a useful hybrid range, lacking the sensitivity of simple

carboxylates to calcium and magnesium whilst retaining excellent detergency; these compounds are more stable to electrolytes than are the conventional nonionics and more suitable for use at high temperatures as they are not susceptible to cloud point problems (section 9.8.2).

Sulphates or sulphuric esters of the long-chain fatty acids were the first alternative to the carboxylates. They are essentially the half esters of sulphuric acid (9.9); the ester incorporating the cetyl hydrophobe (9.10) belongs to the important class of fatty alcohol sulphates. Such sulphates, using C_8–C_{18} hydrophobes, are common.

$$R-OSO_3^-\ Na^+ \qquad\qquad C_{16}H_{33}OSO_3^-\ Na^+$$
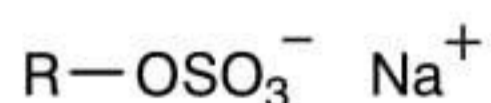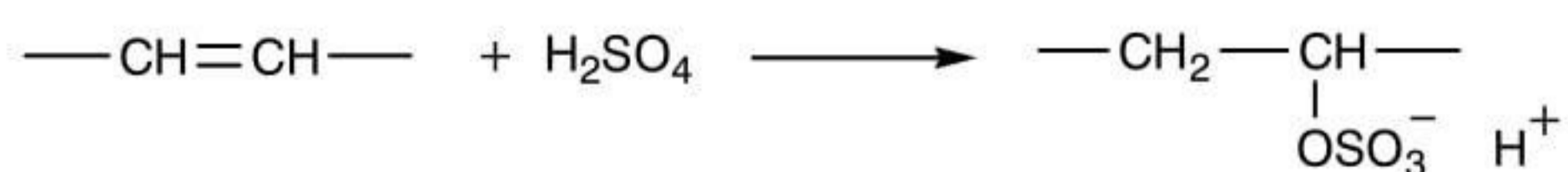
$$\textit{9.9} \qquad\qquad\qquad \textit{9.10}$$

Just as there are mono-, di- and tri-carboxylate surfactants, the sulphates can also be prepared from products bearing mono-, di- and tri-hydrophobes. Indeed, the first sulphates to be used were analogous to soaps in that they were the sulphation products of triglycerides. Although their chemistry can be represented in simple terms, it is worth re-stating that most commercial products are highly complex mixtures. For example, a sulphated triglyceride may contain the following:
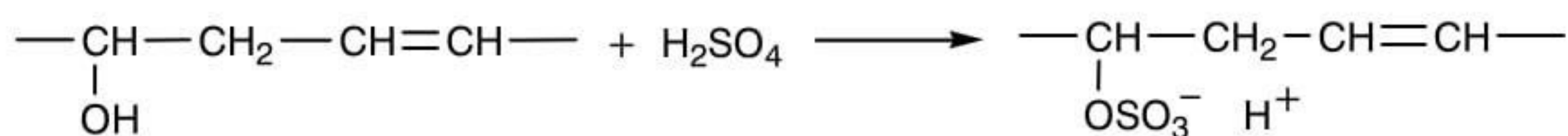– the sulphated glyceride proper
– sulphated free fatty acid
– unsulphated glyceride
– unsulphated fatty acid
– inorganic salts
– traces of glycerol.

The range of hydrophobes present may also be unexpectedly broad, since the raw materials often consist of mixtures of symmetrical and/or mixed glycerides. As little as 60% of an oil may be sulphatable; sulphation is never carried to theoretical completion and is often far below 100%. With these provisos in mind, the chemistry of the sulphated oils can be considered.

Many oils are used as starting materials: olive, castor, tallow, neatsfoot, cotton seed, rape seed and corn oils are examples. Sulphated olive oil was the first sulphated oil to be produced and was used as a mordant in dyeing as long ago as 1834. Sulphation usually occurs at the double bonds of any unsaturated fatty acids in the glyceride (Scheme 9.1). On the other hand, in the preparation of the best-known of these products, Turkey Red Oil or sulphated (often wrongly termed 'sulphonated') castor oil, sulphation of the main component, the glyceride of ricinoleic acid (12-hydroxy-9-octadecenoic acid), takes place preferentially at the hydroxy group rather than at the double bond (Scheme 9.2). Such products possess useful wetting, emulsifying and dye-levelling properties.

$$-CH=CH- \ +\ H_2SO_4 \longrightarrow \ -CH_2-\underset{\underset{OSO_3^-\ H^+}{|}}{CH}-$$

Scheme 9.1

$$\begin{array}{c} -CH-CH_2-CH=CH- \\ | \\ OH \end{array} + H_2SO_4 \longrightarrow \begin{array}{c} -CH-CH_2-CH=CH- \\ | \\ OSO_3^- \ H^+ \end{array}$$

Scheme 9.2

At the present time, however, the long-chain alcohol sulphates already mentioned, such as structure 9.10, and particularly the sulphated ethers are of greater importance. The stability of the sulphates to mildly acidic conditions and to hard water is much better than that of the carboxylates and is sufficient for most purposes. Under more stringent acidic conditions, however, hydrolysis may take place.

Another type of sulphated product, an ester sulphate, can be prepared by esterifying a fatty acid such as ricinoleic or oleic acid with a short-chain (C_3–C_5) alcohol and then sulphating. Such products are particularly useful foaming, wetting and emulsifying agents; an example is sulphated butyl ricinoleate (9.11).

$$\begin{array}{c} CH_3(CH_2)_5CHCH_2CH=CH(CH_2)_7COO(CH_2)_3CH_3 \\ | \\ OSO_3^- \ H^+ \end{array}$$
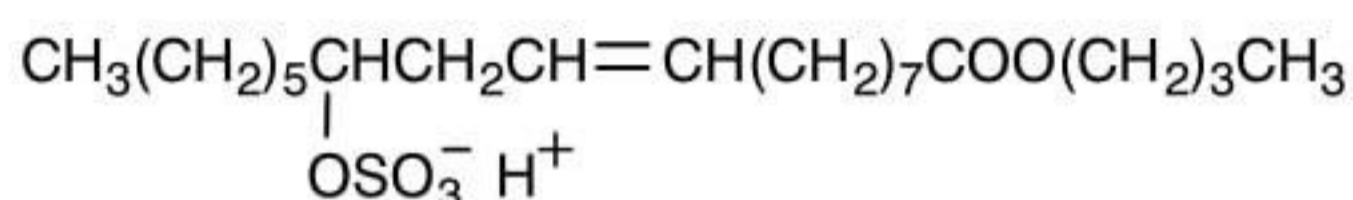
9.11

More recent developments amongst anionic surfactants are the sulphated polyethers or alcohol poly(oxyethylene) sulphates (9.12, 9.13), prepared by ethoxylating the fatty alcohol to give a polyether containing a terminal hydroxy group that is then sulphated. Aromatic hydrophobes may also be used to produce, for example, alkylphenol poly(oxyethylene) sulphates. In a general sense, a poly(oxyethylene) sulphate can be viewed as a partly anionic and partly nonionic surfactant, although the degree of ethloxylation of these products is generally much lower than that of the purely nonionic surfactants. Hence they are sometimes referred to as 'lightly ethoxylated alcohol sulphates'; again, their actual composition may be a good deal more complex than indicated by their nominal structural formulae. There has been increasing use of these derivatives in domestic detergents.

$$R-(OCH_2CH_2)_x-OSO_3^- \ Na^+ \qquad\qquad C_{16}H_{33}-(OCH_2CH_2)_x-OSO_3^- \ Na^+$$
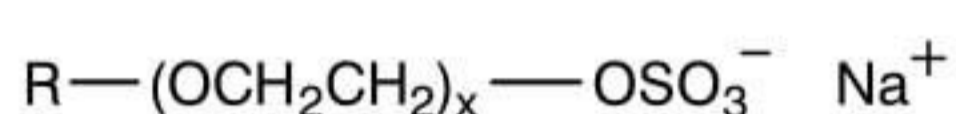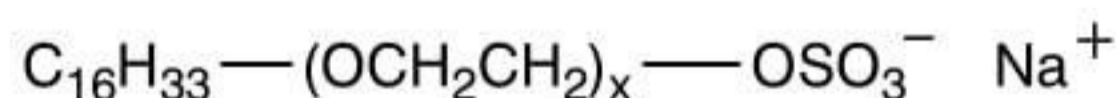
*9.12*   *9.13*

Sulphonated anionic surfactants have the general structure 9.14, which should be compared with that of the sulphates (9.9). As well as the simple alkyl derivatives such as structure 9.15, aromatic and particularly alkylated aromatic (alkylaryl) types are technically and commercially important. Indeed, sodium dodecylbenzenesulphonate (9.16) has long been of great importance in domestic washing powders. Although it is no longer the only surfactant used in domestic washing powders, its economy, efficacy and environmental properties are such that it is likely to remain the dominant anionic surfactant in heavy-duty concentrated powder detergents for some time [15]. Environmental studies have shown that 90% of such linear alkylbenzenesulphonates are removed by conventional sewage treatment, the remainder being virtually completely biodegradable in topsoil with half-life values varying from 3 to 25 days [16,17].

$$H_{25}C_{12} \longrightarrow SO_3^- \ Na^+$$

$$RSO_3^- \ Na^+ \qquad C_{16}H_{33}SO_3^- \ Na^+$$
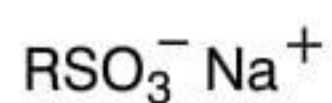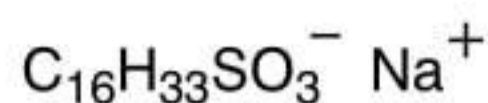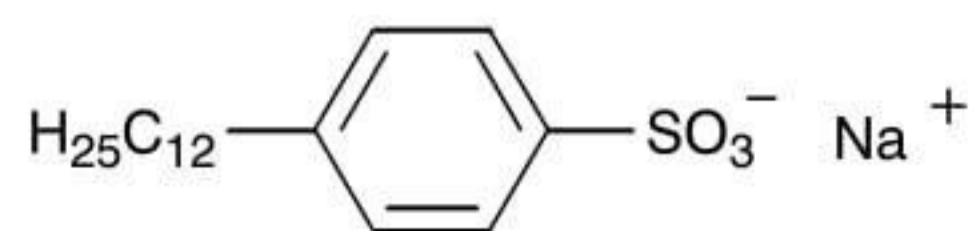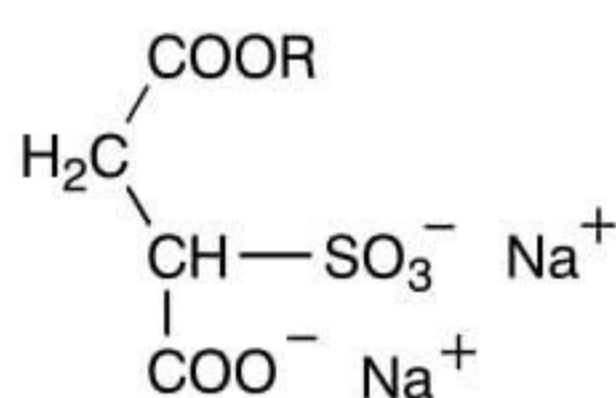
9.14   9.15   9.16

Nowadays these compounds are usually blended with other surfactants, including nonionic types (section 9.6). In 1990 a typical low- or non-phosphate domestic detergent contained 7% linear alkylbenzenesulphonate and 6% nonionic fatty alcohol ethoxylate [16]. There is increasing use of the long-chain fatty alcohol poly(oxyethylene) sulphates previously described (e.g. 9.12) as a partial or complete replacement for linear alkylbenzenesulphonates [15] since they are made from renewable feedstocks such as tallow and palm oil [16].

Naphthalene and other aromatic hydrophobes are also used to produce sulphonates, such as structure 9.17. Of greater importance, however, are the more complex condensation products that form the basis of many excellent dispersing, resist and aftertreating (syntan) agents. Typical examples are the condensation products of naphthalenesulphonates with formaldehyde, and the lignosulphonates derived from pulping processes; these are described in more detail in section 10.6.1.
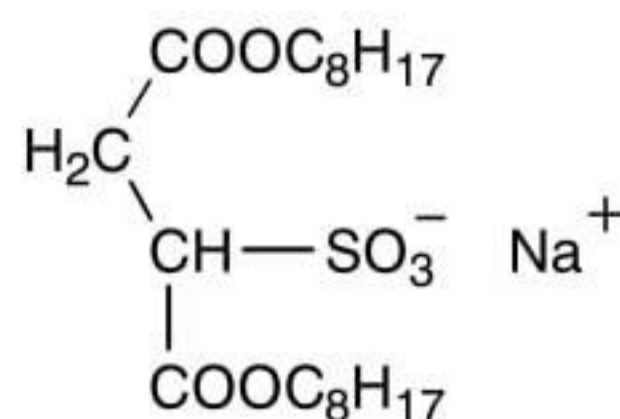
$$C_3H_7$$
$$SO_3^- \ Na^+$$
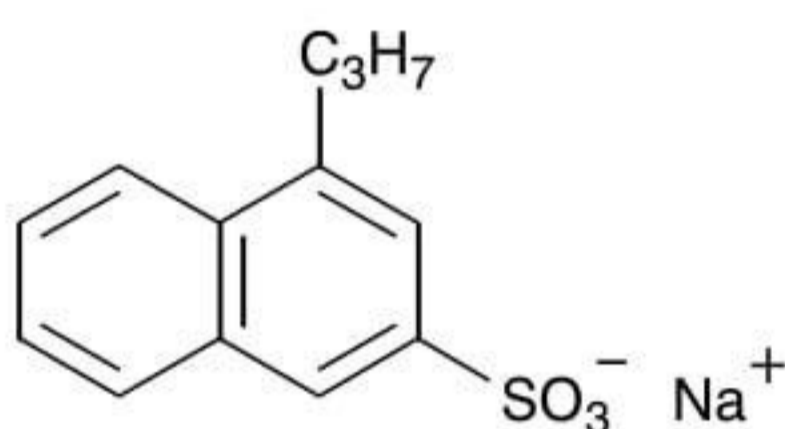
9.17

Sulphosuccinates are of particular interest not only for their technical properties but also because structurally they combine the two hydrophile functions described earlier – the sulphonate and carboxylate moieties – in a single molecule (9.18). The sulphosuccinate diesters, however, are probably of greater commercial importance in textile processing than are the monoesters. The most important example is sodium dioctylsulphosuccinate (9.19), but the dinonyl, dimethylamyl and di-isobutyl analogues are also used commercially. As usual, a wide choice of hydrophobes is available and includes alcohols, lightly ethoxylated alcohols, alkanolamides and combinations of these.

$$\begin{array}{ll} COOR \\ H_2C \\ \quad CH - SO_3^- \ Na^+ \\ \quad COO^- \ Na^+ \end{array} \qquad \begin{array}{ll} COOC_8H_{17} \\ H_2C \\ \quad CH - SO_3^- \ Na^+ \\ \quad COOC_8H_{17} \end{array}$$

9.18   9.19

Phosphate esters (9.20) represent a different class of hydrophile-characterised anionic surfactants; mono- or di-esters can be formed depending on whether one or two alkyl groups are present. Most phosphate esters are based on alcohols and especially their ethoxylates,

including aliphatic and alkylaryl types. Whereas the sulphates tend to be based on lightly ethoxylated alcohols, the phosphate esters are also made from more highly ethoxylated products. Commercial products are complex mixtures (9.21) of monoester, diester, free phosphoric acid and free nonionic surfactant [18].
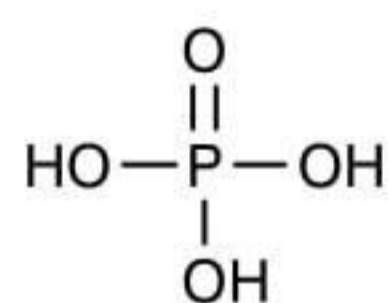
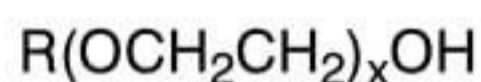$$\underset{\text{OH}}{\overset{\displaystyle \overset{O}{\|}}{R-O-P-OH}} \qquad \underset{\text{OH}}{\overset{\displaystyle \overset{O}{\|}}{R-O-P-O-R}}$$

9.20

$$\underset{\text{OH}}{\overset{\displaystyle \overset{O}{\|}}{R(OCH_2CH_2)_xO-P-OH}} \qquad \underset{\text{OH}}{\overset{\displaystyle \overset{O}{\|}}{R(OCH_2CH_2)_xO-P-O(CH_2CH_2O)_xR}}$$

Monoester surfactant   Diester surfactant

9.21

$$\underset{\text{OH}}{\overset{\displaystyle \overset{O}{\|}}{HO-P-OH}} \qquad\qquad R(OCH_2CH_2)_xOH$$

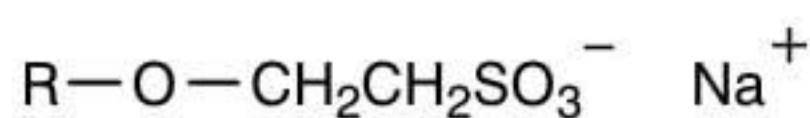Free phosphoric   Free nonionic
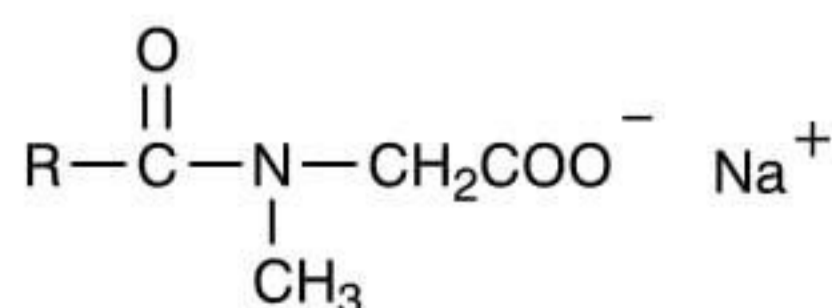acid   surfactant

Phosphate esters are particularly useful for their alkali stability and wettability. It has been shown [18] that a certain amount of ethoxylation of the hydrophobe is required to obtain alkali resistance, and that as the relative molecular mass (M_r) of the hydrophobe increases, the proportion of ethylene oxide required also increases. The greater the degree of ethoxylation, the greater the degree of alkali resistance, few materials showing good alkali resistance with less than six moles of ethylene oxide per mole of hydrophobe. The same study [18] showed that wetting power decreased with increasing M_r of the hydrophobe. Incorporating 2–3 moles of ethylene oxide per mole of hydrophobe seems to give optimum wetting. It appears that as one attempts to increase the rate of wetting, alkali tolerance decreases.
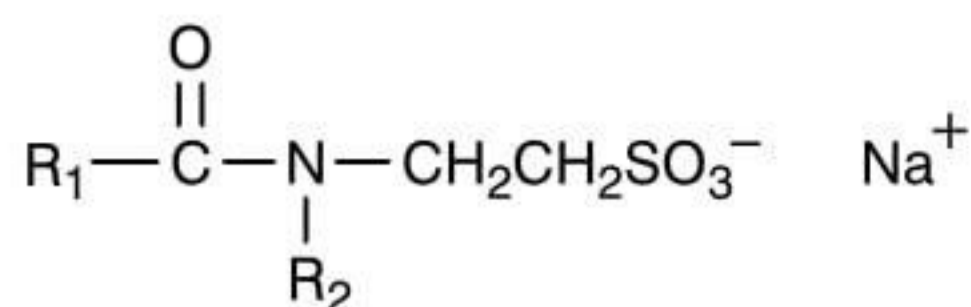
Other anionic surfactant types include the alkylisethionates (9.22), N-acylsarcosides (9.23), N-acyltaurides (9.24) and perfluorinated carboxylates, sulphonates (e.g. 9.25), sulphates and phosphates [13].
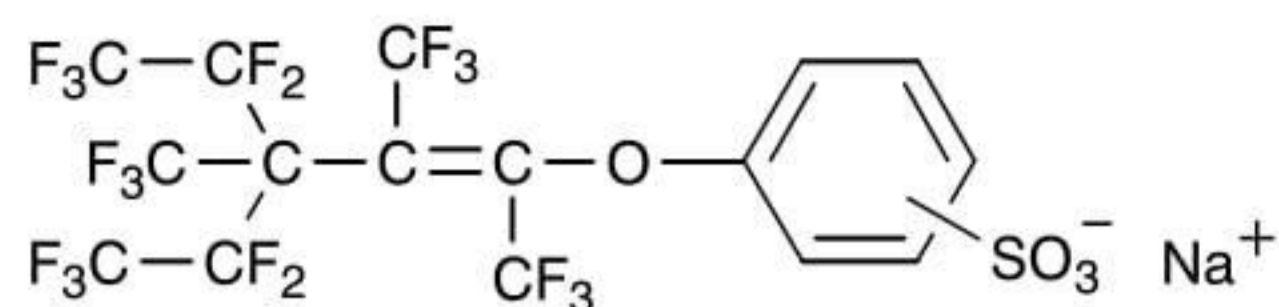
$$R-O-CH_2CH_2SO_3^-\ Na^+ \qquad\qquad \underset{\text{CH}_3}{\overset{\displaystyle \overset{O}{\|}}{R-C-N-CH_2COO^-\ Na^+}}$$

9.22   *9.23*

$$R_1-\overset{\overset{O}{\|}}{C}-\underset{\underset{R_2}{|}}{N}-CH_2CH_2SO_3^- \quad Na^+$$

9.24

9.25

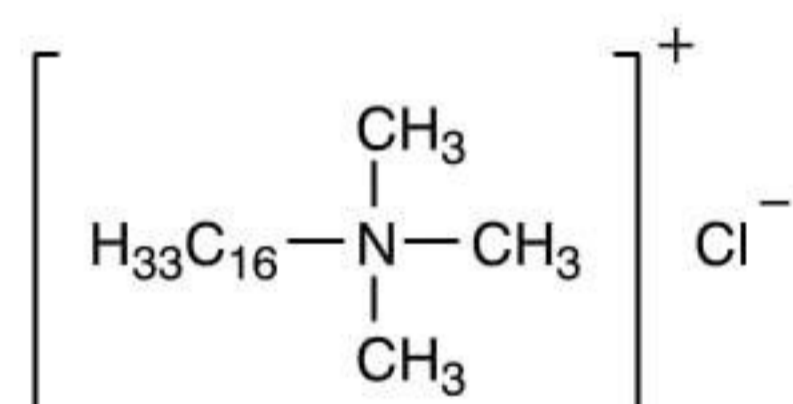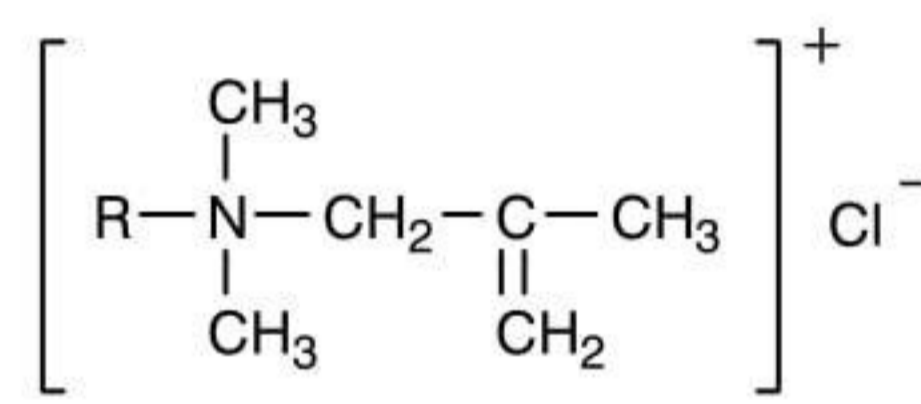## 9.5 CATIONIC SURFACTANTS

By far the most important types of cationic surfactant used in textile processing are the quaternary ammonium salts (9.26), in which R is usually a long-chain hydrophobe and R_1, R_2, R_3 are lower alkyl groups. The most common anions in these and other cationic surfactants are chloride and bromide: thus cetyltrimethylammonium chloride (9.27) is typical of this class of cationic surfactants. In fact, however, all four alkyl groups on the nitrogen atom can be varied to alter the balance of properties of the products. In the alkyldimethylmethallylammonium chlorides (9.28), an unsaturated aliphatic group is used. Aromatic components are also used, as in the important alkyldimethylbenzylammonium chlorides (9.29), and both the aromatic nucleus and the alkyl groups in such products may contain substituents (9.30 and 9.31). As important as the quaternary ammonium surfactants are the pyridinium salts (9.32; R is a long-chain alkyl group), such as cetylpyridinium chloride (9.33).
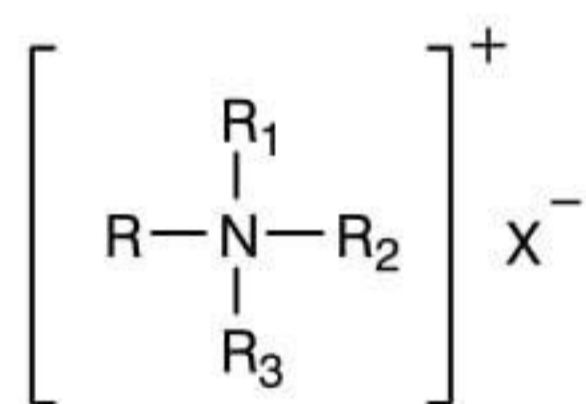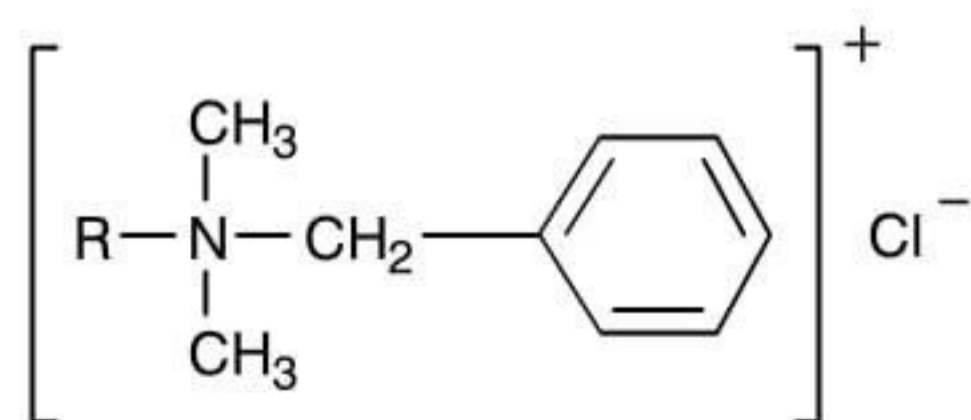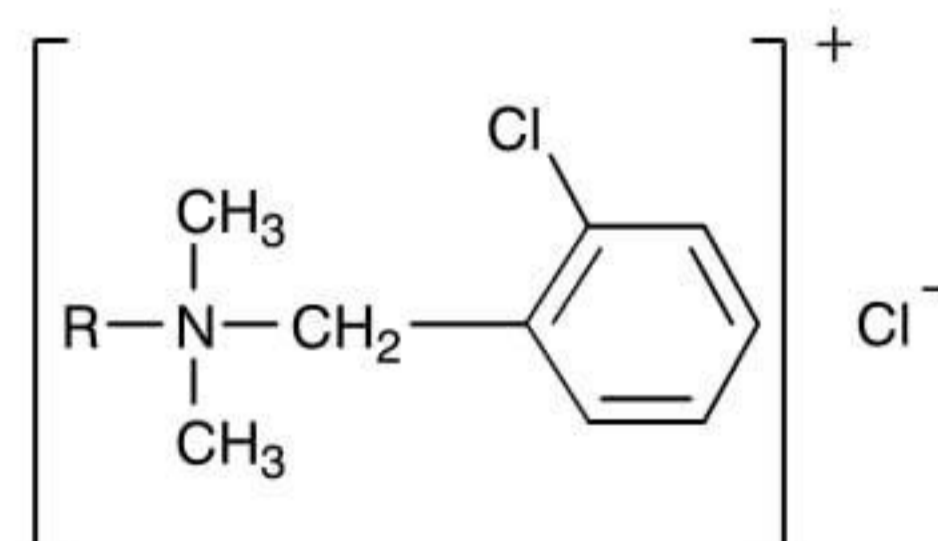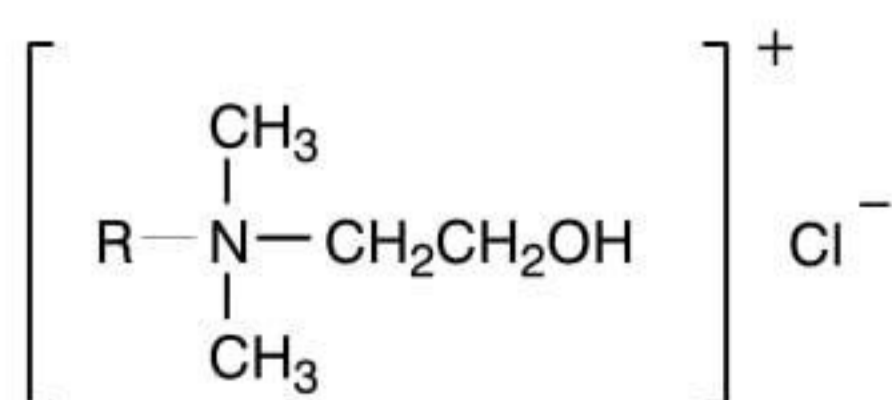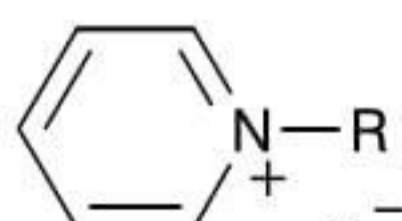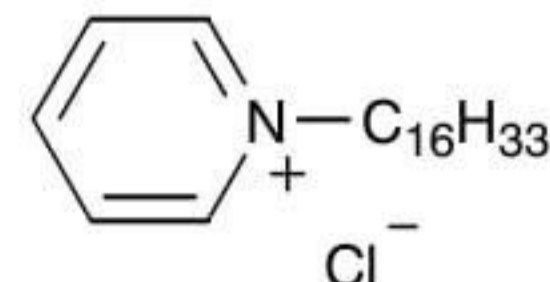
9.26

9.27

9.28

9.29

9.30

9.31

9.32

9.33

Imidazoles can be quaternised to yield cationic surfactants (such as structures 9.34 and 9.35). Long-chain alkyl primary, secondary and tertiary amines can also be used as cationic surfactants, but their use in textile processing is limited as a result of their insolubility in other than acidic aqueous media. The range of products available as cationic surfactants is truly enormous, including, for example, such complex products as alkylated mono- and di-guanidines and polyamines (9.36) containing more than one basic nitrogen atom.

9.34   9.35

$$R\text{---}(NHCH_2CH_2)_x NH_2$$
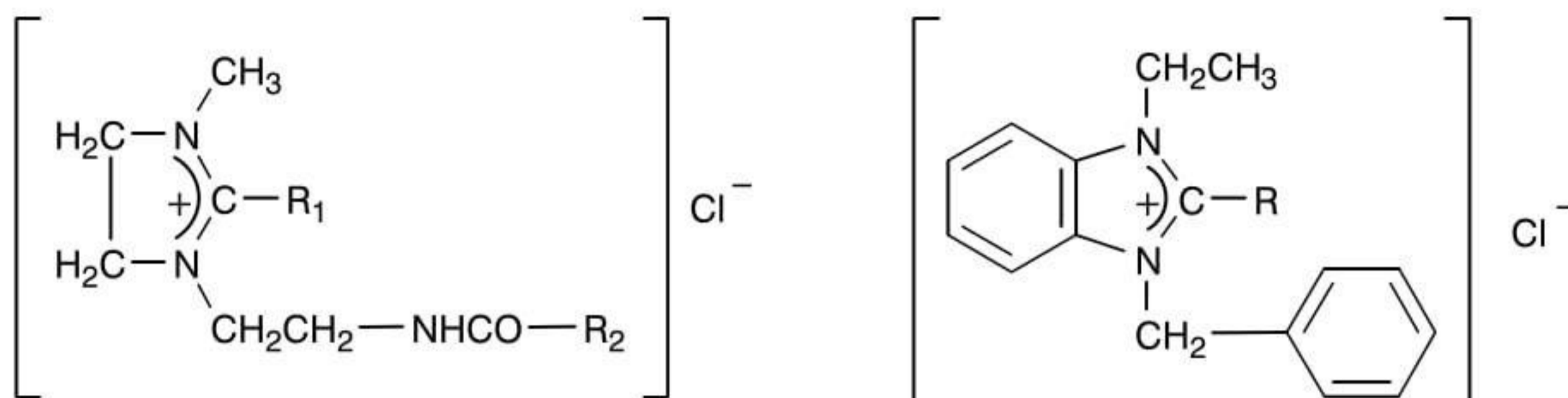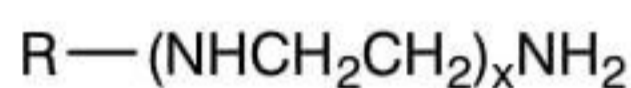
9.36

Many of these cationic products, including the quaternary amines and imidazoles, can be ethoxylated (9.37, 9.38), forming cationic analogues of the ethoxysulphates and ethoxyphosphates in the anionic series. They are essentially cationic/nonionic hybrid surfactants, variously described in manufacturers' promotional literature as 'modified cationic', 'weakly cationic' or even 'modified nonionic'. Their value lies in the fact that the cationic nature can be controlled by varying not only the alkyl substituents but also the degree of ethoxylation. In addition the ethoxylate moiety confers useful emulsifying properties. Fluoro-containing cationic surfactants (9.39) can also be obtained [13].

9.37   9.38

$$C_7F_{15}\text{---}CONH\text{---}(CH_2)_3\text{---}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|+}}{N}}\text{---}CH_3 \quad I^-$$
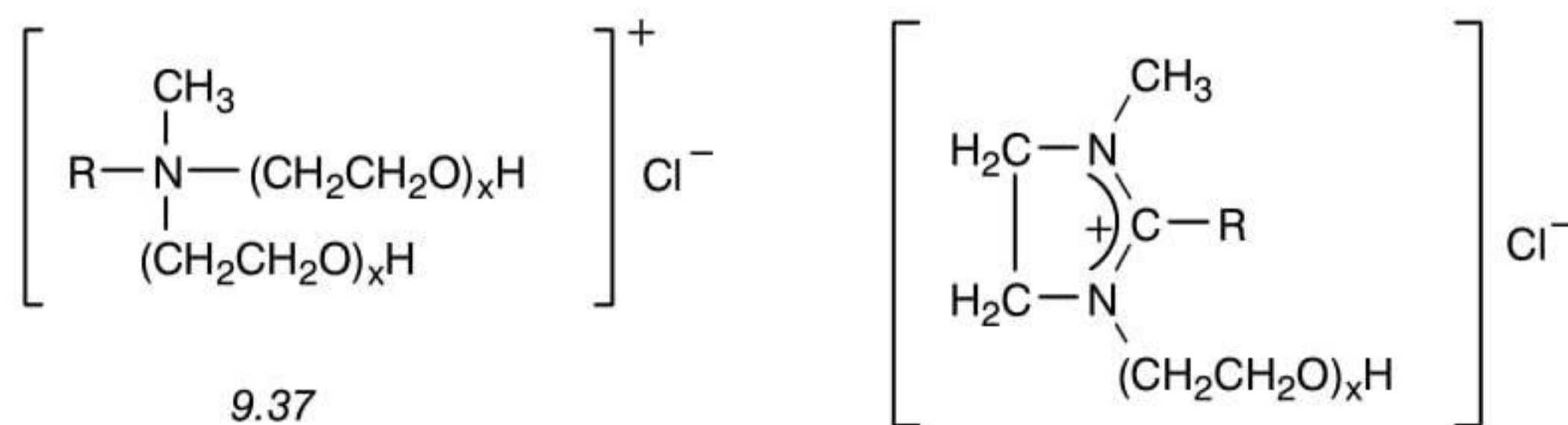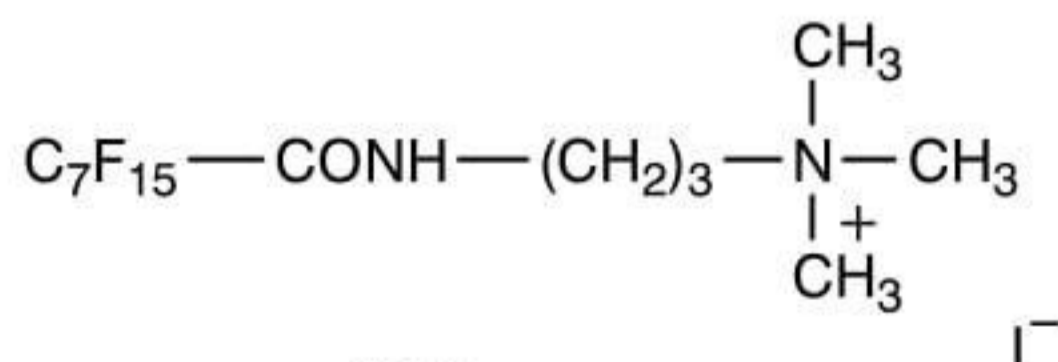
9.39

9.6 NONIONIC SURFACTANTS

Nearly all nonionic surfactants contain the same type of hydrophobes as do anionic and cationic surfactants, with solubilisation and surfactant properties arising from the addition of ethylene oxide to give a product having the general formula 9.40. Usually, depending on the

hydrophobe, aqueous solubility and detergent properties begin to be evident when $x = 6$, but in theory the degree of ethoxylation can be continued almost indefinitely. Optimal surfactant properties are generally found when $x = 10$–15, although higher homologues (for example, $x = 50$) are known. The 'lightly ethoxylated' su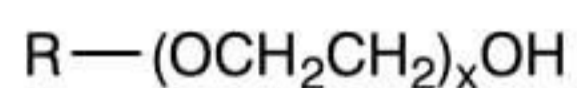lphates mentioned earlier usually contain only 2–4 oxyethylene units per molecule. Thus a typical nonionic surfactant can be represented by structure 9.41.

$$R-(OCH_2CH_2)_xOH \qquad\qquad H_{33}C_{16}-(OCH_2CH_2)_{12}OH$$

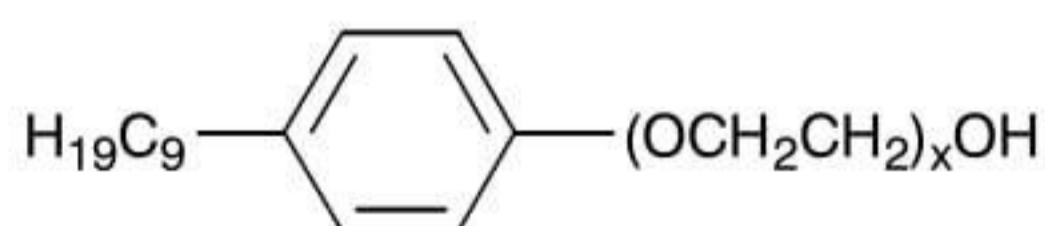$$\textit{9.40} \qquad\qquad\qquad\qquad\qquad \textit{9.41}$$

Although there are other types of nonionic surfactant, the great majority are adducts of ethylene oxide with hydrophobes derived from three sources:
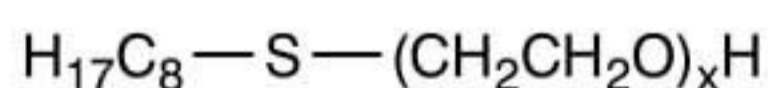– fatty alcohols and alkylphenols
– fatty acids
– fatty amines and amides.

For many years the most common of these have been adducts with p-nonyl- and p-octylphenol, and to a lesser extent 2,4-dinonylphenol, p-dodecylphenol and 1-alkylnaphthols. Since the hydrophobes used may be variable products conforming to an average nominal structure, and since the quoted degree of ethoxylation can also only be regarded as an average value, products having the same name (such as, for example, p-nonylphenol dodecaoxyethylene) may in fact differ in detailed composition and properties when obtained from different manufacturers. These provisos should be borne in mind when considering the examples below, even though there is a trend in some cases towards the manufacture of narrower fractions.

An example of an alcohol-based nonionic (9.41) has already been given. An alkylphenol adduct (9.42) is essentially similar; both alcohols and phenols give rise to the relatively strong and stable ether link, a valuable property of this type of product. Analogues based on alkylthiols (9.43) may also be used.

$$H_{19}C_9-\!\!\!\bigcirc\!\!\!-(OCH_2CH_2)_xOH \qquad H_{17}C_8-S-(CH_2CH_2O)_xH \qquad \begin{array}{c} (OCH_2CH_2)_xOH \\ \diagup \\ R \\ \diagdown \\ (OCH_2CH_2)_xOH \end{array}$$
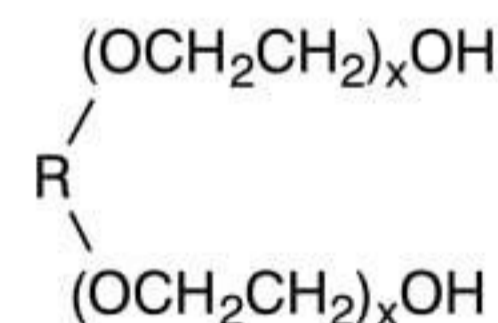
$$\textit{9.42} \qquad\qquad\qquad\qquad \textit{9.43} \qquad\qquad\qquad\qquad \textit{9.44}$$

Polyfunctional alcohols of varying complexity, such as polyethylene glycols (9.44) and polypropylene glycols of varying chain length, also provide useful nonionic agents. A polypropylene glycol molecule has a hydroxy group at each end to which ethylene oxide can be added, forming random segments of poly(oxyethylene) and poly(oxypropylene). This results in block copolymers, which can be engineered by control of starting materials and processing conditions to give products specifically suited to a wide variety of purposes by virtue of wide variations in segment length and degree of polymerisation.

Whereas the alcohol and phenol derivatives are characterised by ether linkages, adducts of ethylene oxide with fatty acids give rise to both monoesters (9.45) and diesters. These are

$$H_{33}C_{16}CO(OCH_2CH_2)_xOH \qquad\qquad H_{23}C_{11}NH(CH_2CH_2O)_xH$$

9.45   *9.46*

$$H_{23}C_{11}-N\Big\langle \begin{matrix}(CH_2CH_2O)_xH \\ (CH_2CH_2O)_xH\end{matrix}$$

9.47

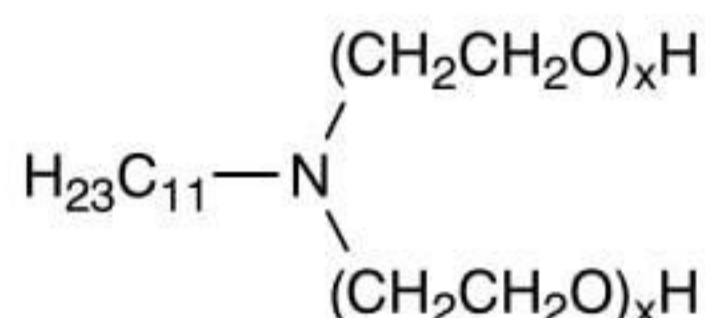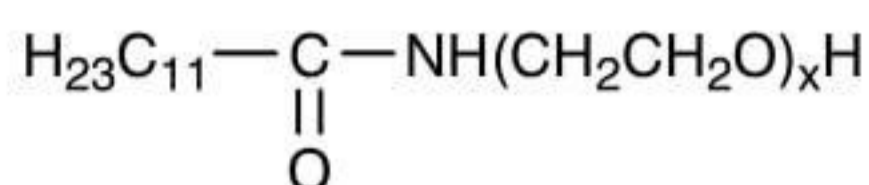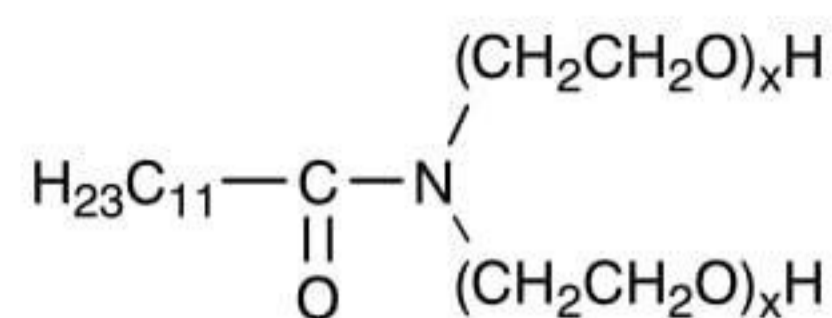$$H_{23}C_{11}-\underset{\underset{O}{\|}}{C}-NH(CH_2CH_2O)_xH$$

9.48

$$H_{23}C_{11}-\underset{\underset{O}{\|}}{C}-N\Big\langle \begin{matrix}(CH_2CH_2O)_xH \\ (CH_2CH_2O)_xH\end{matrix}$$
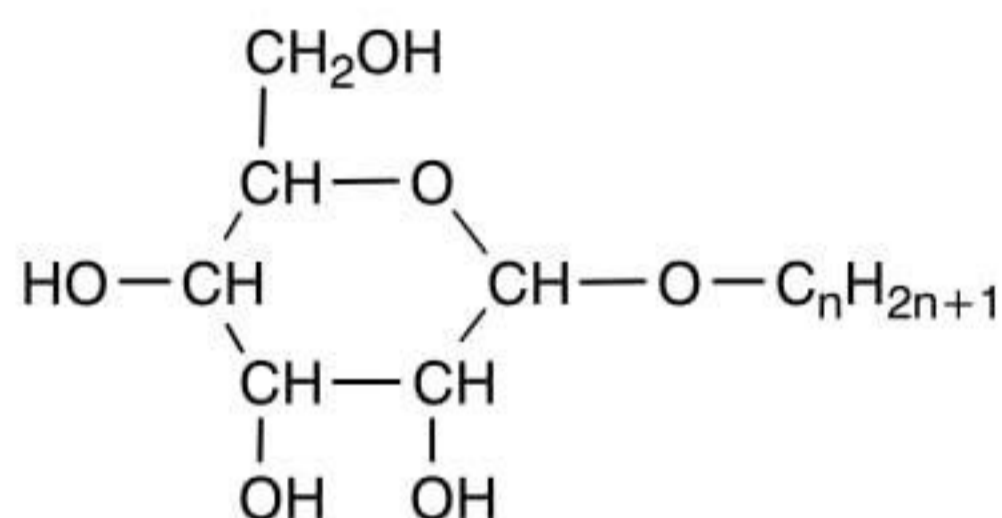
9.49

less stable than the ethers in strongly acidic or alkaline media, however, hydrolysing to the original fatty acid and polyethylene glycol.

Adducts of ethylene oxide with fatty amines can yield mono- (9.46) or di-substituted (9.47) products, as can the adducts with fatty amides (9.48, 9.49). In practice the products formed are far from being as simple or as symmetrical as represented by these formulae since, amongst other things, the ethylene oxide addition takes place randomly.

A recent introduction in the area of nonionic surfactants is the alkylglycoside series. These are long-chain acetals of saccharides (9.50). Commercial products currently have an average alkyl chain length of 10–12 carbon atoms. These are manufactured from non-petroleum sources, being synthesised from glucose and fatty alcohols. Such acetals are regarded as eco-friendly, being said to be completely biodegradable [19] and having low skin irritancy. These surfactants possess wetting, foaming and detergency properties similar to those of the corresponding alcohol ethoxylates but with higher solubility in water and in solutions of electrolytes. They are soluble and stable in sodium hydroxide solutions and show no inverse solubility characteristics.

$$
\begin{array}{c}
CH_2OH \\
|\\
CH-O \\
\diagup \qquad \diagdown \\
HO-CH \qquad\qquad CH-O-C_nH_{2n+1} \\
\diagdown \qquad\qquad \diagup \\
CH-CH \\
|\qquad | \\
OH \quad OH
\end{array}
$$

9.50

The nonionic types so far discussed form the great majority used in textile processing. Of course, a great many more can be synthesised, as the possible range of permutations and combinations is truly enormous. Given appropriate conditions, ethylene oxide will react with almost any proton-donating compound, but the choice in practice is restricted by economic factors. Not all nonionic surfactants are ethoxylates, however. Analogous propylene oxide adducts are known; rather more different products include sucrose and sorbitan esters, alkanolamides and fatty amine oxides. The fatty acid esters of compounds such as sucrose and sorbitol exhibit surfactant properties. Some, such as the sorbitan fatty esters, are insoluble in water but being oil-soluble they can be used as emulsifiers in oil-based systems, or they can be ethoxylated to render them water-soluble. Mention has already been made of fatty amide poly(oxyethylene) adducts formed by condensation of a fatty acid with an alkanolamine which is then ethoxylated; some complex alkanolamides have in themselves (i.e. without ethoxylation) some surfactant properties, however. They are made by the

reaction of a fatty acid (such as lauric acid or a coconut fatty acid) with a secondary alkanolamine (such as diethanolamine) to yield an amide, which then reacts further with diethanolamine to give the water-soluble alkanolamide surfactant. Typical fatty amine oxides (9.51 and 9.52) are derived, for example, from the peroxide oxidation of tertiary amines containing at least one fatty-chain group.


9.51   9.52
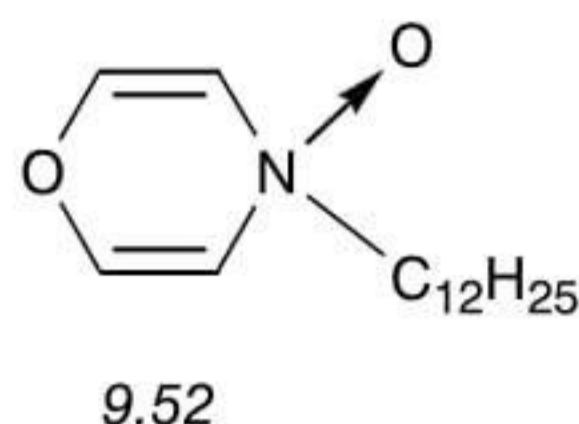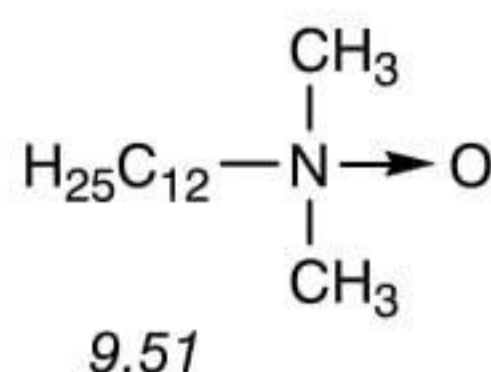
9.7 AMPHOTERIC SURFACTANTS

As mentioned in Table 8.1, amphoteric surfactants contain both an anionic and a cationic group. In acidic media they tend to behave as cationic agents and in alkaline media as anionic agents. Somewhere between these extremes lies what is known as the isoelectric point (not necessarily, or even commonly, at pH 7), at which the anionic and cationic properties are counterbalanced. At this point the molecule is said to be zwitterionic and its surfactant properties and solubility tend to be at their lowest. These products have acquired a degree of importance as auxiliaries in certain ways [20–25], particularly as levelling agents in the application of reactive dyes to wool.

The simplest type is represented by the higher alkylaminoacids, such as compound 9.53; disubstituted amines can also be synthesised (9.54).

Ethoxylated products can also feature as amphoteric surfactants; an example is compound 9.55, an alkylamine poly(oxyethylene) sulphate. Of particular interest in textile processing are the trisubstituted alkylamino acids known as betaines; N-alkylbetaines (9.56; R = C_8–C_{16} alkyl) and acylaminoalkylbetaines (9.57; R = C_{10}–C_{16} alkyl) are typical [30].

Sulphate and sulphonate analogues of the carboxylates, such as the sulphobetaine 9.58, can also be used as amphoteric agents.

9.53

9.54

9.55

9.56

9.57

9.58
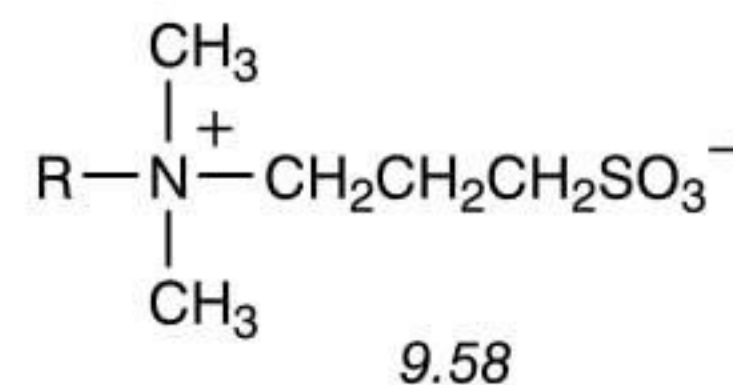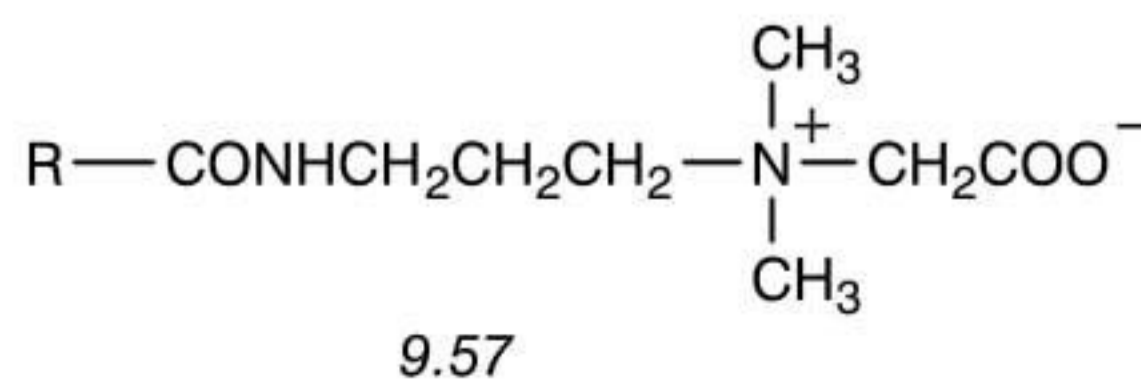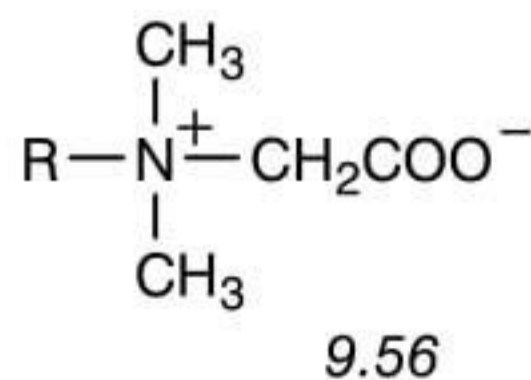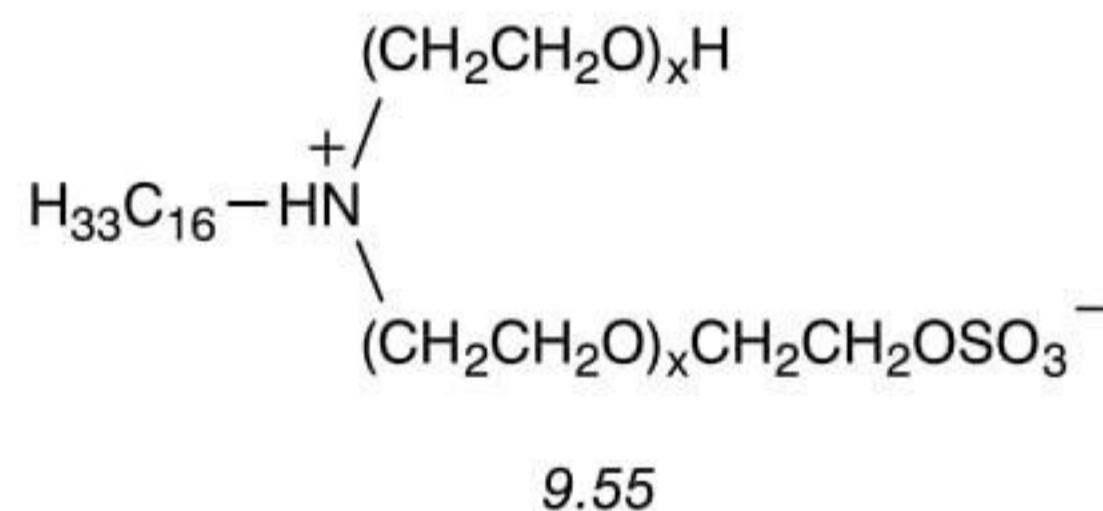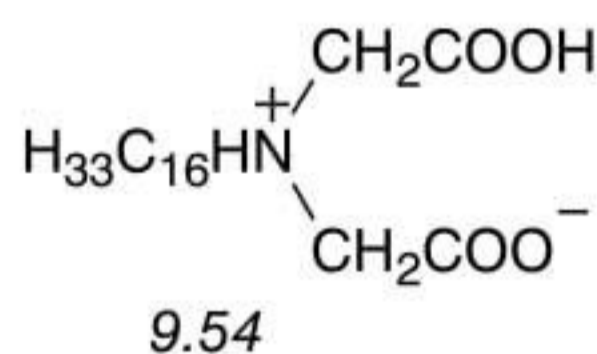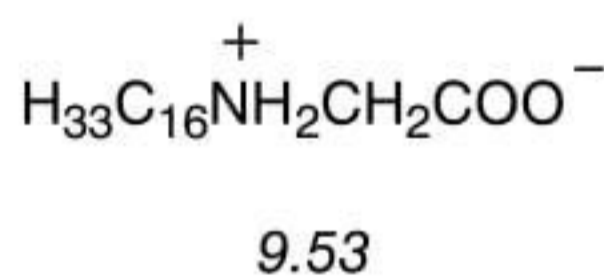
9.8 THE GENERAL PROPERTIES OF SURFACTANTS

9.8.1 Effects on the environment

The widespread use of these products focused attention on their environmental properties long ago, owing to the persistent foam-creating tendency of many surfactants when discharged. However, the surfactants industry has a very good track record of responding to environmental problems, stretching back as long ago as the 1960s; that is, quite some time before the present environmental bandwagon began to roll. Karsa has provided a pointed reminder of this: 'The most significant development in the West in the 1960s was the growing environmental awareness and concern for biodegradable components to overcome problems at sewage treatment plants and foam in watercourses. The result was an under-publicised and often forgotten fact that industry on both sides of the Atlantic voluntarily changed from branched-chain alkylbenzenesulphonates'. Since then, 'detergents have been based on biodegradable components, contrary to the impression given with some of the information supplied with today's 'green' detergents, which would have one believe biodegradability is something new and exclusive to these products. This was among the first major environmental moves by any industry and was ten years ahead of any UK or EEC legislation' [16].

Major works dealing with environmental aspects of surfactants are available [26–30].

The excellent biodegradability of the linear alkylarylsulphonates has already been mentioned (section 9.4). The alcohol sulphates have low toxicity and alcohol poly(oxyethylene) sulphates are even less toxic. Alkane sulphonates have high COD, BOD and an MBAS degradation rate of 90%. Polyether carboxylates have excellent environmental properties and are non-toxic to the extent that they are used in cosmetics and household detergents. Sodium-α-olefin sulphonates show rapid biodegradation due to their linear structures. The α-sulphomonocarboxylic esters show good to excellent environmental properties and are also used in cosmetics and household detergents. Sulphosuccinates generally show 90% biodegradation after seven days and have a long history of safe use, being ranked as relatively non-toxic. Phosphorus-containing anionics are very mild to the skin and are used in cosmetics, shampoos and lotions.

The toxicology of perfluorinated surfactants varies greatly; most are harmless, whilst some are amongst the most toxic non-proteins known, the structural differences between the two often being relatively slight. Hence caution is needed in their use, even though they are so strongly surface-active that they can be used in much smaller quantities than other surfactants.

Cationic alkylammonium surfactants have shown 94% biodegradability [27].

Amongst the nonionics, the use of linear primary alcohol ethoxylates has grown rapidly since the 1970s, due in very large measure to their high degree of biodegradability under most test procedures, both rapid primary and ultimate degradation [28]. Biodegradation of such products is retarded by branching of the alkyl chain, this being cumulative. It is also retarded in secondary alcohol structures, by the addition of about 3 equivalents of propylene oxide to the ethoxylate moiety and by an ethoxylate chain of more than 20 units. However, as Talmage points out [28], products containing these features are not present in the simple alcohol ethoxylates most commonly used in detergent formulations.

In contrast to the above trends, during the 1980s and 1990s there has been considerable environmental concern over the alleged effects of the nonionic nonylphenol ethoxylates.

The concern seemed to be centred around possible bioaccumulation and the properties of nonylphenol itself, potentially one of the major metabolites (products of biodegradation) released during the environmental breakdown of nonylphenol ethoxylates. The incomplete biodegradation was attributed to branching in the nonyl group and the presence of the aromatic phenyl ring. In the 1980s, particularly in Europe, there were calls for restrictions and bans on the use of nonylphenol ethoxylates. This concern, not surprisingly, led to much careful and detailed research from which has evolved a clarified and much less alarmist picture.

This research has been excellently reported by Naylor [31], who pointed out the limitations of laboratory methods (the extent of biodegradation of nonylphenol ethoxylates has been variously reported from 0% to 100%!) and the critical importance of determining biodegradability in conventional waste water plants using improved and streamlined analytical methods. This work, on American rivers and treatment plants, showed that nonylphenol ethoxylates exhibited high treatability under conditions of extremely high loadings on waste water treatment plants. It was confirmed that nonylphenol is indeed the metabolite of highest toxicity but it is not a significant metabolite except under anaerobic conditions. It was shown that nonylphenol ethoxylates are extensively biodegraded (92.5–99.8% removal rates) in secondary treatment. Re-aeration studies have shown that nonylphenol and nonylphenol ethoxylates contained in sewage sludge degrade when the sludge is applied to soil.

Thus there is a strong basis for the conclusion that nonylphenol ethoxylates are highly biodegradable, do not accumulate in water, sediment or aquatic organisms and do not pose a credible threat to the environment. Hence, in 1995, Naylor [31] was able to say that, in America, nonylphenol ethoxylates were by far the most important alkylphenol ethoxylates, accounting for 80% of the total volume and commonly found in formulations for fibre sizing, spinning, weaving, scouring and dyeing, as well as for water-based paints, inks, adhesives and many institutional and household cleaning products.

Finally, in considering the environmental properties of surface-active auxiliaries generally, it should be borne in mind that they are more or less complex mixtures and hence the presence of other components, such as solvents, electrolytes or sequestrants, needs to be considered in addition to the surfactants present.

9.8.2 Application properties

Anionic and cationic products generally tend to interact with each other, usually diminishing the surface-active properties of both and often resulting in precipitation of the complex formed. Amphoteric compounds can also be incompatible with anionics in acid solution but are generally compatible with cationics and nonionics. Interaction between anionic and cationic agents can sometimes be prevented by addition of a nonionic. In some cases, if an ethoxylated sulphate or phosphate is used as the anionic component a cationic compound produces no obvious precipitation, since the oxyethylene chain acts as dispersant for any complex that may be formed.

The main disadvantages of the carboxylates are their tendency to react with calcium and magnesium ions in hard water to give insoluble precipitates and their insolubility in acidic media, although they generally have good wetting and detergent properties. The acylsarcosides are less affected by calcium and magnesium ions, however, whilst the

carboxymethyl surfactants are unaffected. The sulphates were specifically developed to overcome the drawbacks of the carboxylates and, like the phosphates, are stable towards calcium and magnesium ions. As well as being outstanding detergents, the sulphonates are also unaffected by strongly acidic or alkaline conditions, and the higher-alkyl members have useful lubricating properties. On the other hand, the sulphates can be hydrolysed by acid and sulphated monoglycerides can also be hydrolysed by alkali. Their wetting properties tend to be inferior to those of the sulphonates but they are particularly valuable as emulsifying agents, especially in combination with nonionics. The sulphosuccinates have a high propensity to foaming and their solubility is not generally good, but the monoesters have good detergency properties and the diesters are particularly rapid wetting agents.

As a group, the phosphates have good stability to acid and alkali for most purposes, have low foaming and good detergency properties and are biodegradable. They tend to be better wetting agents than the sulphates and their solubility in organic solvents makes them useful in, for example, dry cleaning. The perfluoroalkyl anionic surfactants are very expensive, but are powerful surfactants at very low concentrations and are stable in chemically hostile environments; they also exhibit surface activity in organic solvents.

Cationic agents generally are less useful than anionics as detergents but they have useful properties as softeners, germicides and emulsifiers.

Nonionic agents are generally compatible with both anionic and cationic types. They are also stable to calcium and magnesium ions. With the exception of the fatty acid esters, which are readily hydrolysed by acid and alkali, they are stable and effective over a wide range of pH values. A particular characteristic of nonionic surfactants is their inverse solubility: as the temperature rises the solubility decreases, until a point is reached at which the surfactant attains its limiting solubility and therefore begins to precipitate out, causing cloudiness of the solution. The temperature at which this occurs, known as the cloud point, depends on the number of oxyethylene units in the nonionic molecule in relation to the length of the hydrophobe. Thus, for any given hydrophobe, the cloud point increases with the increasing degree of ethoxylation; for example, dodecanol heptaoxyethylene $C_{12}H_{25}(OCH_2CH_2)_7OH$ has a cloud point of 59 °C, while that of the undecaoxyethylene homologue is 100 °C. Conversely, for a fixed number of oxyethylene units, the cloud point decreases with increasing size of the hydrophobe. The cloud points of nonionic agents are also generally lowered by the presence of electrolytes, the effect varying with the electrolyte and its concentration. It is important to bear this in mind when choosing nonionic agents for use in electrolyte-containing processes. This inverse solubility arises from the solubilisation of the nonionic molecules by hydrogen bonding of water with the ether oxygen atoms (9.59). As the temperature rises, the energy within these bonds becomes insufficient to maintain their cohesion and dehydration takes place, with a consequent decrease in solubility. A knowledge of the cloud point of a surfactant is useful, not only because of solubility effects but also because the surface activity tends to be optimal just below the cloud point.

9.59
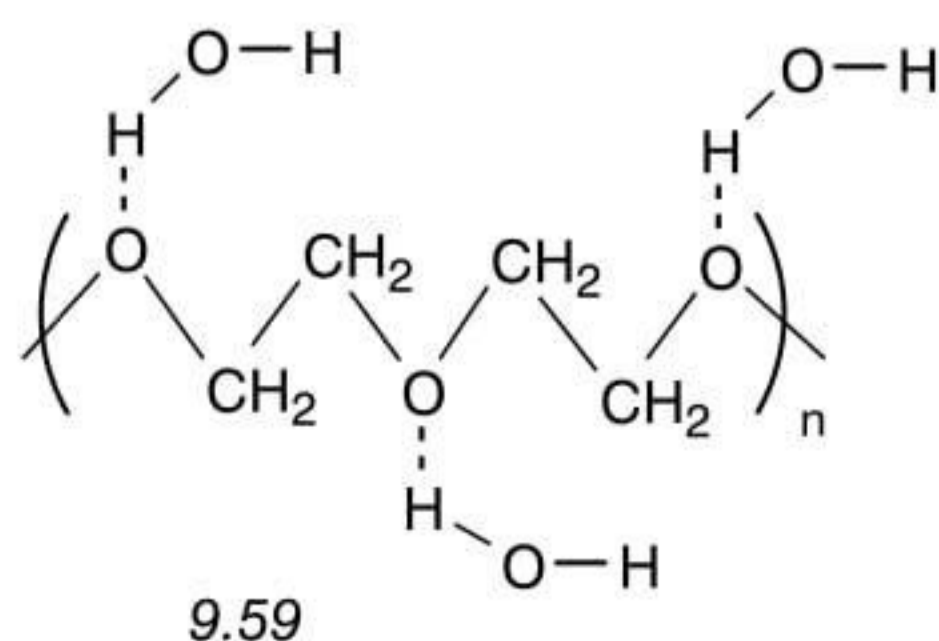
The tendency of nonionics to produce foam varies. Some, such as the block copolymers, are even used as defoamers. Their wetting, detergency and emulsifying properties also vary widely, depending to a large extent on the balance between the hydrophobic and hydrophilic (oxyethylene) portions.

The amphoteric agents exhibit excellent compatibility with inorganic electrolytes and with acids and alkalis. Such is their stability in strongly acidic solution that they are even used in cleaning compositions based on hydrofluoric acid [14].

9.8.3 The theory of surface activity

The physico-chemical theory of surface activity is a vast field and no more than broad principles can be touched on here; major reference sources exist for those who require more detail of the relationship between chemical structure and the various surfactant properties such as wetting, detergency and emulsification-solubilisation [32–36].

Surface activity is generally related to the balance between the hydrophobic and hydrophilic portions of the molecule. For example, among the anionic surfactants C_8–C_{12} alkyl hydrophobes tend to be predominantly wetting agents, whilst the C_{12}–C_{18} homologues exhibit better detergency and emulsifying properties. The alkylsuccinates and sulphosuccinates are particularly powerful wetting agents. Clearly, as the hydrophobic character of the surfactant is increased, aqueous solubility decreases and oil solubility increases. Thus the balance between the hydrophobic and hydrophilic moieties of a surfactant is a critical factor in determining its major characteristics. This is referred to as the hydrophile–lipophile balance, or HLB (the term 'lipophile', of course, being analogous to 'hydrophobe'). Whilst the HLB value is of general use in expressing the characteristics of a surfactant, it is of particular value in describing the formation of emulsions. For some general purposes the HLB can be used qualitatively (referring, for instance, to low, medium or high HLB), but for more precise work it is preferable to use a quantifying scale. Such a scale, put forward in the 1940s [37], covers a range of values from zero (the lipophilic or hydrophobic extreme) to a hydrophilic extreme of 20 or higher, with a value of 10 approximately representing the point at which the hydrophilic and hydrophobic portions are in balance. This scale is especially useful in describing the properties of the nonionic ethoxylates. For example, a low HLB value (4–6) signifies a predominance of hydrophobic groups, indicating that the surfactant is lipophilic and should be suited for preparing water-in-oil emulsions. A value in the 7–9 range indicates good wetting properties. As the value shifts towards increased hydrophilicity other properties predominate, values of 8–18 being typical for surfactants that will give oil-in-water emulsions, and values of 13–15 for surfactants that show useful detergency. The HLB values required for solubilising properties are generally in the range 10–18.

The HLB of a relatively pure poly(oxyethylene) adduct can be calculated from theoretical data [37]. For these agents the HLB is an indication of percentage by mass of the hydrophilic portion, divided by five to give a conveniently small number. For example, if the hydrophilic portion of a purely hypothetical nonionic agent accounted for 100% of the molecule (such a product cannot, of course, exist), its HLB is 20. Similarly, a more plausible product in which 85% of the molecule is accounted for by the hydrophilic portion has an HLB of 85/5 = 17. The ICI Americas Inc. method of calculating the theoretical HLB of a sorbitan monolaurate nonionic having 20 oxyethylene units per molecule is given in

Equation 9.1 (total relative molecular mass = 1226, of which 1044 is contributed by the hydrophilic portion) [37].

$$\text{HLB} = \frac{1044}{1226} \times 100 \times \frac{1}{5} = 17.0 \qquad (9.1)$$

As explained earlier, however, the actual constitution of a surfactant rarely conforms to its nominal structure. Consequently the theoretical method of calculation is of limited utility, practical methods being more reliable. The HLB value may be determined directly by analysis or by comparison with a range of surfactants of known HLB values. An analytical method for the sorbitan monolaurate described above uses Equation 9.2 [37].

$$\text{HLB} = 20\left(1 - \frac{S}{A}\right) = 20\left(1 - \frac{45.5}{276}\right) = 16.7 \qquad (9.2)$$

where S is the saponification number of the ester and A is the acid number of the recovered acid. The saponification value of a product is the mass in milligrams of potassium hydroxide required to saponify one gram of the product; it can be found by saponification of the product with an excess of potassium hydroxide, followed by back-titration of the remaining alkali with hydrochloric acid. The acid value of an acid is the number of milligrams of potassium hydroxide required to neutralise a standard quantity, and can again be found by titration. The comparative methods should always be used for the nonionic surfactants that are not based on ethylene oxide, and also for ionic surfactants since the hydrophilic influence of the ionic group exceeds that indicated by the mass percentage basis (this can lead to apparent HLB values higher than 20).

Once the HLB values of a range of surfactants are known it is an easy matter to calculate the HLB value of a mixture as follows:

Individual HLB		Fractional HLB			
45% of surfactant A	16.7	0.45 × 16.7	=	7.52
35% of surfactant B	4.0	0.35 × 4.0	=	1.40
20% of surfactant C	9.6	0.20 × 9.6	=	1.92
		Total HLB	=	10.84

When preparing an emulsion, emulsification tends to be most efficient when the HLB of the agent matches that of the oil phase. Often a mixture of surfactants makes a more efficient emulsifying agent than a single product having the same HLB value as the mixture; similarly, if the oil phase to be emulsified is itself a mixture, its components will each contribute to the effective HLB value. It is this effective HLB that is the main criterion in designing a suitable emulsifying system. The effective HLB value can be found by carrying out preliminary emulsification tests with agents of known HLB values. A useful procedure [37] uses two such emulsifying agents of widely differing HLB values mixed in various proportions so as to give a range of intermediate HLB values. The HLB value of the mixture that gives the best emulsion of the oil phase under test then corresponds to the effective

HLB value of the oil phase. Further tests can then be carried out with different chemical types of agents around this effective HLB value in order to find the optimum emulsifying system.

9.8.4 Micelle formation

All surfactants in solution tend to form more or less ordered agglomerates of molecules, known as micelles. Pure water has a surface tension of about 72×10^{-3} N/m. As surfactant is added gradually to it, the surface tension falls quite rapidly (Figure 9.1) until, at a certain concentration of surfactant, it begins to level off more or less sharply. At the point at which this levelling out takes place, the critical micelle concentration (CMC in Figure 9.1), the surfactant molecules begin to orient themselves in clusters within the body of the solution, these clusters being more or less lamellar or spherical (Figure 9.2).
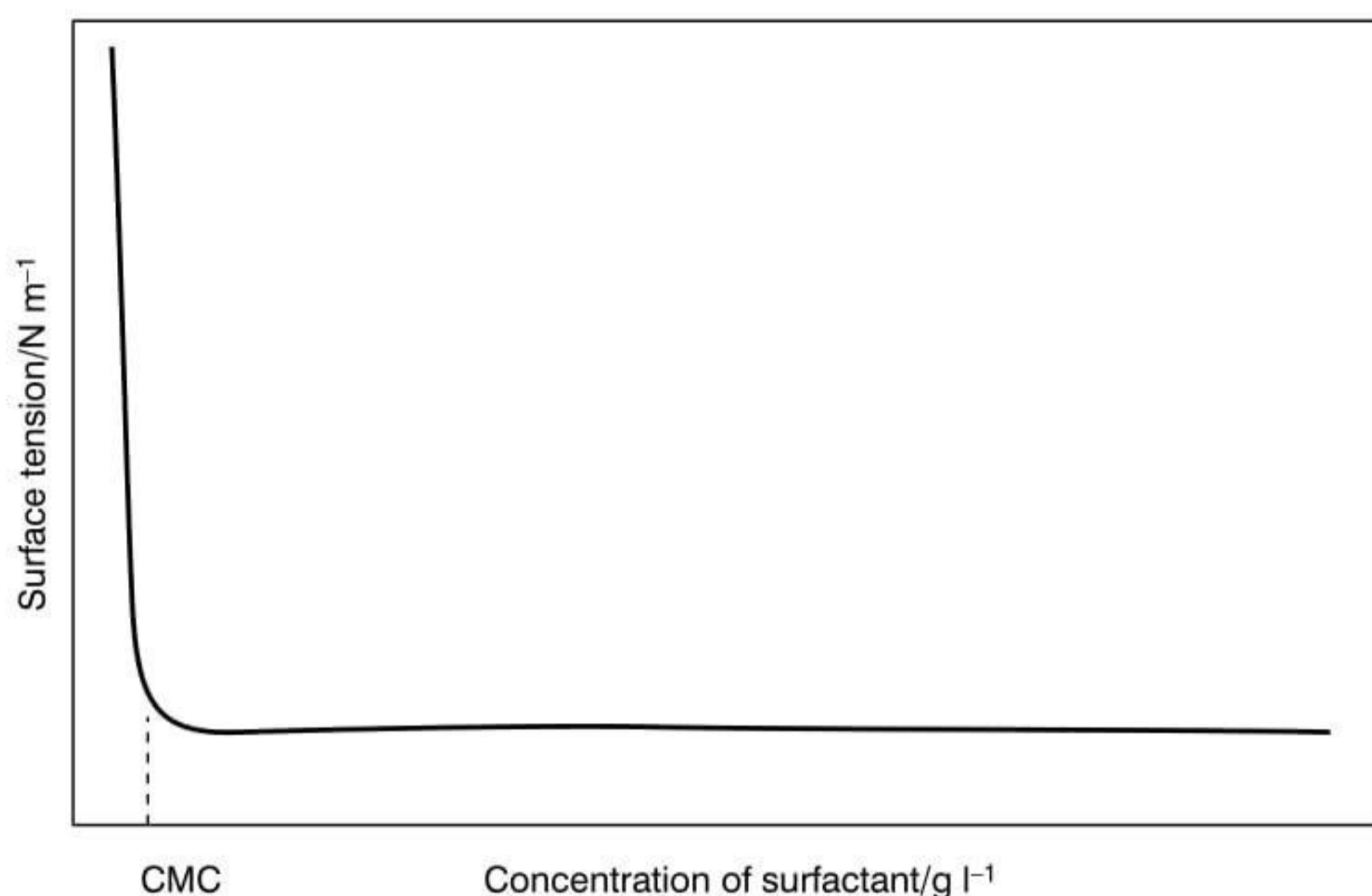

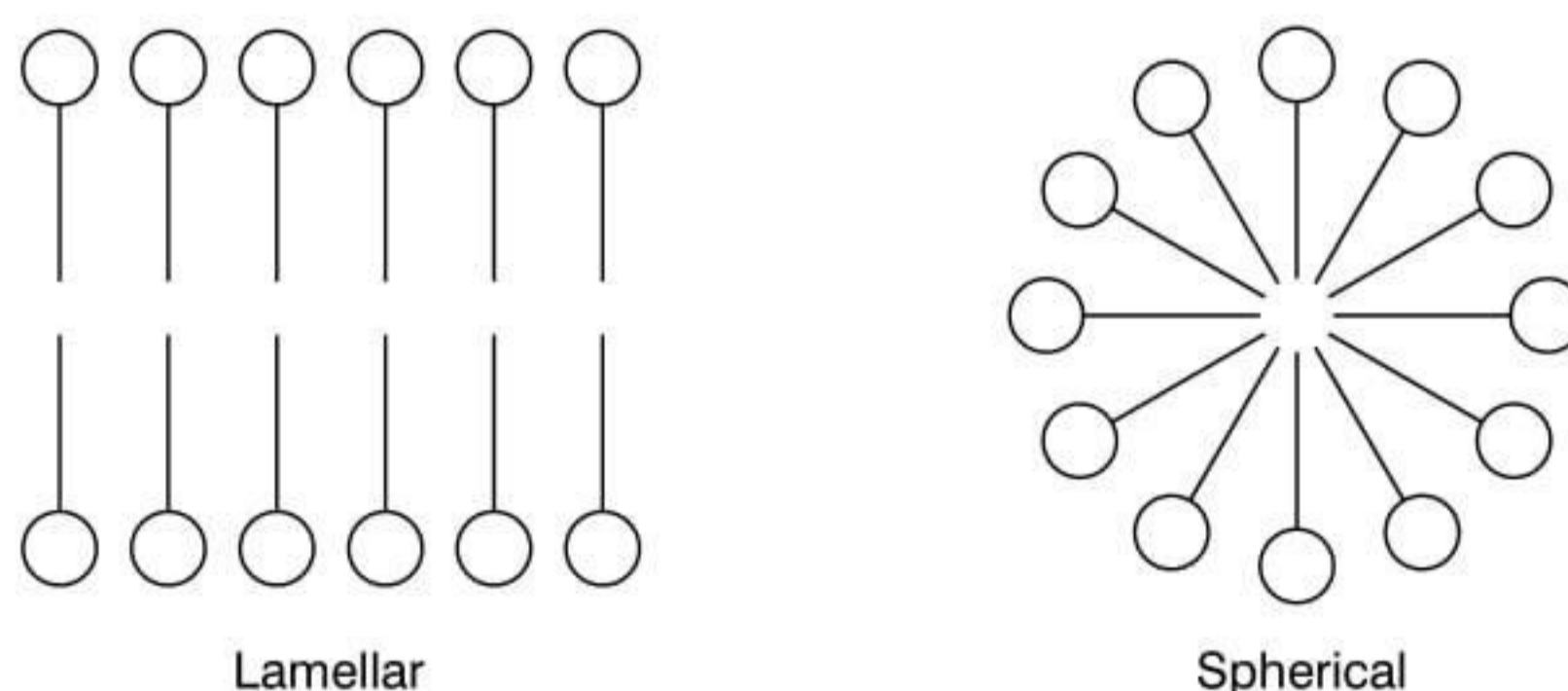**Figure 9.1** Surface tension of water against surfactant concentration

Figure 9.2 Micelle formation

In water the surfactant molecules orient themselves with their hydrophobes at the centre of the cluster. The CMC is typically quite low, perhaps 0.5–0.2 g/l. At concentrations lower than this the molecules orient themselves only at the interfaces of the solution, and it is this effect which brings about the lowering of surface tension. Once the CMC is reached the

interfaces become saturated and as the concentration increases micellar clusters of molecules begin to form in the bulk of the solution; there is little further reduction in surface tension beyond the CMC, nor are there changes in the other surfactant properties such as wetting and foaming. In general, the CMC decreases with increasing size of the hydrophobe, and the CMCs of nonionic agents tend to be lower than those of ionic types, since with the nonionics micelles can form more easily in the absence of polar charges. This ability to form micelles is vital to the efficacy of surfactants as emulsifying, dispersing and solubilising agents.

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