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9.1 Introduction

Chemical admixtures are nowadays very important for concrete design, and are essential for the formulation of concrete with a low environmental impact (Flatt et al., 2012).

Chemical admixtures can modify the properties of fresh or hardened concrete or, in some cases, both. Superplasticizers and viscosity-modifying admixtures, discussed in more detail in Chapters 16 (Nkinamubanzi et al., 2016) and 20 (Palacios and Flatt, 2016) respectively, modify the rheological behaviour of fresh concrete. Retarders and accelerators modify cement hydration, with implications for concrete placing, and are discussed in Chapters 18 and 19 (Aïtcin, 2016b,c). Admixtures such as air entrainers and shrinkage reducers enhance durability; these are dealt with in Chapters 17 and 23 (Gagnè, 2016a,b).

Besides their main effect, many admixtures have secondary effects. For example, most compounds used as water reducers or high-range water reducers can cause some retardation of cement hydration, depending on factors such as dosage and molecular structure. In some circumstances these secondary effects can be beneficial, while in others they are undesired. The influence that chemical admixtures have on cement hydration (Marchon and Flatt, 2016a, Chapter 8) is dealt with in Chapter 12 (Marchon and Flatt, 2016b).

Many chemical admixtures are effective at low or very low dosages, and the reason for this is that they act at the interface, either solid–liquid (as for superplasticizers) or liquid–vapour (as for shrinkage-reducing and air-entraining admixtures). The adsorption of chemical admixtures at an interface is discussed in Chapter 10 (Marchon et al., 2016). The working mechanisms of admixtures are discussed in various chapters of this book, requiring in many cases a good knowledge of their chemical structure.

The main objective of this chapter is to regroup the information about molecular structure of chemical admixtures to make it easier to compare compounds among each other. It also serves as a source of chemical structures that may be consulted if this information is needed for any other chapters.

In preparing this chapter we decided to focus our presentation on organic chemical admixtures. This choice was guided by the fact that this is where the real added value of molecular structure comes into play in terms of design of new or modified chemical admixtures. It is therefore our hope that the chapter may serve not only as a general reference for people wanting to know about chemical admixtures, but also that it

may give chemists a comprehensive overview of molecular structures used in practice and inspire them to design new and/or improved compounds.

9.2 Water reducers and superplasticizers

9.2.1 Introduction

In this section the chemistry of the main types of superplasticizers (SPs), also called high-range water-reducing admixtures, is presented.

The first part is dedicated to natural polymers, which are rather plasticizers or mid-range water-reducing admixtures. The use of such dispersants dates back to the 1930s. Although the performance of natural polymers is limited compared to synthetic ones, it is worth mentioning them as they are still widely used in the concrete industry—mainly because of their low cost of production.

Next, synthetic linear polymers are described. This category includes some of the most commonly used SPs, such as polynaphthalene sulphonates (PNS), polymelamine sulphonates (PMS) and vinyl copolymers. The higher dispersing ability of these compounds qualifies them as true SPs or high-range water reducers (in contrast to lignosulphonates or other low- or mid-range water reducers). They were introduced during the 1960s and are generally referred to as electrostatic dispersants, although some show predominant steric effects. They made it possible to develop high-performance concrete as a reliable form now used in numerous structures. The practical use of SPs is dealt with in Chapter 16 (Nkinamubanzi et al., 2016).

Finally, the new generation of SPs, namely comb-shaped copolymers, is introduced. The development of comb-shaped SPs in the 1980s represented a breakthrough in concrete technology, as they allow use of a very low water/cement ratio (w/c of 0.20 or less) while keeping good workability. In this regard, one should in particular acknowledge that the formulation and large-scale use of self-compacting concrete (Okamura and Ouchi, 1999) have greatly benefited from the introduction of such admixtures. But these polymers have also found a place in ultra-high-strength concrete (Mitsui et al., 1994). Comb-shaped copolymers are steric admixtures, meaning that their dispersing ability is due to steric effects rather than electrostatic repulsion (even if, as mentioned previously, linear polymers often also work via steric hindrance, this terminology persists and it would be better to qualify comb-copolymer as “more effective” steric dispersants). The successful use of these SPs comes mainly from the possibility of tailoring their design, in terms of both chemical groups and molecular structure, to obtain SPs with different performance and applications (ready-mix concrete, pre-cast concrete, etc.).

9.2.2 Natural polymers

9.2.2.1 Lignosulphonates

Lignosulphonates (LSs) were the first dispersants added as water-reducing admixtures to concrete. LSs have been used since the 1930s as plasticizers and water reducers (Scripture, 1937) and ready-mix concrete represents their largest application.

LSs are obtained as by-products of bisulphite pulping of wood, which is used to separate pure cellulose fibres by dissolution of hemicellulose and lignin. Lignin is a natural and renewable biopolymer present in wood and is, after cellulose, the second most abundant organic molecule on Earth. The lignin content depends on the wood species: it is higher in softwood (27–37%) than in hardwood (16–29%). The production of extracted lignin amounts to 70 million tons per year: the majority is burnt for energy recovery and regeneration of pulping chemicals, and only 5% is used as a chemical product. Native lignin is water-insoluble, and presents a complex three-dimensional network built from randomly cross-linked monolignols, such as coumaryl, conyferil and synapyl alcohols.

The chemical process of sulphite pulping (delignification) involves the use of sulphite (SO_3^{2-}) or bisulphite (HSO_3^-) salts (typically sodium, magnesium, ammonium or calcium) at high temperatures (140–170 °C). During this process, lignin with a reduced molecular weight is formed because of the breaking of ester bonds that interconnect lignin units (fragmentation). At the same time the introduction of sulphonic groups on the aliphatic chains makes the lignin water-soluble (sulphonation). The insoluble cellulose fibres are separated from LSs by filtration. The resulting by-product, called ‘spent liquor’, contains poorly sulphonated lignins of different molecular size, inorganic salts, extracts from wood and pentose and hexose sugars coming from the acidic hydrolysis of the hemicellulose. LSs for concrete applications are further modified to achieve the desired properties.

Earlier presented as a spherical microgel unit, the structure of LSs has now been described as randomly branched polyelectrolyte macromolecules (Myrvold, 2008). The structure is formed by phenyl propane units connected in a non-regular manner by ether or C–C bonds, the latter between the aromatic rings. To optimize both water solubility and plasticizing effect, the degree of sulphonation is increased, typically up to 0.5–0.7 per phenyl propane unit, by sulphomethylation with sodium sulphite and formaldehyde. The sulphonate groups are distributed foremost on the surface of LS molecules.

LSs contain numerous functional groups, such as carboxylic acid, phenolic hydroxyl, catechol, methoxyl, sulphonic acid and various combinations of these. The structure of a commercial LS is shown in Figure 9.1.

The solubility in water is influenced not only by the degree of sulphonation and polymerization, but also by the cation, usually sodium or calcium, used in the admixture production. Unlike calcium LSs, sodium LSs are generally more soluble, even at low temperatures (below –10 °C), preventing precipitation under cold conditions. Moreover, at constant concentration of counterion, the degree of ionization is higher in sodium LSs. However, calcium LSs are typically cheaper than sodium LSs, offsetting the cost of the extra dosage used to achieve a comparable dispersion.

Approximately 25% of the total solids in spent liquor is sugars, which can have a strong retarding effect on concrete setting time (see Marchon and Flatt, 2016b, Chapter 12). LSs can be purified and sugar content reduced by precipitation, alkaline heat treatment, ultrafiltration or amine extraction. However also sugar-free LSs show very pronounced retardation, so that the role of sugars is often stated as either secondary or complimentary. (Reknes and Gustafsson, 2000).

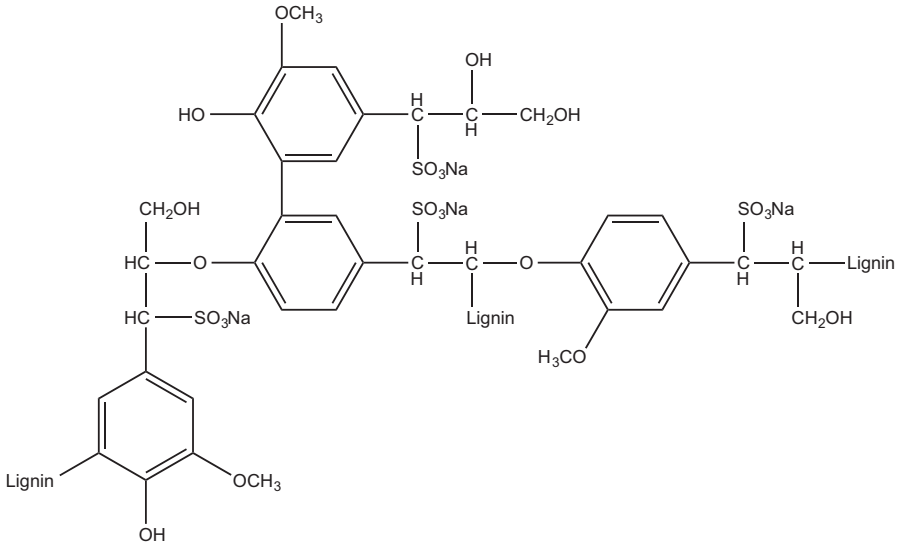


Figure 9.1 Chemical structure of a lignosulphonate.

The molecular weight of commercial LSs ranges from a few thousand to 150,000 Da, showing a much greater polydispersity than synthetic polymers. Ultrafiltration can be applied to narrow the molar mass distribution.

The degree of sulphonation increases with decreasing molecular weight, but it does not depend on the type of wood. Additionally, it was demonstrated that hardwood LSs have significantly lower molecular weights than softwood LSs (Fredheim et al., 2002).

The molecular weight of LSs and their fractions was typically characterized by size exclusion chromatography combined with either ultraviolet (UV) or multi-angle laser light-scattering detectors, but more techniques are available nowadays (Fredheim et al., 2002; Brudin and Schoenmakers, 2010). The study of LS adsorption on cement can be carried out by UV absorption at 280 nm prior to a calibration with the LS under investigation (Gustafsson and Reknes, 2000).

LSs as dispersants in concrete show a limited water reduction capability (8–10%), with an averaged dosage of about 0.1–0.3% by weight of cement. For this reason, although LS is the most used material for the formulation of water-reducing admixtures, it is hardly used in the design of high-performance concrete. To improve their water-reducing effect, many efforts and studies have been made to modify the structure of lignins and LSs. Oxidation, hydroxymethylation, sulphomethylation processes (Pang et al., 2008; Yu et al., 2013), graft copolymerization of LS with carbonyl aliphatics (Chen et al., 2011) and modification of lignin by the introduction of epoxytated polyethylene glycol (PEG) derivatives (Aso et al., 2013) seem to be effective in enhancing the hydrophilicity of LSs, promoting the dispersion of cement particles.

Tests with LSs with different molecular weights have shown that higher-molecular-weight fractions (>80 kDa) cause better plasticizing effects, enabling water reduction

of up to 20% with moderate retardation. Moreover, high-molecular-weight LSs also improve the workability retention (Reknes and Gustafsson, 2000; Reknes and Petersen, 2003).

In concrete, commercial LSs show a low content of entrapped air, of about 2%. This is basically the same as the 1–2% found in ordinary non-admixed concrete. More details are given in Chapter 6 (Aïtcin, 2016a). However, the air entrainment can rise to 8% in the presence of high-molecular-weight fractions (Reknes and Gustafsson, 2000; Ouyang et al., 2006).

LSs are among the cheapest concrete admixtures available on the market, costing about five times less than a commercial polycarboxylate-ether (PCE)-based polymer (Kapielov et al., 2000). In 2005 the annual worldwide production of LSs was estimated at 1.8 million tons with a commercial value of about US\$500 million (Will and Yokose, 2005). In 2007 up to 90% of total LS production was used in concrete constructions (Tejado et al., 2007).

9.2.2.2 Casein

Casein is a phosphoprotein found in bovine milk, and makes up to approximately 80% of the total milk protein. Casein is obtained by acid precipitation from milk, and is easily available in powder with high purity at a low cost.

The casein constituents, α , β , and κ -casein, exist in proportions of approximately 5:4:1 by weight. They differ in the amount of phosphate groups, which are linked to the amino acid serine through esterification. A proposed model for casein structure is shown in Figure 9.2.

Casein solubility is pH-dependent. In aqueous solution at neutral pH, casein is water-insoluble and forms spherical micelles with an average diameter of 150 nm. When dissolved in alkaline solution (pH 12–13), casein micelles dissociate to form

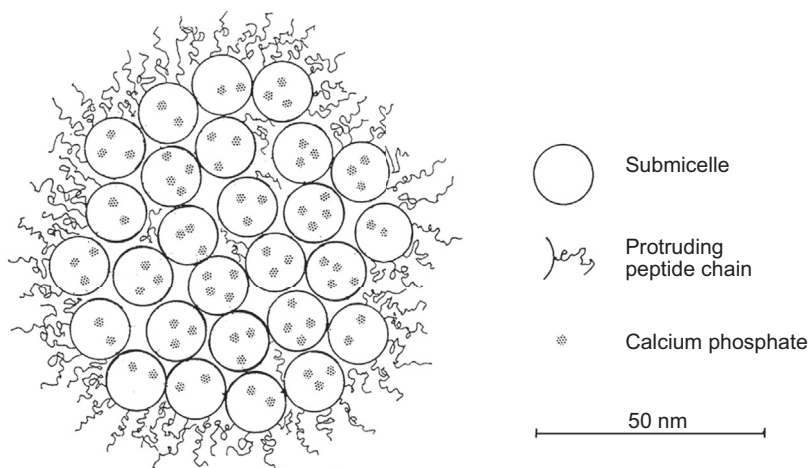


Figure 9.2 Model of a casein micelle (cross-section). Reproduced from Walstra (1999) with authorization.

negatively charged water-soluble submicelles of about 20 nm (Bian and Plank, 2012). Caseins possess high anionic charge density in alkaline media, because of the deprotonation of the amino acid residues.

Casein has been used as a dispersant and stiffening agent for a long time, but has only recently been developed for modern construction applications. When used with an appropriate cement composition, the casein reduces fluidity loss and has minimal effects on thickening time (Vijn, 2001). In self-levelling underlayments, the addition of casein provides good dispersing properties at dosages of 0.1–0.4% and shows a self-healing effect on the surface of the grout. Furthermore, it shows good compatibility with α -hydroxy carboxylic acid-based retarders, such as citric and tartaric acids (Plank and Winter, 2008).

Plank et al. (2008) and Winter et al. (2008) isolated the casein constituents and found that the α -casein has the highest negative net charge (-24 at pH 6.7) with respect to the other fractions, concluding that α -casein is the main fraction responsible for the dispersing effect, adsorbing on cement particles in large amounts. These results are supported by the fact that α -casein barely intercalates into layered double hydroxides. In this way, α -casein should be more available in solution than β -, and κ -caseins for cement dispersion (Yu et al., 2010). Furthermore, it has been observed that the unique self-healing property of casein derives from α -casein (Bian and Plank, 2013a). The plasticizing effect of caseins also depends on the content of κ -casein. A high proportion of κ -casein promotes the formation of submicelles smaller than 10 nm at alkaline pH, leading to an increased negatively charged surface in contact with the cement (Plank and Bian, 2010).

As observed for other biopolymers, casein-based water reducers show some disadvantages related to variability and storage. Indeed, the quality of casein varies depending on the species of animal, sampling season, manufacturing process, etc. Moreover, prolonged exposure to high temperatures (80–100 °C) during its production causes the denaturation of proteins, resulting in reduced plasticizing effectiveness (Bian and Plank, 2013b). A further limitation in using casein in cementitious systems is the unpleasant smell of ammonia due to the biodegradation of proteins under alkaline conditions and the proliferation of pH-tolerant moulds (Karlsson and Albertsson, 1990).

9.2.3 Linear synthetic polymers

9.2.3.1 Polynaphthalene sulphonates (PNS)

PNSs, also known as sulphonated naphthalene formaldehyde condensates (SNFC), were first developed in the 1930s and originally used in textile chemicals and the development of synthetic rubber. In the late 1960s PNSs were introduced into the concrete admixtures market in Japan as the first synthesized high-range water-reducing admixture, more commonly called superplasticizer.

The first step of PNS synthesis is the sulphonation of naphthalene with sulphuric acid, as shown in Figure 9.3(a).

Due to the symmetry of the naphthalene, the substitution of the hydrogen by the sulphonate can take place in two positions, α or β (Figure 9.4).

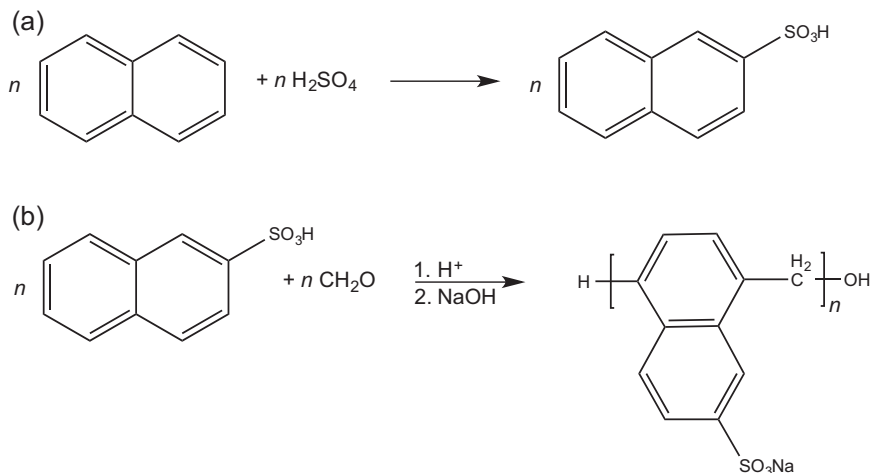


Figure 9.3 Synthetic route for preparation of PNSs. (a) Sulphonation of naphthalene with sulphuric acid and (b) polycondensation in the presence of formaldehyde.

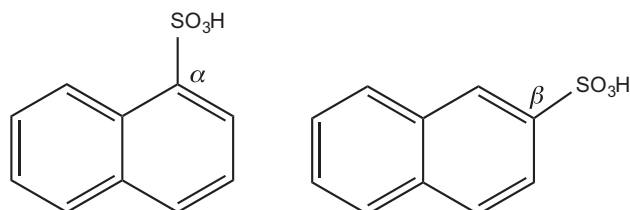


Figure 9.4 Chemical structure of naphthalene with a sulphonate group in α and β positions.

The α -substitution occurs mostly below a temperature of 100 °C, whereas at temperatures higher than 150 °C the β -isomer represents the most thermodynamically stable compound (Piotte, 1993). The quality and type of sulphonation are of great importance, as significant residual amounts of α -naphthalene sulphonic acid, naphthalene and sulphuric acid may influence the condensation of PNS. Furthermore, only PNSs polymerized with β -naphthalene sulphonic acid show the expected dispersing effect (Piotte, 1993). Aïtcin et al. (2001) mentioned that in a well-controlled synthesis of PNS, the sulphonation degree is about 90%. Furthermore, Piotte (1993) and Piotte et al. (1995) showed in a study of the quality of a non-purified batch of sulphonated naphthalene produced in typical conditions, as described in Hattori and Tanino (1963) and Miller (1985), that about 10% of the sulphonated functions were in position α .

The second step of PNS production (Figure 9.3(b)) is the condensation reaction of β -naphthalene sulphonic acid with formaldehyde, producing polymethylene naphthalene sulphonic acid. This polycondensation has been described as being similar to the reaction of phenol-formaldehyde resins (Piotte, 1993): first, after the protonation of its carbonyl function, the formaldehyde in its reactive form is added to the aromatic ring

by electrophilic addition. Then, after condensation, the methylol function of this new compound reacts with a second molecule of naphthalene and forms a methylene bridge between these two naphthalene molecules.

Once the desired degree of polymerization has been obtained (the molecular weight being time-dependent), the third and last step of PNS production consists of neutralizing the polymethylene naphthalene sulphonic acid with sodium hydroxide. When it is necessary to obtain a polymer free of alkalis, lime can be used, but filtration becomes mandatory to remove excess of lime and gypsum.

The conditions of reaction, such as the ratio between the reagents, the steric hindrance and the conformation changing during the polymerization, have a strong effect on the final structure of the PNS molecules and their molecular weight. The structure can be classified into three groups: linear, branched and cross-linked molecules. In a study of characterization of PNSs by ultrafiltration and high-performance liquid chromatography (HPLC), [Piotte et al. \(1995\)](#) showed that commercial products generally exhibit a high degree of polydispersity. They contain up to 10% of oligomers with a degree of polymerization between one and four, the monomers being the most abundant species. Some 20–30% of the polymers are linear molecules with a maximum degree of polymerization equal to 20 (which represents a molar mass of about 5000 g/mol) and a maximum population of around 10 (2500 g/mol). Finally, 35% of the polymers have a degree of polymerization between 20 and 40 (10,000 g/mol), and about 25% of species have a higher degree that can exceed 200 (50,000 g/mol), probably due to strong cross-linking. This indicates that commercial PNSs can contain a large amount of non-linear molecules with a more or less stiff three-dimensional conformation.

The structural composition of PNSs is an important factor in their dispersing properties. For example, the monomers and oligomers (degree of polymerization smaller than four) as well as the cross-linked molecules with a high molar mass do not disperse cement suspensions. PNS molecules show a dispersing ability when the degree of polymerization is between 5 and 80, with an optimum around 10 ([Aïtcin et al., 2001](#)). This optimum comes from the fact that at higher degrees of polymerization highly branched and, in the worst cases, cross-linked molecules cannot be completely avoided during the reaction, although the branching degree can be controlled by the amount of formaldehyde used in the condensation process ([Miller, 1985](#)). As the mode of action of these polymers involves adsorption on the solid particles, and thus the degree of particles coverage, these large molecules with high stiffness prevent a good covering of the particle surface and therefore lead to a low dispersing effect.

As seen above, characterization of the composition, structure and molar masses of PNSs is of great importance for determining and approaching the expected dispersing ability. As for other types of SPs, HPLC has shown its advantage in providing detailed profiles of the structural composition of commercial PNSs. Furthermore, the amount of molecules with a low degree of polymerization can be determined by UV spectroscopy ([Piotte, 1993](#)). These two methods can be applied to monitor the evolution of condensation reactions. Besides ultrafiltration to separate the polymeric fractions by molecular weight, selective precipitation allows the removal of oligomers with alcohols, as the solubility of the polymer changes with its polymerization degree and the type of alcohol.

The effect of PNSs on concrete fluidity has been intensively studied, as they were the most used SPs until the beginning of 2000. These studies include, for example, the effect of molar mass on adsorption and dispersing effect (Pieh, 1987; Pagé et al., 2000; Kim et al., 2000; Aïtcin et al., 2001), as discussed earlier, and the effect of the counterions on the performance of PNS in cement paste (Piotte, 1993), as well as their impact on hydration of cement phases (Singh et al., 1992; Uchikawa et al., 1992; Mollah et al., 2000). One of the great advantages of PNS is that their use does not alter the stability of the pore network in air-entrained concrete with freeze–thaw resistance, which explains their wide use in North America (Nkinamubanzi et al., 2016, Chapter 16). One of the most reported limitations of PNSs as concrete dispersants has been their incompatibility with low-alkali cement; but here PNSs containing a significant amount of residual sulphate can improve the situation.

9.2.3.2 Polymelamine sulphonates

The dispersing properties of another family of sulphonate-based SPs, called polymelamine sulphonates (PMSs) or sulphonated melamine formaldehyde condensates (SMFC), were discovered in the 1970s, and they are nowadays still widely used in the concrete industry.

As for PNSs, the synthesis of PMSs involves several steps. First, formaldehydes react with the amino groups of the melamine under alkaline conditions, leading to a methylolated melamine. Under the same alkaline conditions, sodium bisulphite is used to sulphonate one of the methylol groups (Figure 9.5).

Finally, polymerization by polycondensation is performed under acidic conditions. Increasing the pH to basic values stops the reaction.

As for PNSs, molecular weight distributions of PMSs are broad. Cunningham et al. (1989) measured by high-performance size exclusion chromatography a distribution between 1200 and 44,000 g/mol, with an average molecular weight of 7900 g/mol. Pojana et al. (2003) mentioned that a PMS exhibits a much higher average number of oligomeric units (around 50–60) with respect to a PNS (with its average number around 10). This would imply that PMSs can exhibit a more complex structure with possibly branched molecules.

As PNSs and PMSs are produced in the same way and were developed and used in the same period, there is a certain number of comparative studies on use, stability and toxicity of both admixtures. For example, they have the same water reduction or plasticizing ability, but cement pastes with a PMS show a higher slump loss. However, PMSs retard cement hydration less, which is why they are often preferred in the pre-cast industry (Flatt and Schober, 2012). It should be noted that the use of PMSs can be limited due to the probable presence in the solution of free formaldehydes, which have been listed since 1981 as a human carcinogen (Report on Carcinogens, 2011).

Another important aspect in toxicity is the impact on the environment when these SPs are used in concrete at construction sites (Redín et al., 1999; Ruckstuhl and Suter, 2003; Pojana et al., 2003). Ruckstuhl and Suter (2003) showed that oligomers of PNSs (up to a polymerization degree of four) were found in groundwater close to a tunnel

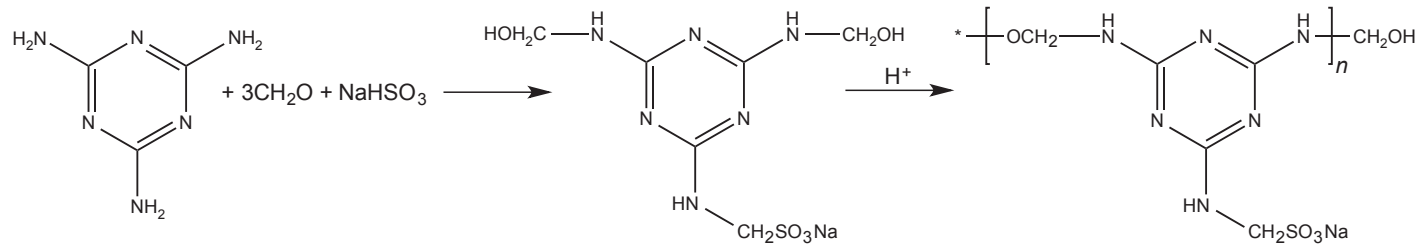


Figure 9.5 Sequence of reactions in the synthesis of polymelamine sulphonates.

being constructed in Switzerland. Similarly, [Pojana et al. \(2003\)](#) observed that released components of a PMS solution from leaching tests were composed only by shorter molecules. It seems that in both cases larger molecules that are strongly adsorbed on cement particles could not be washed out of the cement.

9.2.3.3 Phosphonate-terminated PEG brushes

Polyoxyethylene phosphonates or diphosphonates were developed at the beginning of the 1990s ([Guicquero et al., 1999](#)). These polymers are composed of one PEG chain with one or two phosphonate groups on one end ([Figure 9.6](#)).

The objective of developing such a molecule was to use a functional group with a higher affinity for cement surface than carboxylic or sulphonate groups. Indeed, phosphonates are known to have strong complexing ability for calcium, which means that they have a strong affinity for cement particles owing to the high calcium concentration in cement suspensions. The steric stabilization of these polymers then arises from the polyethylene glycol chain, which does not adsorb onto the surface and forms a layer on the particle surface from which other polymer-coated particles are expelled. The high adsorption and dispersion efficiency in CaCO_3 suspensions were shown by [Mosquet et al. \(1997\)](#) and [Chevalier et al. \(1997\)](#).

Polyoxyethylene phosphonates are polymerized in two steps, as shown in [Figure 9.7](#).

First, the primary or secondary amino-terminated PEG is produced by anionic polymerization of ethylene oxide, initiated by potassium aminoalcoholates. The presence of the primary or secondary amine group at one end of the chain allows obtaining the mono- or diphosphonate end group, more specifically called the aminomethylene-phosphonate group, by Moedritzer reaction with orthophosphorous acid and formaldehyde ([Moedritzer and Irani, 1966](#)).

The structure of the adsorbed polymer layer on particles consists of free end-anchored chains, and depends on the polymer molecular weight, solvent quality and the density of molecules adsorbed on the surface. Two regimes have been observed ([Figure 9.8](#)).

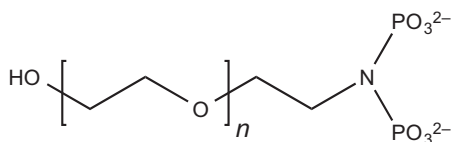


Figure 9.6 Chemical structure of a polyoxyethylene diphosphonate.

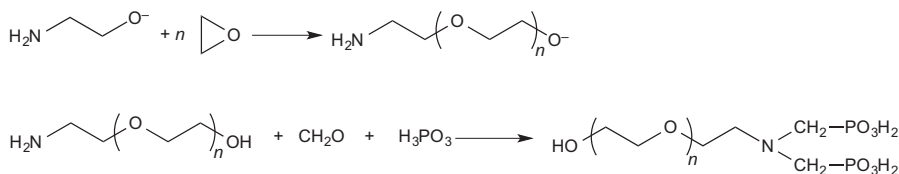


Figure 9.7 Scheme of the two-step synthesis of polyoxyethylene diphosphonate.

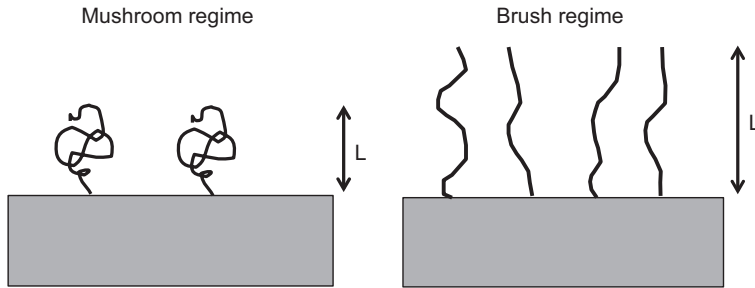


Figure 9.8 Schematic illustration of the change in conformation of end-anchored chains from a mushroom to a brush regime as a result of an increase in the density of surface occupancy.

At low coverage, adsorbed macromolecules are independent of each other and have an unperturbed coil conformation similar to that of non-functional PEG chains in bulk water. This is the ‘mushroom’ regime (Chevalier et al., 1997; Mosquet et al., 1997), where the thickness of the polymer layer, L , has been shown to be equal to the polymer radius of gyration. When the density of adsorbed polymers increases such that the adsorbed macromolecules cannot be considered as dilute and start to influence each other, a ‘brush’ regime is reached where the polymer chains stretch away radially from the surface, increasing the thickness of the adsorbed polymer layer and enhancing the steric repulsion.

Beside high dispersing ability, this type of SP has important advantages. They show an increased slump life (Guicquero et al., 1999) and a good resistance to soluble alkali sulphates due to their specific mode of adsorption and dispersion. Nevertheless, they induce strong retardation of hydration of C_3S , as Comparet et al. (2000) showed. This is discussed further in Chapter 12 dealing with the retardation of hydration by chemical admixtures (Marchon and Flatt, 2016b). Due to these properties, the phosphonates are particularly adapted to extreme conditions, such as hot weather, long slump requirement, long-distance pumping or oil-well cementing (Mosquet et al., 2003).

9.2.3.4 Vinyl copolymers

With the development of new concrete technologies, requirements for synthetic SPs with mixed functionality became more demanding to fulfil the expected performance. PNSs and PMSs already showed improved properties when polymerized with other chemical functionalities (Pagé et al., 2000; Shendy et al., 2002). However, the specific conditions of the condensation reactions limit the number and type of functional monomers, and thus the development of PNS- or PMS-based polymers with novel structures. Under these circumstances, a new type of linear polyacrylate-based polymers, first developed in the 1970s, found its place in the admixtures market in the 1980s and 1990s.

These polymers are produced by radical copolymerization, which allows greater possibilities in structural design due to the large number of monomers compatible with this type of reaction. For example, the monomers can bear sulphonate, carboxylate

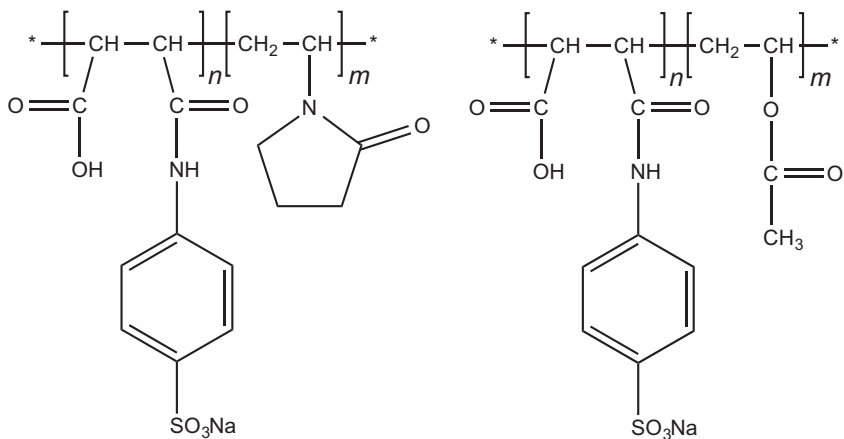


Figure 9.9 Chemical structure of two vinyl copolymers.

or phosphonate groups as anionic functional groups, as well as ether, amide or amine groups as bridging functions. This leads to a large variety of copolymers designed for specific applications and thus expected performance (Bradley and Szymanski, 1984; Jeknavorian et al., 1997; Bürge et al., 1994). Two examples are illustrated in Figure 9.9.

Unlike a PNS, which shows a molecular weight depending on reaction time, the molecular weight of these vinyl copolymers depends on the conditions of the radical polymerization, such as the quantity of initiator, the chain transfer agent and the type and reactivity of the monomers. In general, these molecules show a higher dispersing efficiency than PNSs and a significantly longer slump life (Mäder et al., 1999), but induce higher hydration retardation.

Vinyl copolymers represent the first step towards a new type of copolymers with side chains, called polycarboxylate ethers and developed later in the 1990s. These polymers, described below, mostly replaced vinyl copolymers in the 2000s as they showed a greater variety of structural design for better performance.

9.2.4 Comb-shaped copolymers

Comb-shaped copolymers are the last-generation SPs and were introduced in the mid-1980s (Tsubakimoto et al., 1984). This category includes many types of SPs exhibiting the same common comb-like structure.

The structure of comb-shaped SPs generally consists of a main chain, the so-called backbone, bearing carboxylic groups, to which non-ionic side chains made of polyethers are attached (Figure 9.10). These SPs are also called polycarboxylate ethers, polycarboxylate esters or polycarboxylates (PCEs).

The carboxylic groups, dissociated in water, confer a negative charge to the backbone. The negatively charged backbone is responsible for the adsorption of the SP onto the positively charged cement particles. The resulting charge of cement particles

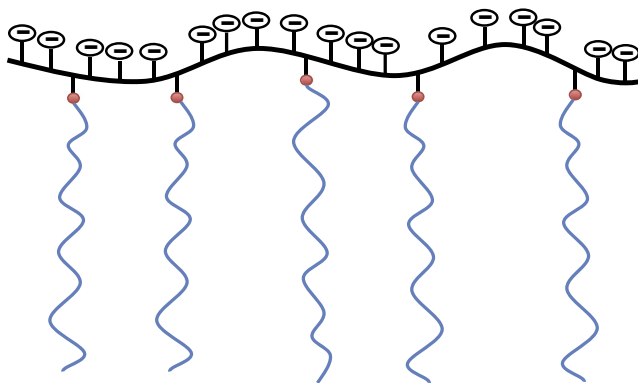


Figure 9.10 Schematic drawing of the comb-like structure of a PCE.

is lower compared to that induced by LSs, PNSs and PMSs. The dispersing ability of PCEs comes from the non-adsorbing side chains, which are responsible for the steric hindrance effect. While the adsorption depends strongly on the number of free carboxylic groups, the steric stabilization depends on the amount and length of the side chains of the adsorbed polymer (Flatt et al., 2009; Nawa et al., 2000). More precisely however, adsorption is affected by all structural parameters of the polymer, but to different extents (Marchon et al., 2013, 2016). More details about the dispersion mechanism of comb-shaped SPs are given in Chapter 11 (Gelardi and Flatt, 2016).

The key to the success of PCE SPs lies in the fact that they offer a broad range of possible molecular structures. Since the molecular structure greatly affects the performance of PCEs, tailoring their molecular structures enables the production of SPs with quite different properties that can be used in a broader range of applications.

The main factors determining the performance of polycarboxylates are:

- length of the backbone
- chemical nature of the backbone (acrylic, methacrylic, maleic, etc.)
- length of the side chains
- chemical nature of the side chains (PEG, polypropylene oxide, etc.)
- distribution of the side chains along the backbone (random, gradient)
- anionic charge density
- linkage between backbone functionalities and side chain (ester, ether, amide, etc.).

Two main synthetic approaches are used for producing PCEs. One is the free radical copolymerization of a monomer bearing carboxylic groups and a monomer bearing the side chain. This route is the most common, especially in industry, as it has a simpler experimental procedure and is cost-effective. Moreover, radical copolymerization is ideal for the incorporation of different kinds of monomer into the main chain. This procedure leads to a gradient distribution of the side chains along the backbone. It also gives rise to PCEs with a high degree of polydispersity, in terms of both statistical distribution of the monomers and size of the polymers. Since the reactivity of the two monomers can be different, PCEs synthesized by free radical copolymerization may

have a gradient distribution of side chains along the backbone. The typical polydispersity index (PDI) for such PCEs is between two and three.

The other approach is the polymer analogous esterification or amidation of a preformed backbone bearing carboxylic groups with monofunctional PEG. This procedure can lead to PCEs with a narrower distribution of structures and molecular weights, due to the fact that the length of the backbone is fixed, and also the side chains introduced this way are more uniformly distributed along the backbone.

A schematic representation of the two main synthetic routes is shown in Figure 9.11.

Recently, controlled radical polymerization techniques, such as reversible addition-fragmentation chain-transfer or RAFT polymerization, have been used for the production of methacrylic-based PCEs with a well-controlled structure (Rinaldi et al., 2009). These approaches should provide relatively monodisperse SPs that can serve as models for fundamental studies on the working mechanism of PCEs.

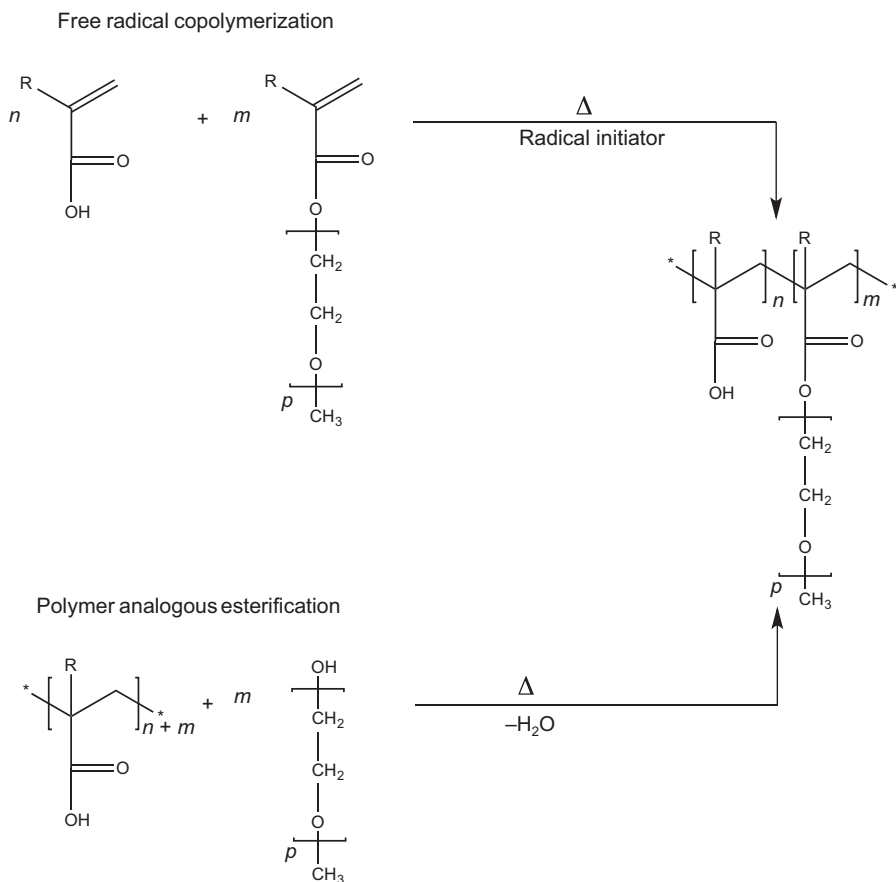


Figure 9.11 Schematic representation of the two main routes for synthesizing an acrylic or a methacrylic-based PCE ($R = H, CH_3$).

9.2.4.1 Chemical nature of the backbone

In acrylic-based copolymers the monomer unit of the backbone is acrylic acid, while the bond between these units and the side chains is an ester or amide bond (Figure 9.12).

The ester bond of acrylic-based as well as maleic-based SPs is prone to undergo hydrolysis in an alkaline medium, such as the aqueous phase of a cementitious system. The cleavage (detachment) of some of the side chains leads to an increase in the number of free carboxylic groups. Thus PCEs with higher charge density, and therefore adsorption ability, are formed over time. The change of adsorption ability can compensate for the flow loss of cement paste. Indeed, this feature has been exploited for the production of cement dispersants with improved slump-retention ability.

Cross-linked acrylic-based SPs show similar retention ability. A recent example of such dispersants is the PCE with a hyperbranched structure described by Miao et al. (2013). In this case the hydrolysis of the ester bond provides a continuous supply of SPs for adsorption on cement grains (Figure 9.13).

If methacrylic acid is used instead of acrylic acid, the resulting PCEs will be more stable towards hydrolysis of their side chains.

The hydrolysis of the ester bond can be overcome by substitution with more stable bonds. Amide, imide and ether bonds are examples, and are frequently introduced in the structure of PCEs for this purpose (Figure 9.14).

Allyl ether macromonomers are also frequently copolymerized with acrylic acid, maleic acid or maleic anhydride to produce PCEs. Compared to methacrylic-based PCEs, allyl ether-based SPs show generally a lower adsorption but better slump retention (Liu et al., 2013). Moreover, it has been demonstrated that they are more effective with silica fume (Schröfl et al., 2012). Plank and Sachsenhauser (2006) synthesized α -allyl- ω -methoxypolyethylene glycol-maleic anhydride copolymers with a well-defined primary structure of alternating monomer units. This was possible because

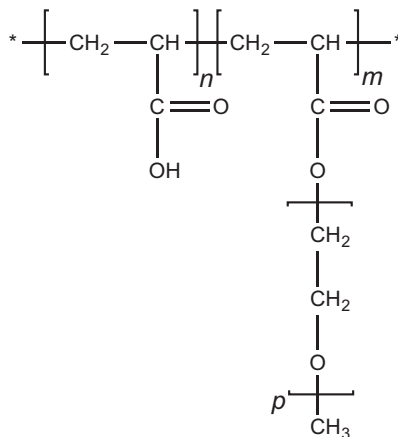


Figure 9.12 Structure of a PCE with an acrylic backbone and PEG side chains.

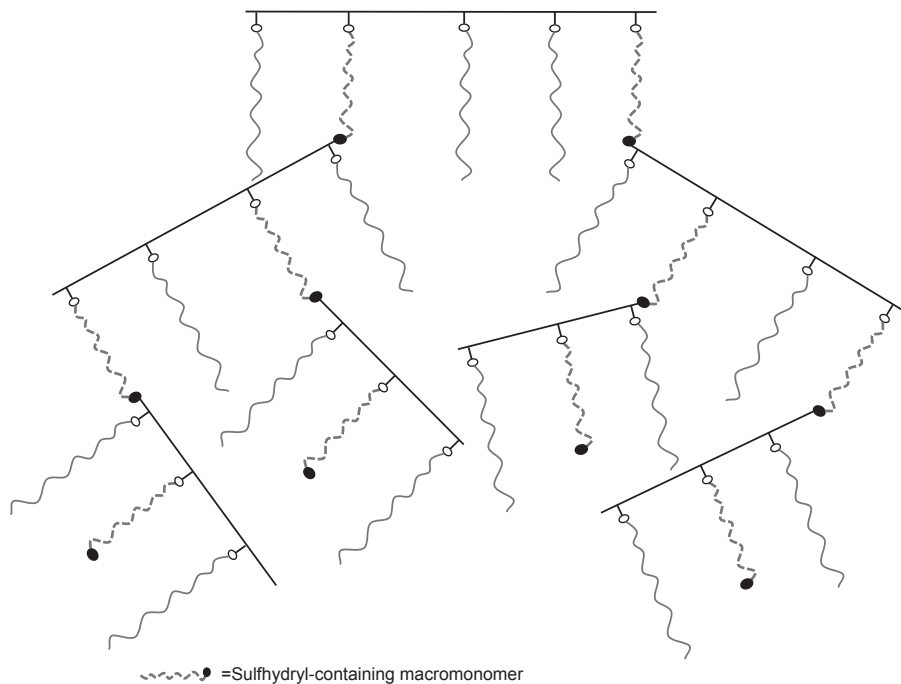


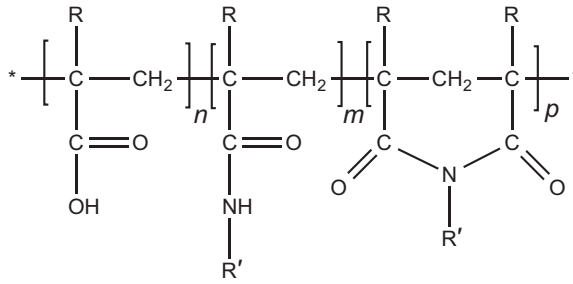
Figure 9.13 Possible structure of a hyperbranched PCE.
Adapted from Miao et al. (2013).

neither maleic anhydride nor allyl ether monomer undergoes homopolymerization. Isoprenyl oxypoly(ethylene glycol) macromonomers have been copolymerized with acrylic acid to produce PCEs with side chains connected by ether bonds (Yamamoto et al., 2004).

The type of monomer constituting the backbone of a PCE affects its performance as an SP. For instance, although the chemistry of the backbone of acrylic- and maleic-based SPs may look the same, such PCEs show different adsorption behaviour. This is due mainly to the additional chelating ability of the vicinal carboxylic groups of the maleic units. Methyl groups in α -position with respect to the carbonyl, as for methacrylic- and methallylic-based SPs, reduce the mobility of the main chain and can thus change the adsorption behaviour of the polymer. The flexibility of the backbone can be modified by the introduction of so-called spacer molecules, like for example styrene monomers (Figure 9.15).

The adjustment of the SP chemistry allows tailoring polymers with peculiar properties – for instance sulphate tolerance, as for allyl ether-based PCEs containing a five-membered lactone ring (Habbaba et al., 2013), or clay tolerance, as for terpolymers made of methacrylic acid-monoalkyl maleate-HBVE (Lei and Plank, 2014).

Recently, silyl functionalities were introduced in the methacrylate backbone of PCEs (Witt and Plank, 2012). The incorporation of such groups into the main chain of methacrylic-based SPs with a high grafting degree was found to increase the



$$\text{R} = \text{H}, \text{CH}_3$$

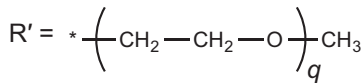


Figure 9.14 Chemical structure of PCEs with imide (top) and ether (bottom) bonds between the backbone and the side chains.

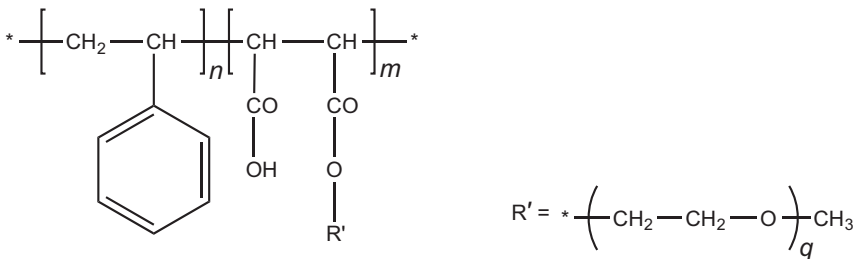


Figure 9.15 Structure of a comb-shaped copolymer made of styrene with a maleate bearing the side chain.

adsorption of such SPs. [Fan et al. \(2012\)](#) showed that incorporation of organosilane (trimethoxysilane) functionalities leads to SPs with high sulphate tolerance ([Figure 9.16](#)).

Methallyl sulphonic acid has been copolymerized in the acrylic backbone chain ([Yamada et al., 2000](#)).

water-insoluble gel. However, PCEs with hydroxyl-terminated PEG side chains can be prepared by radical copolymerization of methacrylic acid and ω -hydroxy PEG methacrylate macromonomer (Plank et al., 2008). In terms of performance these PCEs behave similarly to methoxy-terminated PCEs.

The market for comb-shaped copolymers is dominated by PCEs with PEG or PEG/PPO as side chains. However, some attempts have been made to use other types of side chains. For instance, it has been demonstrated that PCEs with ethoxylated polyamides and PEG as side chains can be very effective as dispersants and allow use of a w/c ratio as low as 0.12 (Amaya et al., 2003).

9.2.4.3 Characterization of comb-shaped superplasticizers

Comb-shaped SPs, like polymers in general, are not monodisperse. PCEs are characterized by a high degree of polydispersity, as they can differ in the length of both backbone and side chains, as well as in the grafting degree. With respect to other SPs, PCEs are more complex than linear ones, such as PNSs or PMSs; but their polydispersity is limited compared to that of LSs.

The first step of the characterization of such complex polymers is the determination of their average properties. The anionic charge density of comb-shaped SPs can be easily determined by acid–base titration or titration with cationic polyelectrolytes, such as polydiallyldimethylammonium chloride (Plank and Sachsenhauser, 2009). The grafting degree of a comb-shaped acrylic-based SP, as well as the number average molecular weight of the PEG side chains, can be estimated by proton nuclear magnetic resonance (NMR). The $^1\text{H-NMR}$ spectrum of an acrylic-based PCE is shown in Figure 9.17.

Carbon-13 NMR has been shown to be a powerful tool to investigate the microstructure of these polymers, in particular in studying the repartition of the comonomers along the backbone (Borget et al., 2005). Moreover, the conformation in solution of comb-shaped SPs can be studied by static and dynamic light scattering, which provide average gyration and hydrodynamic radii, respectively. However, in many cases PCEs are on the lower end of the detection level, so these results must be treated with care.

Besides the determination of average properties, there is a need to consider the distributed properties. The role of the molar mass distribution of PCEs in adsorption behaviour has already been pointed out (Winnefeld et al., 2007). Furthermore, it has been shown that the distribution of the side chains along the backbone also plays an important role. For instance, for a same average grafting degree, polymers with a statistical and a gradient distribution of side chains do not show the same adsorption (Pourchet et al., 2012).

HPLC has been successfully used to distinguish between adsorption of different polymeric fractions (Flatt et al., 1998). However, understanding of the structure–activity relationships requires the use of more advanced techniques. Two-dimensional chromatography is a promising technique for this purpose (Adler et al., 2005).

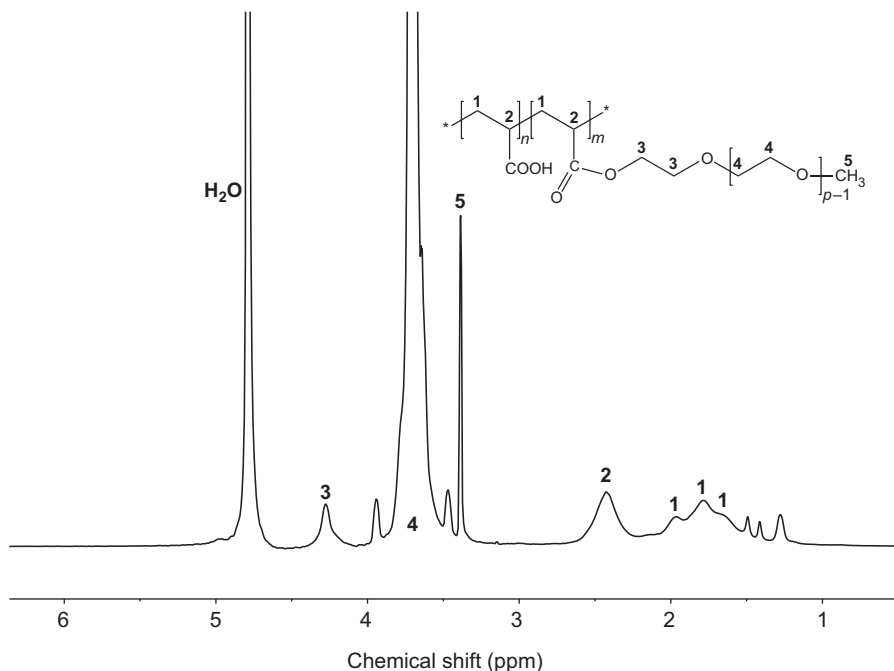


Figure 9.17 $^1\text{H-NMR}$ spectrum of a PCE made of an acrylic backbone and methoxy-PEG side chains.

9.2.4.4 Conformation of PCEs in solution

Conformation of comb-shaped copolymers in solution can be derived from the model by Gay and Raphaël (2001) for comb-shaped homopolymers in a good solvent. According to this model, comb-shaped homopolymers can be seen as an assemblage of n repeating units, each containing N monomers along the backbone and one side chain of P monomers (Figure 9.18).

Depending on the relative magnitude of these three structural parameters, the homopolymers can assume five different conformations (Figure 9.19). The possible conformations, shown in the phase diagram in Figure 9.19, are as follows.

1. Decorated chain (DC).
2. Flexible backbone worm (FBW).
3. Stretched backbone worm (SBW).
4. Stretched backbone star (SBS).
5. Flexible backbone star (FBS).

The PCEs used as dispersing agents most often belong to the FBW regime. This regime is typical of comb-shaped polymers whose side chains are short compared to the backbone. In this conformation, the comb-shaped homopolymer can be seen as a chain of cores, each having a radius of gyration R_C . Both the radius of gyration of

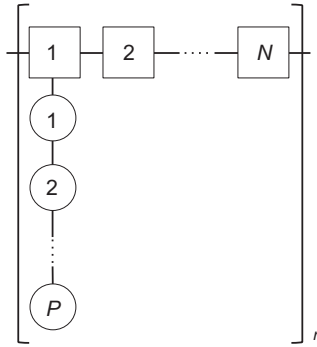


Figure 9.18 Schematic notation of the structure of a comb-shaped copolymer or homopolymer made of n repeat units each carrying one side chain made of P monomers and a backbone segment of N monomers.

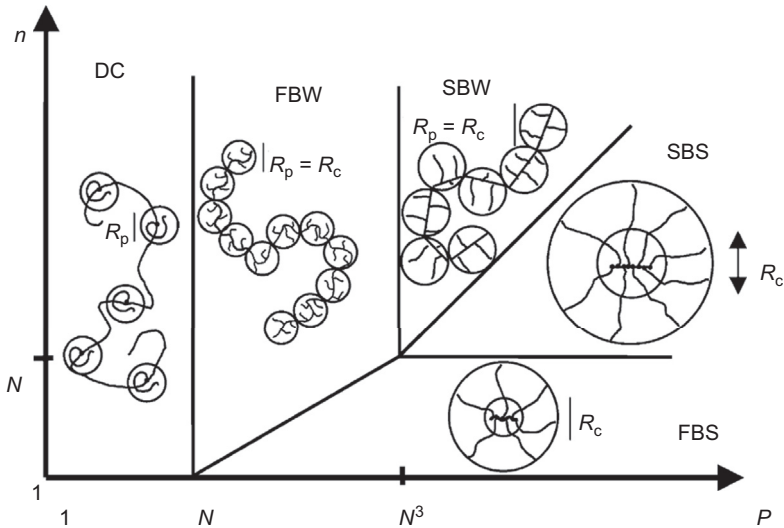


Figure 9.19 Phase diagram for comb-shaped homopolymers with the structure defined in Figure 9.18.

Reproduced from Gay and Raphaël (2001) with authorization.

the core and the overall chain follow a Flory scaling law. By minimizing the Flory free energy, the following expression for the overall radius of gyration of a comb-shaped homopolymer in the FBW conformation can be derived:

$$R = R_C \left(\frac{n}{n_C} \right)^{3/5} = (1 - 2\chi)^{1/5} a P^{2/5} N^{1/5} n^{3/5} \tag{9.1}$$

where

n_C = number of side chains per core

χ = Flory parameter

a = monomer size.

Flatt et al. (2009) extended this equation to comb-shaped copolymers having monomers of different size along the backbone and in the side chains. Equation (9.2) can be rewritten as:

$$R = \left(\left(\frac{a_N}{a_P} \right)^2 \frac{(1 - 2\chi)}{2} \right)^{1/5} a_P P^{2/5} N^{1/5} n^{3/5} \quad (9.2)$$

with a_N and a_P being the size of the backbone and side-chain monomers, respectively. For methacrylic backbones $a_N = 0.25$ nm, and for PEG side chains $a_P = 0.36$ nm and $\chi = 0.37$.

9.3 Retarders

9.3.1 Introduction

There are a very large number of compounds that may be used as retarders. Examples of these and their applications are given in Chapters 12 (Marchon and Flatt, 2016b) and 18 (Aïtcin, 2016b). Many retarders also have a water-reducing action, and many water reducers also have a retarding action on cement hydration — as stated by Collepari (1996), who chose to treat retarders and water reducers together in a single chapter of a handbook of chemical admixtures. In this chapter we give only a very brief overview of the chemistry of retarders, and then focus more extensively on the case of sugars.

LSs (discussed earlier) may be considered as retarders that additionally have a decent water-reducing ability, or vice versa. Other compounds, such as hydroxycarboxylic acids or salts thereof, as well as carbohydrates lean more clearly towards the role of retarders that may additionally offer some (small) water-reducing ability.

Various inorganic salts are also known to retard cement hydration (see Aïtcin, 2016b, Chapter 18). However, as they are higher priced than organic alternatives, they are not used much in practice (Collepari, 1996). This contrasts with LSs and sugar derivatives that can offer powerful retardation. For even longer retardation, phosphonates that have been described as superretarders may be considered (Ramachandran et al., 1993).

In this section we mainly examine the chemistry of sugars and their derivatives. Indeed, this is where a large range of controllable variations in chemistry can be achieved, giving a greater flexibility in design and a powerful tool for better understanding cement hydration. The information presented here constitutes a basis for Chapter 12, which discusses the retarding action of chemical admixtures on cement hydration (Marchon and Flatt, 2016b).

9.3.2 Carbohydrates

The terminology of carbohydrates comes from their average composition, which is analogous to a hydrate of carbon, $C_m(H_2O)_n$, where m and n can be different and m is typically equal to or larger than three. Carbohydrates offer a very large spectrum of structural variations, including, but not limited to, functionalization and polymerization. As a result, many criteria may be used to classify carbohydrates.

One criterion concerns the number of basic sugar units they contain. Only in a case where the units are identical, this does correspond to a degree of polymerization. This classification contains four groups: monosaccharides (e.g. glucose), disaccharides (e.g. sucrose), oligosaccharides (e.g. raffinose) and polysaccharides (e.g. starch).

9.3.2.1 Monosaccharides

Monosaccharides are the basic building groups for the higher-order saccharides (di, oligo and poly). Their general formula is $H-(CHOH)_x(C=O)-(CHOH)_y-H$. If either x or y is zero they are aldehydes, otherwise they are ketones. Another characteristic is that all other carbon atoms carry a hydroxyl group.

Let us consider the open form of the monosaccharide D-glucose illustrated in the centre of Figure 9.20. It contains four chiral centres, and therefore is one compound of a family of 16 (2^4) stereoisomers. Additionally, it may self-react to form a six-member ring, leaving the hydroxyl closest to the oxygen in the ring either on the opposite or the same side of the $-CH_2OH$ group with respect to the ring plane (noted α and β , respectively) (Vollhardt and Schore, 2010). Figure 9.20 illustrates this, in addition to how both ring forms are in equilibrium with D-glucose and therefore also with each other. Resulting from these equilibria, D-glucose is found mainly in ring forms, with about 38% α -D-glucose and about 62% β -D-glucose (Robyt, 1998).

The stereochemistry of sugars plays a very important role in their chemical behaviour. In particular, in the cases we are interested in, it affects their ability to complex

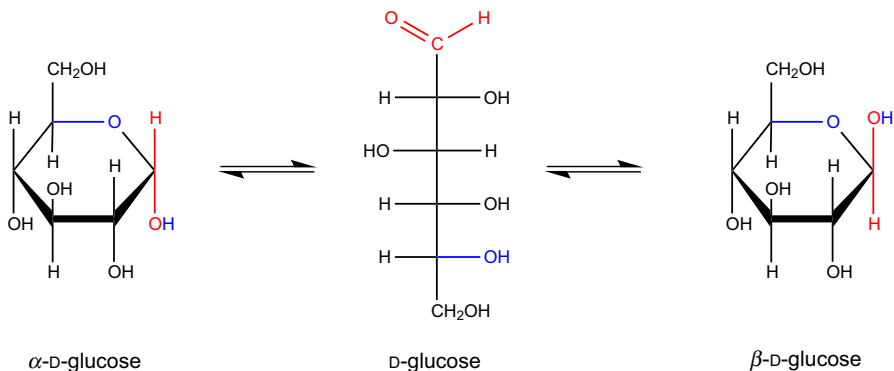


Figure 9.20 Schematic representation of the equilibrium between α - and β -D-glucose with an intermediate opened form.

metal cations in solution (Angyal, 1980; Pannetier et al., 2001), and can be expected to do so on surfaces for which such cations have an affinity. As explained in Chapter 12, complexation can be viewed as a necessary but not sufficient condition for retardation (Marchon and Flatt, 2016b).

The complexing ability of aldehyde sugars can be increased if they are partially oxidized to the corresponding carboxylic acids. Reducing sugars are subject to this, as they can suffer ring opening, forming an aldehyde group that can then be oxidized to an acid. Although this reaction is spontaneous, it is slow unless a catalyst is used. However, alkaline conditions such as those that prevail in cementitious systems can catalyse this process (de Bruijn et al., 1986, 1987a,b,c; Yang and Montgomery, 1996). This can lead to many different degradation products carrying carboxylate functions.

One must therefore consider that reducing sugars will be converted to salts of their corresponding acids, or even to smaller fragments (Thomas and Birchall, 1983; Smith et al., 2012). In contrast, non-reducing sugars such as sucrose, which is discussed below in the disaccharides section, are stable. This difference in behaviour has recently been evidenced in cementitious systems using NMR, showing explicitly that glucose degrades at 95 °C but sucrose does not (Smith et al., 2011, 2012). Earlier work also established by chromatography that sucrose is stable in alkaline solutions up to pH 13.5 at ambient temperature (Luke and Luke, 2000). From a structural point of view, reducing sugars are differentiated from non-reducing ones in that they have a free anomeric carbon (one that carries a hydroxyl group).

9.3.2.2 Disaccharides

Two monosaccharides can bond together in a reaction involving the elimination of water and the formation of a $-C-O-C-$ bond between them. In polymer chemistry this is referred to as condensation, while in carbohydrate chemistry it would rather be called dehydration.

The bond between saccharides is part of a broader family of chemical bonds called glycosidic. They cover covalent bonds that link a chemical group to a saccharide, regardless of the nature of this chemical group (here another saccharide). If the formation of a glycosidic bond involves the hydroxyl on an anomeric carbon, then the associated ring is stabilized against ring opening. The formation of such bonds consequently influences the redox reactivity of sugars, including their stability in alkaline solutions, which is of particular interest for cementitious systems.

To illustrate this, let us consider two examples of disaccharide: maltose and sucrose (Figure 9.21). In both cases the aldehyde group of the left glucose ring is stabilized by the glycosidic bond. In maltose the right ring is not stabilized, as it has a free aldehyde, but in sucrose it is stabilized. This explains why maltose (and glucose) degrades in the alkaline aqueous phase of cementitious materials, but not sucrose (Thomas and Birchall, 1983; Smith et al., 2012).

It has also been found that sucrose can lose a proton in aqueous solutions above pH 11 without reacting further (Popov et al., 2006). Probable important implications

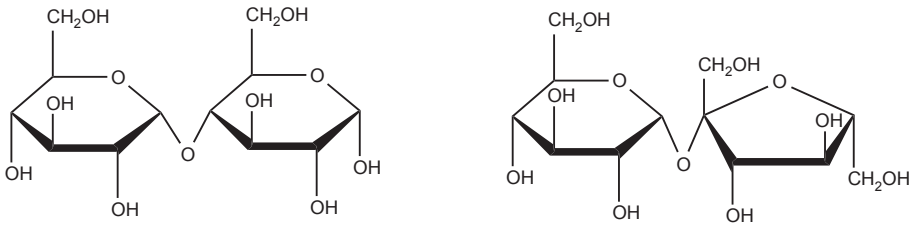


Figure 9.21 Illustration of two common disaccharides: left, maltose; right, sucrose.

of this in terms of complexation and cement hydration are discussed in Chapter 12 (Marchon and Flatt, 2016b).

9.3.2.3 Oligosaccharides

Oligosaccharides are molecules containing a small number of monosaccharides, typically from three to nine. With respect to cement chemistry, the case of raffinose is of particular interest as it acts as a very powerful retarder (Thomas and Birchall, 1983).

As can be seen in Figure 9.22, raffinose can be considered as a derivative of sucrose (Figure 9.21, right). It additionally has a α -D-galactose unit connected to the pendant $-\text{CH}_2\text{OH}$ of the glucose unit. As with sucrose, this sugar is non-reducing.

9.3.2.4 Polysaccharides

Polysaccharides are saccharides that have a higher number of monosaccharide units than oligosaccharides. They are very abundant components in natural products for energy storage (e.g. starch) or structural functions (e.g. cellulose). Their solubility decreases with molecular weight, which is further driven by an increasing number of intermolecular hydrogen bonds.

The most important use of polysaccharides in concrete technology is for viscosity-modifying admixtures, which are discussed in further detail below.

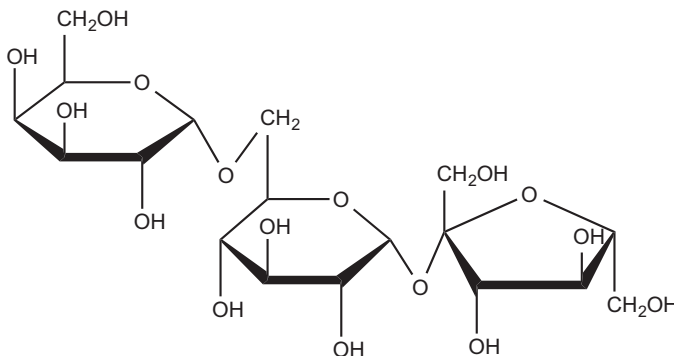


Figure 9.22 Chemical structure of raffinose.

9.4 Viscosity-modifying admixtures

9.4.1 Introduction

Viscosity-modifying admixtures (VMAs) are widely used to increase the stability, cohesion and robustness of self-compacting concrete, underwater concrete, shotcrete and cement grouts. These applications require highly fluid mixes to enable pouring but at the same time segregation and bleeding must be avoided. SPs are commonly used in these mixes to reach high flowability with low w/c ratio, while the use of VMAs increases stability. VMAs are also used to reduce the water loss of mortars due to evaporation or capillary suction when they are placed on a porous support (Cappellari et al., 2013; Khayat, 1998).

VMAs, specifically Xanthan gum, were introduced in the construction field in the 1960s (Plank, 2005), and since then their use has progressively increased. VMAs are also known as water-retaining or anti-washout admixtures. Most are hydrophilic, water-soluble organic polymers, although inorganic compounds such as nano-silica are also used as VMAs.

Table 9.1 shows a classification of the organic VMAs proposed by Kawai (1987) according to their nature. The most commonly used VMAs in cementitious systems are cellulose-ether derivatives and welan gum, although the use of starch has been progressively increasing in recent years. A more detailed explanation of the most relevant VMAs is given later in this chapter.

Table 9.1 Classification of VMAs

Natural polymers	Starch
	Welan gum
	Diutan gum
	Guar gum
	Xanthan gum
	Alginates
	Agar
Semi-synthetic polymers	Cellulose-ether derivatives
	Guar gum derivatives
	Modified starch
	Alginates derivatives
Synthetic polymers	Polyethylene oxide
	Polyvinyl alcohol, etc.

Adapted from Khayat and Mikanovic (2012).

9.4.2 Natural polymers

9.4.2.1 Welan gum and diutan gum

Welan gum and diutan gum are high-molecular-weight microbial polysaccharides produced by aerobic fermentation (Khayat and Mikanovic, 2012). They both belong to the sphingans group.

Welan gum is synthesized by the fermentation process of the *Alcaligenes* sp. ATCC 3155. It contains a tetrasaccharide backbone chain with L-mannose, L-rhamnose, D-glucose and D-glucuronic acid. The side chains contain a single unit of either L-mannose or L-rhamnose substituted in C3 of every 1,4-linked glucose molecule (Kaur et al., 2014). This polysaccharide has an approximate molecular weight of 10^6 g/mol.

Diutan gum has a similar structure to welan gum, but the side chains of the former consist of two units of L-rhamnose. In addition, diutan gum has a molecular weight up to three times higher than welan gum, of about $3-5 \times 10^6$ g/mol (Khayat and Mikanovic, 2012).

Figure 9.23 shows the structure of both polysaccharides. The presence of D-glucuronic acid in both gums gives them anionic charges and the ability to adsorb onto the surface of cement particles. Welan and diutan gum exhibit good rheological

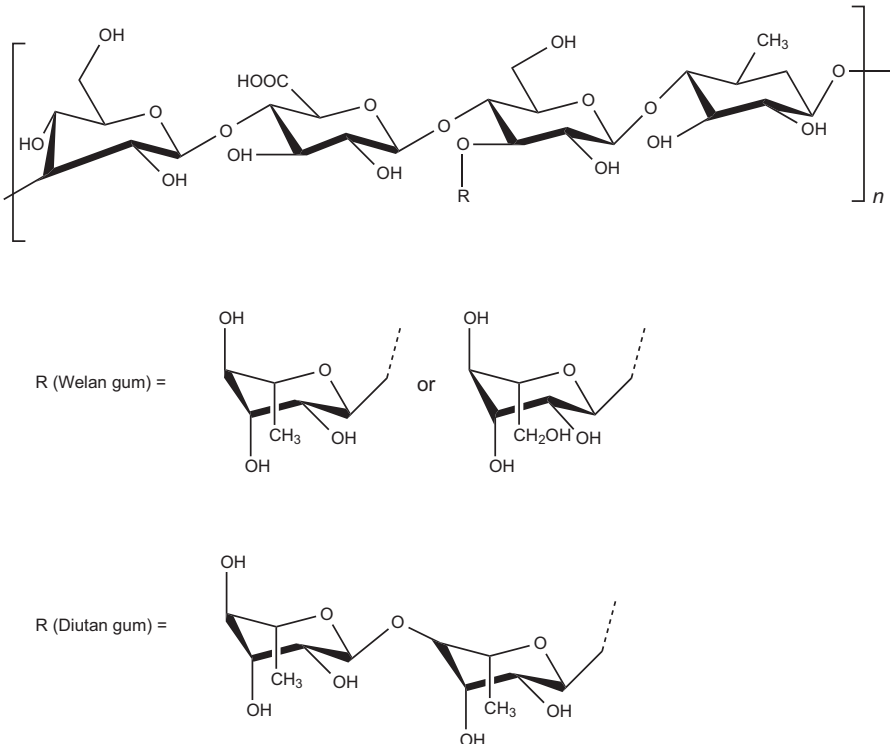


Figure 9.23 Chemical structure of welan gum and diutan gum.

properties and are stable at extreme temperature and pH. In aqueous solution, both gums adopt a double-helical conformation where the side chains screen the carboxylate groups of the backbone and prevent cross-linking by calcium ions. The shielding might be higher in the case of diutan gum due to its longer side chains compared to welan gum (Sonebi, 2006). This screening gives both gums high stability in media with high Ca^{2+} concentrations, as in cement pore solutions (Campana et al., 1990). With all these properties, welan and diutan gums are suitable VMAs for application in cementitious systems. However, their production is still rather expensive, so new and less costly synthesis methods need to be developed (Kaur et al., 2014).

9.4.3 Semi-synthetic polymers

9.4.3.1 Cellulose-ether derivatives

Cellulose-ether (CE) derivatives are the most widely used and effective water-retaining admixtures. It has been estimated that around 100,000 tons of cellulose derivatives are annually consumed by the construction industry (Plank, 2005), mainly for producing rendering mortars.

Cellulose is a uniform, linear glucose polymer and the most abundant of all natural substances (Khayat and Mikanovic, 2012). Cellulose consists of several hundreds to many thousands of β -1,4-linked D-glucose units, as shown in Figure 9.24. It is insoluble in water: to make it soluble, it is normally modified by attachment of small substituents in the hydroxyl groups of C2, C3 and C6.

In the case of CE derivatives, etherification occurs in alkaline conditions. The most widely used CE derivatives in building materials are hydroxypropyl methyl cellulose, hydroxyethyl methyl cellulose and hydroxyethyl cellulose (Figure 9.25). These admixtures have proved to be stable in the highly alkaline conditions of cementitious systems (Pourchez et al., 2006).

The behaviour of CE derivatives depends on its degree of substitution (DS), the nature of the substituent group and its structural parameters, such as molecular mass and amount of substitution groups (Brumaud et al., 2013). In general, the molecular weight is between 10^5 and 10^6 g/mol.

The DS is the number of substituted hydroxyl groups per glucose molecule, and ranges between zero and three. The solubility of cellulose derivatives will depend on the DS. Derivatives of cellulose with a DS lower than 0.1 are generally insoluble. Those with a DS between 0.2 and 0.5 are soluble in aqueous alkaline solutions. Cellulose derivatives with a DS between 1.2 and 2.4 are soluble in cold water (Richardson and Gorton, 2003; Brumaud, 2011; Khayat and Mikanovic, 2012). The substitution of hydroxyl groups in glucose molecules by chemical groups with additional free hydroxyl groups for further substitution is quantified by the molar substitution and has no theoretical upper limit.

9.4.3.2 Guar gum derivatives

Guar gum is a polysaccharide extracted from the seeds of *Cyamopsis tetragonolobus*. Its structure is based on a β -1,4-linked D-mannopyranose backbone with random

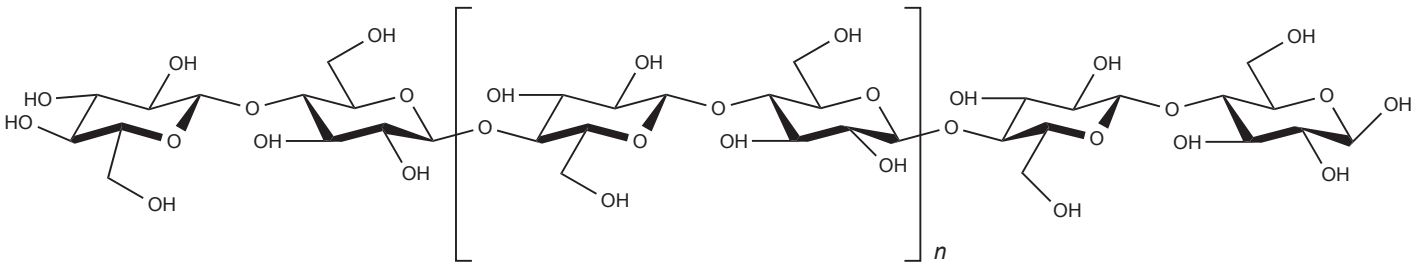


Figure 9.24 Chemical structure of cellulose.

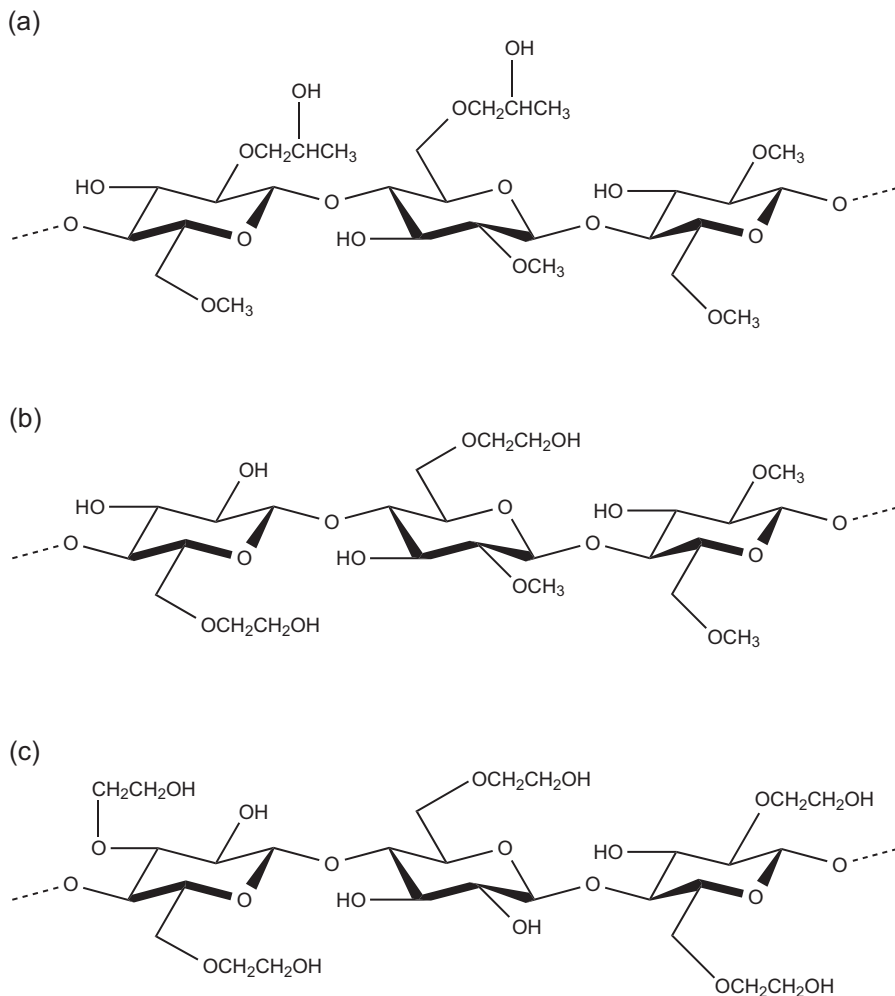


Figure 9.25 Chemical structure of cellulose ethers: (a) hydroxypropyl methyl cellulose; (b) hydroxyethyl methyl cellulose; (c) hydroxyethyl cellulose.

branch points of galactose via an α -1,6-linkage (Poinot et al., 2014) (Figure 9.26). Guar gum has a molecular weight in the order of 1×10^6 to 2×10^6 g/mol.

Guar gum is soluble in water, but its use causes problems such as solution clarity, alcohol solubility, uncontrolled rate of hydration, decrease of viscosity with time and microbial contamination susceptibility. To overcome this limitation, derivatives are produced (Iqbal and Hussain, 2013; Risica et al., 2005).

Hydroxypropylguar is the most commonly used derivative of guar gum (Figure 9.27). It is obtained from the guar gum by an irreversible nucleophilic substitution, using propylene oxide in the presence of an alkaline catalyst (Pourchez et al., 2006). It is highly soluble and shows high thermal stability. Functional

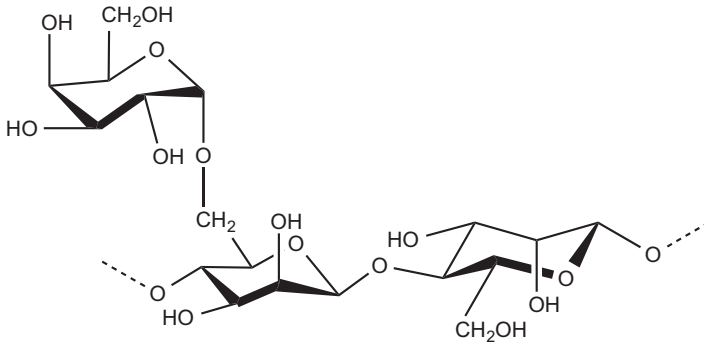


Figure 9.26 Chemical structure of guar gum.

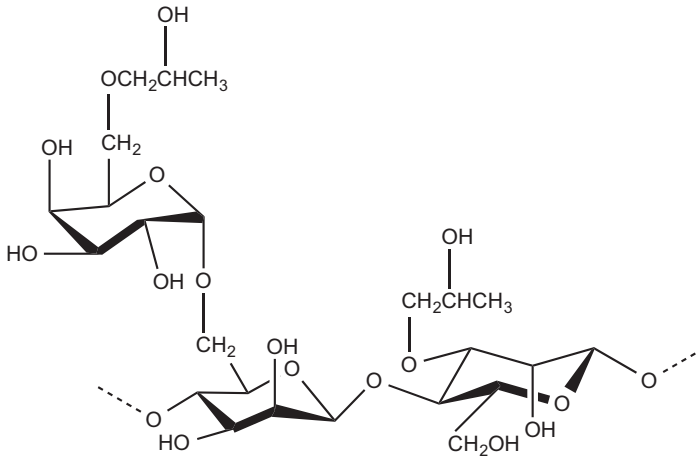


Figure 9.27 Chemical structure of hydroxypropylguar.

properties of hydroxypropylguar depend on its DS. As in the case of cellulose, the maximum DS is three, as three hydroxyl groups are available in each sugar unit for derivatization. As substituents are introduced in the molecule, additional hydroxyl groups can be also included for possible further derivatizations. The primary hydroxyl group at C6 is more susceptible to reacting than C2 and C3 (Brumaud et al., 2013).

9.4.3.3 Modified starch

After cellulose and hemicellulose, starch is the principal carbohydrate found in nature (Richardson and Gorton, 2003). Starch is a polysaccharide composed of two homopolymers of D-glucose: amylose and amylopectin (Figure 9.28). Amylose consists mainly of long linear chains of α -1,4-linked glucose, although a low degree of branching has

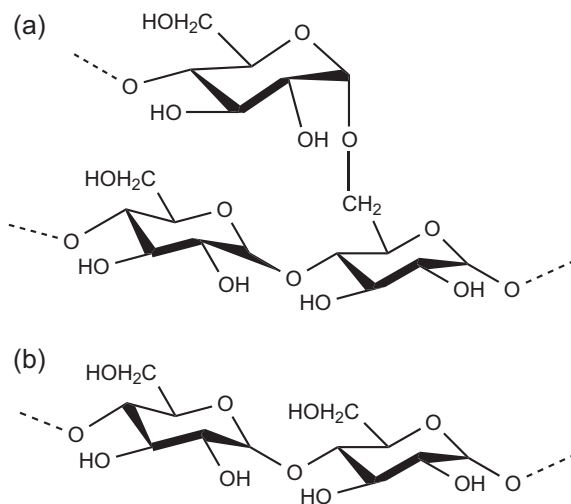


Figure 9.28 Chemical structures: (a) amylopectin and (b) amylose.

been identified. Amylopectin is a highly branched molecule (about once every 20 to 25 glucose units) with shorter α -1,4-linked glucose molecules and more frequent α -1,6 branches. The molecular weight of amylose is around 150,000–600,000 g/mol, while that of amylopectin is 10^7 – 10^9 g/mol. The percentage of amylose and amylopectin varies with the source of starch, ranging from 10% to 30% of amylose and 70–90% of amylopectin (Banks and Muir, 1980; Vollhardt and Schore, 2010). The main raw materials used for the extraction of starch are maize, potato, tapioca and wheat (Khayat, 1998).

Native starch is insoluble in cold water. For application in concrete, starches are normally modified through etherification or esterification to become soluble in cold water and stable at the high pH of cementitious systems. During etherification and esterification, hydroxyl groups of amylose and amylopectin are generally substituted (Khayat and Mikanovic, 2012). In construction, carboxymethyl and hydroxypropyl starch are the most used modified starches (Plank, 2005; Khayat and Mikanovic, 2012).

9.4.4 Synthetic polymers

9.4.4.1 Polyethylene oxide

PEO is a high-molecular-weight and non-ionic polymer. It is hydrophilic, linear and not cross-linked, and highly soluble in both aqueous and organic solvents.

Figure 9.29 shows the chemical structure of the repeating unit of ethylene oxide. This repeating unit contains a hydrophobic ethylene group and hydrophilic oxygen, which is also a hydrogen bond site (Zhang, 2011).

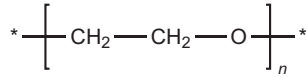


Figure 9.29 Structure of the repetitive unit in polyethylene glycol.

PEOs are synthesized by polymerization of ethylene oxide using a metallic catalyst. They are available in a very wide molecular weight range, from 200 to 7.0×10^6 g/mol, and the low-molecular-weight PEOs are called PEGs. They are completely soluble in cold and warm water.

9.4.4.2 Polyacrylamides

Polyacrylamides are a family of high molecular weight, water-soluble polymers. Anionic polyacrylamides (aPAMs) are used in the construction field as a thickener or flocculent. Their chemical structure is shown in [Figure 9.30](#). APAMs are synthesized by free radical polymerization of acrylamide and acrylic acid salts or by partial hydrolysis of non-ionic polyacrylamide ([Cheng 2004](#); [Bessaies-Bey et al., 2015](#)). Their molecular weight ranges from 10^3 to 20×10^6 g/mol.

APAMs can vary in molecular weight, structure (linear or branched) and charge density providing them different properties. At the high pH of cement pore solutions, aPMAs are susceptible to hydrolysis ([Cheng 2004](#)).

9.4.5 Inorganic powders

The stability of highly flowable concrete mix designs can be increased by the addition of high specific surface area inorganic powders such as colloidal silica, fine calcium carbonate, silica fume or fly ash. In addition, swelling powders such as bentonite can increase the water retention in cement mixes.

9.5 Air-entraining admixtures

9.5.1 Introduction

In this section the chemistry of air-entraining admixtures (AEAs), also called air entrainers, is presented. These molecules are surfactants, and understanding their

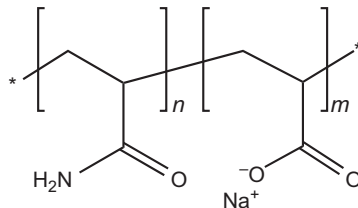


Figure 9.30 Structure of anionic polyacrylamide

working mechanisms therefore requires introducing some concepts about surfactant science. In particular, the parameter known as the hydrophile-lipophile balance (HLB), which gives an indication of the hydrophilic character of a surfactant, is introduced. While this concept has serious limitations, it is used in this chapter to show how this balance can be influenced through surfactant molecule architecture.

A first categorization of commercial AEAs dates back to 1954 (Torrans and Ivey, 1968), and distinguishes them into:

- salts of wood resins (pinewood stumps)
- synthetic detergents (petroleum fractions)
- salts of sulphonated lignin (paper pulp industry)
- salts of petroleum acids (petroleum refining)
- salts of proteinaceous materials (processing of animal hides)
- fatty and resinous acids and their salts (paper pulp and animal hide processing)
- salts of sulphonated hydrocarbons (petroleum refining).

The list indicates that the initial classification of AEAs was mainly based on the source of the raw materials and their treatment. A more recent screening conducted in the USA (Nagi et al., 2007) subdivided 41 commercially available AEAs into five categories based on infrared analysis:

- alpha olefin sulphonate (six admixtures)
- benzenesulphonate (four admixtures)
- resin/rosin and fatty acids (13 admixtures)
- vinsol resin (14 admixtures)
- combination (surfactants, urea, tall oil, and others).

Concrete Admixtures and the Environment; State-of-the-Art Report (2011), published by Deutsche Bauchemie, distinguishes two main categories: soaps made from natural resins (root resins, tall resins, gum resins and derivatives) and synthetic surfactants (alkyl polyglycol ethers, alkyl sulphates and alkyl sulphonates). The use of synthetic surfactants has increased due to a scarcity of natural sources, in particular wood resin/rosin. However, the classification of AEAs still contains terms relating to sources as well as types of synthetic surfactants in use.

There is abundant literature in which air entrainers are selected, named in one or another form and applied to concrete. However, few give a direct indication of the nature and properties of the surfactants or AEAs used.

In this section, a way to classify AEAs according to their surfactant nature is proposed. In doing this, we try to bridge a gap in surfactant science that has unfortunately grown since air entrainers have been introduced in concrete. First, a brief overview of the main characteristics of surfactants is provided.

9.5.2 General features of surfactants

9.5.2.1 Basic structural features

This subsection summarizes general features of surfactants, taken from Rosen (2004), that are of concern considering their use as AEAs for concrete.

Surfactants are surface-active amphiphilic molecules that consist of a hydrophobic ‘tail’, usually a long alkyl chain, and a hydrophilic ‘head’, ionic or polar. When a surfactant is in an aqueous environment, the tail tends to minimize its contact with the solvent. As a result, at the liquid–vapour interface a monolayer of surfactant molecules is formed, in which the tails are away from the solvent and oriented towards the air (non-polar). The presence of the hydrophilic group prevents the surfactant from being expelled completely from the solvent as a separate phase.

Based on the chemical nature of the hydrophilic head, surfactants can be distinguished into:

- anionic
- cationic
- amphoteric
- non-ionic.

Many changes can be brought to the hydrophobic portion of surfactants to tailor its properties. These modifications can include:

- Increasing the *length of the hydrophobic chain*. This decreases solubility in water and increases solubility in oil or organic solvents; can cause a closer packing of molecules at the interface; increases the tendency to adsorb from solution at an interface or to self-associate into micelles; and increases precipitation from water by counterions in case of ionic surfactants.
- The introduction of *branching or unsaturated bonds* that increase solubility in water or organic solvents with respect to the corresponding linear or saturated ones; and decrease the tendency towards self-association into liquid crystal (a process that can reduce the surfactant availability and therefore performance).
- The presence of an *aromatic nucleus* will increase the adsorption of the surfactant onto the positively charged substrates, e.g. cement surfaces; and may cause looser packing at the liquid–vapour interface.

9.5.2.2 The concept of hydrophile-lipophile balance

The HLB was introduced by Griffin (1949) and indicates the emulsification behaviour of a surfactant. It quantitatively expresses the balance between the hydrophilic and lipophilic (hydrophobic) parts of the molecule. The larger the HLB, the more hydrophilic the surfactant.

The HLB value determines the most appropriate use for a given surfactant. Table 9.2 shows the main applications of surfactants with the corresponding HLB range.

Davies (1957) developed a cumulative concept in which the HLB value can be obtained from the individual contributions of the hydrophilic and hydrophobic portions of the molecule defined by group numbers (Table 9.3). While the first method used to calculate the HLB was strictly limited to non-ionic surfactants, Davies’s method of individual group contributions broadened the applicability of the HLB concept to ionic surfactants.

The HLB of a surfactant calculated using group numbers according to Davies is:

$$\text{HLB} = \sum_{k=0}^n (i_k \text{GN}_k) \quad (9.3)$$

Table 9.2 Examples of surfactant applications with the corresponding most adapted HLB range and dispersability in water

HLB-range	Application	HLB range for dispersion in water
3–6	Water in oil emulsifier	<4 No dispersion 3 < Poor dispersion < 6
7–9	Wetting agent	6 < Milky dispersion after vigorous agitation < 8
8–18	Oil in water emulsifier	8 < Stable milky dispersion < 10; 10 < Translucent to clear dispersion < 12 >13 Clear solution
13–15	Detergent	Clear solution
15–18	Solubilizer	Clear solution

Adapted from Tadros (2005).

where:

k : 0, ..., n individual groups (hydrophilic and lipophilic)

i : quantity of group k

GN: group number according to Table 9.3.

Further development of this method includes the concept of effective chain length and leads to the values shown in Table 9.3 (Guo et al., 2006).

In Table 9.3 it can be seen that anionic head groups make a relatively high contribution to hydrophilicity (high group numbers). This contrasts with the individual contribution of an ethylene oxide (EO) group. Therefore to reach the same hydrophilicity as when using ionic groups, one must use very large head groups of non-ionic ethoxylated surfactants.

Tables 9.2 and 9.3 show that modifications of the molecular architecture of a surfactant, whether ionic or not, affect the HLB and the corresponding application range.

9.5.3 Sources for air-entraining admixtures

Traditional sources for AEAs are acids from wood resins and animal and vegetable fats and oils. The main compounds found in wood resins are abietic acid, pimaric acid (Figure 9.31) and their isomers, whereas natural fats and oils are sources of glycerides from which fatty acids can be derived by hydrolysis. Natural fatty acids are medium- to long-chain carboxylic acids with an even number of carbon atoms between 4 and 26 (Black, 1955). The structure of a saturated fatty acid is shown in Figure 9.32.

Another source of acids for AEAs is crude tall oil, a by-product of the Kraft process for paper manufacture. Among other compounds, it contains resin acids (see above) and fatty acids, mainly palmitic acid (C16, saturated), oleic acid (C18, unsaturated);

Table 9.3 HLB group numbers

Hydrophilic groups	Group number		Lipophilic groups	Group number	
	According to Davies	According to Guo et al.		According to Davies	According to Guo et al.
$-\text{SO}_4^- \text{Na}^+$	38.7	38.4	$-\text{CH}-$; $-\text{CH}_2-$; CH_3- ; $=\text{CH}-$	-0.475	-0.475
$-\text{COO}^- \text{K}^+$	21.1	20.8	$-\text{CF}_2-$	—	-0.87
$-\text{COO}^- \text{Na}^+$	19.1	18.8	$-\text{CF}_3$	—	-0.87
$-\text{SO}_3 \text{Na}^+$	—	10.7	Phenyl	—	-1.601
<i>N</i> (tertiary amine)	9.4	2.4	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ (PO)	-0.15	-0.15
Ester (free)	2.4	2.316	$-\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-$	—	-0.15
$-\text{COOH}$	2.1	1.852	$-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-$	—	-0.15
$-\text{OH}$ (free)	1.9	2.255	Sorbitan ring	—	-20.565
$-\text{CH}_2\text{OH}-$	—	0.724			
$-\text{CH}_2\text{CH}_2\text{OH}-$	—	0.479			
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}-$	—	0.382			
$-\text{O}-$	1.3	1.3			
$-\text{CH}_2\text{CH}_2\text{O}-$ (EO)	0.33	0.33			
$-\text{CH}_2\text{CH}_2\text{OOC}-$	—	3.557			
OH (sorbitan ring)	0.5	5.148			
Ester (sorbitan ring)	6.8	11.062			

From Davies (1957) and Guo et al. (2006).

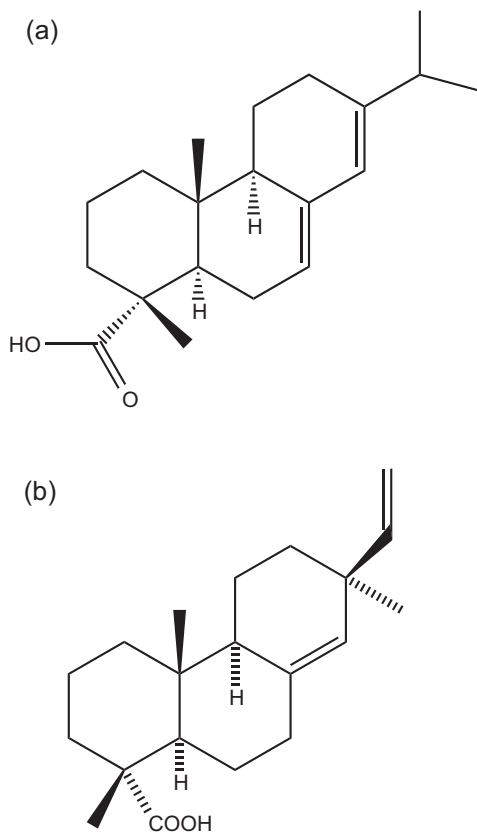


Figure 9.31 Chemical structures: (a) abietic acid and (b) pimaric acid.

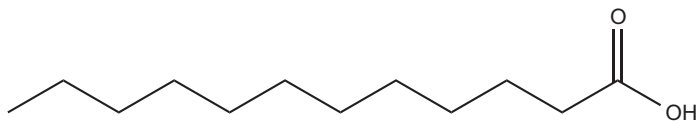


Figure 9.32 Chemical structure of lauric acid or dodecanoic (C12) acid.

one double bond; (9Z)-Octadec-9-enoic acid) and linoleic acid (C18, unsaturated; two double bonds; (9Z,12Z)-9,12-Octadecadienoic acid). Through further fractional distillation and reduction of the tall oil, fatty acids, mostly consisting of oleic acid (Figure 9.33), can be obtained.

Salts of petroleum acids are gained through alkaline extraction from crude oil containing naphthenic acids. Naphthenic acids are mostly mixtures of cyclopentyl and cyclohexyl carboxylic acids. An example of a naphthenic acid is shown in Figure 9.34.

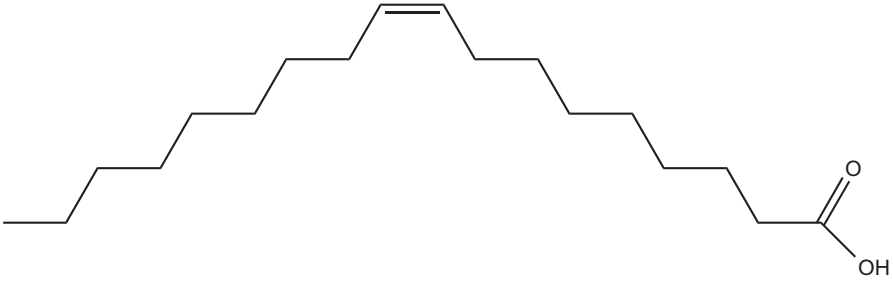


Figure 9.33 Chemical structure of oleic acid, or (9Z)-Octadec-9-enoic acid.

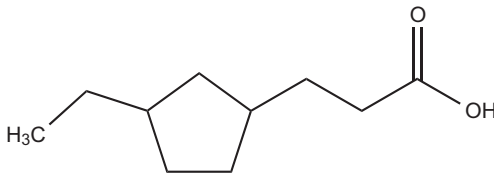


Figure 9.34 Chemical structure of a naphthenic acid.

9.5.4 Anionic surfactants

The hydrophilic portion of anionic surfactants has a negative charge. According to [Tadros \(2005\)](#), the most used head groups of anionic surfactants are carboxylates, sulphates, sulphonates and phosphates. [Table 9.4](#) shows general formulae and characteristics for such anionic surfactants.

The presence of a negatively charged head renders the surfactant water-soluble, but is also responsible for its tendencies to adsorb onto cement particles and precipitate in

Table 9.4 Types of anionic surfactant and HLB group numbers

Surfactant type		Group and group number		HLB	Application
Head group	Formula	Sodium head group	C12-alkyl		
Carboxylates	$C_nH_{2n+1}COO^-X$	18.8	-5.7	20.1	Oil in water emulsifier
Sulphates	$C_nH_{2n+1}OSO_3^-X$	38.4		39.7	Wetting agent
Sulphonates	$C_nH_{2n+1}SO_3^-X$	10.7		12.0	Oil in water emulsifier
Phosphates	$C_nH_{2n+1}OPO(OH)O^-X$	—		—	—

cement pore solutions due to the presence of di- or trivalent cations. This has advantages and disadvantages.

Surfactants anchored or aggregated onto particle surfaces can catch and stabilize entrained air bubbles through hydrophobic interactions. However, early adsorption leads to some extent to a loss of active admixture and the consequent increase of the specific dosage needed for entrainment of a certain volume of air into concrete.

The same is true for surfactant precipitation in cement pore solutions. Indeed, while there is wide agreement in the scientific community that precipitation, or salting out, of anionic surfactants stabilizes air bubbles, it is also clear that early precipitation, prior to air bubble formation, results in an undesired loss of surfactant.

In general, one can consider that anionic surfactants from natural sources are rather robust admixtures that allow controllable adjustments of air content. However, this is at a rather high dosage compared to their synthetic competitors.

The influence of the hydrophobic group was summarized by [Rosen \(2004\)](#). In particular, it is stated that while the charged head of anionic surfactants used in cementitious material determines adsorption onto solids, changes in the length of the hydrophobic group increase adsorption efficiency from the aqueous solution.

Examples of anionic surfactants, whether from natural resources or synthetic, are given in the next subsections.

9.5.4.1 Carboxylic acid salts

From a categorization of commercial products in [Torrans and Ivey \(1968\)](#), carboxylic acid-based surfactants can be grouped as:

- salts of wood resins (abietic acid and pimaric acid)
- salts of petroleum acids (petroleum refining)
- fatty and resinous acids and their salts (paper pulp and animal hide processing).

According to [Rosen \(2004\)](#), such compounds are easily prepared by neutralization of the acids or saponification of triglycerides found in natural fats or vegetable oil. The surfactants obtained are soaps (RCOO^-M^+), and can be seen as a very early type of AEA. As previously stated, in cementitious systems they have the disadvantage of forming water-insoluble soaps with di- and trivalent metallic ions and are insolubilized readily by electrolytes.

However, experience teaches us that the advantage of such admixtures can be seen in their relative robustness and ease of controlling air entrainment. Furthermore, according to [Mayer and Axmann \(2006\)](#), this gives air void contents that are relatively independent of external conditions, such as agitation intensity and stirring time. Moreover, precipitation in the presence of Ca-ions of soaps prepared from wood resins is less significant than that of soaps obtained from other raw materials.

The issue of precipitation can be overcome by including additional SO_3H -groups in the oleoresin acid skeleton of anionic surfactants based on abietic acid ([Mayer and Axmann, 2006](#)). Another solution is to add lime soap-dispersing agents, i.e. sulpho-nates and sulphates (compatible anionic surfactants, discussed later in this section) ([Rosen, 2004](#)).

One specific compound in anionic AEAs is based on the neutralization of resin acid and fatty acids using amines, in particular triethanolamine and diethanolamine,

a process well known to lead to surfactants (McCorkle and Brow, 1955). Through this process, quasi-synthetic soaps can be produced with the robustness of metal salts of anionic surfactants but better efficiency and less tendency to precipitate or be adsorbed on solid surfaces (Sychra and Steindl, 1998).

9.5.4.2 Sulphonic acid salts

In sulphonates, the sulphur atom is directly attached to the carbon atom of the alkyl group. This renders the molecule stable against hydrolysis, also in alkaline media, when compared with sulphates (described in the next subsection) (Tadros, 2005).

An example of such a surfactant used as an AEA is linear alkylbenzenesulphonate of the generic structure $RC_6H_4SO_3^-M^+$. The chain length of the alkyl portions is about 12 carbons in most cases. Linear alkylbenzenesulphonate is relatively cheap.

Regarding the hydrophilic head, salts with different cations have different characteristics. Calcium and magnesium salts are water-soluble, and therefore not affected by hard water. Sodium salts are sufficiently soluble in the presence of electrolytes for most uses.

A commercially available surfactant for AEAs is linear sodium dodecylbenzenesulphonate, shown in Figure 9.35.

Other surfactants, with HLB values ranging from about 11 to 14, are also used in commercial products:

- Sodium C10–16 benzenesulphonate
- Triethanolamine dodecylbenzenesulphonate.

α -Olefin sulphonates are produced by reacting a linear α -olefin with sulphur trioxide. This typically yields a mixture of alkene sulphonates (60–70%), hydroxyalkane sulphonates (~30%) and some disulphonates and other species (Tadros, 2005).

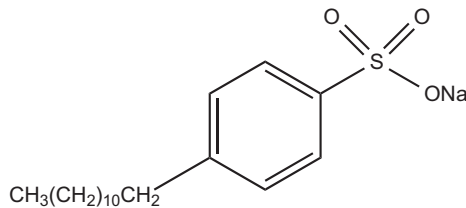


Figure 9.35 Chemical structure of sodium dodecylbenzenesulphonate.

1. 3,4 Olefin sulphonate:	$R-CH=CH(CH_2)_2SO_3^-$
2. 4-Hydroxy alkane sulphonate:	$R-CHOH-(CH_2)_3SO_3^-$
3. Disulphonate (sulphatosulphonate):	$R-CH_2-\underset{\substack{ \\ OSO_3^-}}{CH}-CH_2-SO_3^-$

Such surfactants are commercially available for concrete AEAs with C14 or C16 hydroxy alkane sulphonate (even numbered and C14–16 olefin sulphonate, respectively; $10 < \text{HLB}_{\text{calculated}} < 11$).

9.5.4.3 Sulphuric acid ester salts

Sulphates are synthetic anionic surfactants that are produced by reaction of an alcohol with sulphuric acid, and are therefore esters of sulphuric acid. Sulphates carrying alkali metals counterions show good solubility in water, but tend to be affected by the presence of electrolytes (Tadros, 2005). Ammonium alkyl sulphates can also be found.

Sulphates are usually prepared using alcohols with chain lengths ranging from dodecyl to hexadecyl (Rosen, 2004). The presence of a methyl branch in the hydrophobic group gives the surfactant a higher tolerance towards calcium ions in water.

An important sulphate surfactant is sodium dodecyl sulphate (or sodium lauryl sulphate), shown in Figure 9.36. It is extensively used for fundamental studies and in many industrial applications, as well as in air entrainers for concrete and gypsum. Sodium alkyl sulphates with chains of 8 and 10 carbons also have application in air entrainers.

Through modification of the hydrophobic group by introducing some EO units, better solubility and less sensitivity compared to straight alcohols are achieved, and the surfactant becomes more compatible with electrolytes in aqueous solution. These sulphates are then referred to as alcohol ether sulphates or sulphated polyoxyethylated straight-chain alcohols (Tadros, 2005). Commercial products mostly include C12 and EO units with a broad range of distribution in polyoxyethylated chain length (Rosen, 2004; Tadros, 2005). Recent products have a narrow range of chain lengths and contain fewer unreacted (non-ethoxylated) hydrophobic residues, making them more tolerant towards hard water (Rosen, 2004).

To the authors' knowledge, commercially available sodium alkyl ether sulphates for air entrainment of concrete include:

- sodium alkyl ether sulphate with two EO units and C12–14 chain
- sodium alkyl ether sulphate with three EO units and C12–15 chain.

Commercial ammonium alkyl ether sulphates can be found as:

- ammonium alkyl ether sulphate with 2.2 EO units and C8–10 chain
- ammonium alkyl ether sulphate with 2.5 EO units and C9–11 chain
- ammonium lauryl (C12) ether sulphate with three EO units.

It is important to note that in the above cases the HLB of the surfactant can be adjusted through modifications to both the hydrophilic head, via the salt type, and the hydrophobicity of the chain by the addition of certain number of EO units.

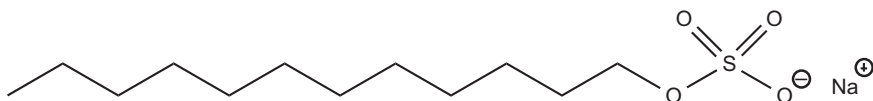


Figure 9.36 Chemical structure of sodium lauryl sulphate.

The advantages of alkyl ether sulphates over alkyl sulphates were summarized by Rosen (2004) as being:

- more water-soluble
- more electrolyte-resistant
- much better lime soap-dispersing agents
- foam is more resistant to water hardness and protein soil.

Of these four advantages, the second and the third are the most important for use as air entrainers in concrete.

9.5.4.4 Taurates

Surfactants of the group of taurates (taurides) are rather mild anionic surfactants. They show good compatibility with non-ionic and other anionic surfactants, and provide good stability against hydrolysis as well as good lime soap-dispersing power. Because of this, they find application in air entrainers as ‘cosurfactants’ to support the efficiency of the main active surfactant.

A general representation of taurates is shown in Figure 9.37, where R mostly comes from saturated C12–C18 fatty acids, oleic acid or coconut fatty acid. According to Rosen (2004), the solubility, foaming, detergency and dispersing powers of the *N*-methyl derivatives (Figure 9.37 with $R_1 = \text{CH}_3$) are similar to those of the corresponding fatty acid soaps, and are effective in hard and soft water.

Examples of commercially available products are sodium salts of oleic acid methyl taurate and coconut fatty acid methyl taurate.

9.5.5 Cationic surfactants

Cationic surfactants have a positively charged hydrophilic head; their advantage is their compatibility with non-ionic and amphoteric surfactants. They are mostly incompatible with ionic surfactants (Rosen, 2004; Tadros, 2005).

Ethoxylated amines are sometimes referred to as ‘cationic’ surfactants, but this is true only for low pH and low numbers of EO units. Considering the high pH of cement pore solution, their surfactant nature will be rather that of a ‘non-ionic’ compound (discussed later in this section).

Examples of pH-insensitive cationic surfactants are quaternary ammonium salts. On the quaternized amine group the electrical charge on the molecule is unaffected by pH changes, which means that the positive charge remains in acidic, neutral and alkaline media.

It is reported that using cationic surfactants can maintain the efficiency of air entrainers in the presence of clay contaminations in concrete (Hill et al., 2002).

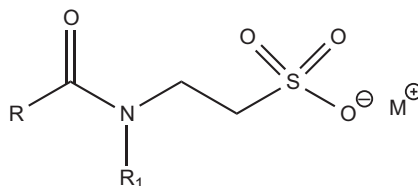


Figure 9.37 Chemical structure of an alkali metal salt of *n*-acyl-*n*-alkyl taurate.

In patents for AEAs one can find references to cationic surfactants. However, these compounds appear to be used as by-products or additions.

9.5.6 Amphoteric surfactants

The hydrophilic group of amphoteric surfactants bears both a negative and a positive charge, so the net charge of the molecule is zero. The main characteristic of amphoteric surfactants is that their behaviour depends on pH. For acidic 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. At their individual isoelectric point, the properties of amphoteric surfactants resemble those of non-ionic surfactants very closely (Tadros, 2005).

Examples of amphoteric surfactants used in air entrainers are betaines, amine oxides and amines. However, these compounds are mostly used as components in surfactant mixes of formulated products.

In patent literature on AEAs, betaines or their salts and derivatives are found in combination with non-ionic surfactants, i.e. ethoxylated alcohols or alkylaryl polyether alcohol, polyoxyalkylene copolymer surfactants and others. This family of surfactants is used in AEAs compatible with shrinkage-reducing admixtures (SRAs) based on mixtures of non-ionic surfactants and cosolvents or hydrotropes. It can be speculated that the presence of cosolvents and hydrotropes increases the solubility of the AEA. The energy gain in stabilizing air bubbles is then reduced, but betaines probably compensate for that.

Betaine-type surfactants found in patent literature are derivatives of trimethylglycine (Figure 9.38(a)) with $R = \text{CH}_3$ (Bour and Childs, 1992; Kerkar and Dallaire, 1997; Kerkar et al., 2001; Budiansky et al., 2001a; Hill et al., 2002). Several types of betaine derivatives can be obtained by modifying the nature of both hydrophobic and hydrophilic portions of the surfactant. For example, the head group of an alkyl betaine can undergo sulphonation with formation of an alkyl sulphobetaine (Figure 9.38(b)). Other betaine-type surfactants are shown in Figure 9.38.

An example of a commercially available betaine is alkyl amidopropylsulphobetaine, for which, according to Bour and Childs (1992), the hydrophobic group can be decyl, cetyl, oleyl, lauryl and coco ($\text{C}_{6-18} \text{H}_{13-37}$) radicals.

To the authors' knowledge, commercial products can be found that include the following compounds:

- coco amidopropyl betaine
- coco amidopropyl hydroxy sulphobetaine.

A second important surfactant type of an amphoteric nature used in AEAs is the group of amine oxides which are sometimes referred to as cationic, but would be non-ionic according to Tadros (2005) and amphoteric according to Rosen (2004).

A commercial product designated for use in concrete air entrainment is coco alkyl dimethyl amine oxide (Figure 9.39). Coconut fatty acids have a distribution of alkyl chain lengths in the range of C8–C20. Commercial products listed as air entrainers are found to have more or less narrow ranges, such as C12–18, C12–16, C12–14 or even C14.

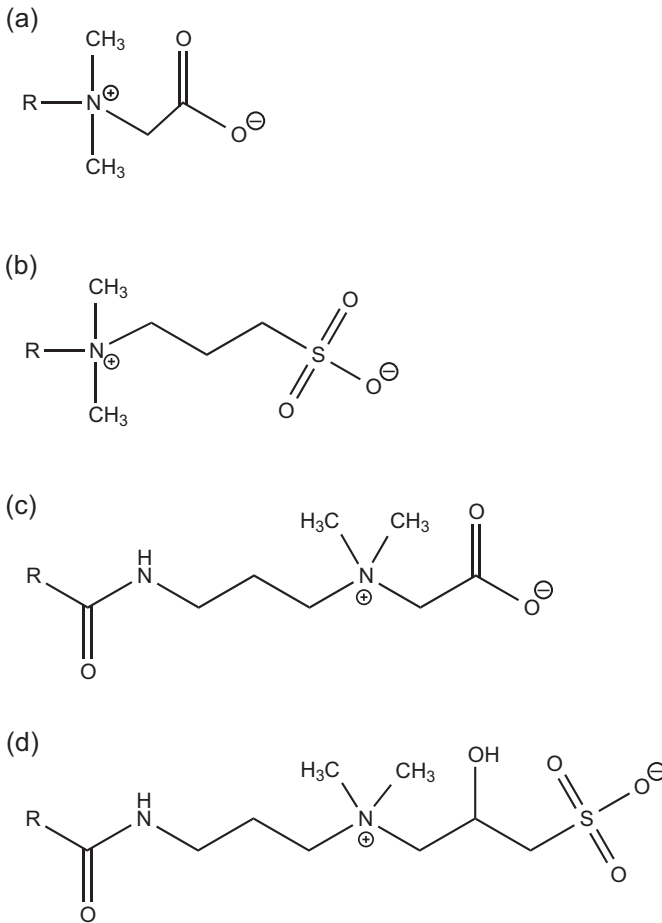


Figure 9.38 Chemical structure of betaine-type surfactants (with R = long hydrophobic chain): (a) alkyl betaine, (b) alkyl sulphobetaine, (c) alkyl amidopropyl betaine, (d) alkyl amidopropyl hydroxy sultaine.

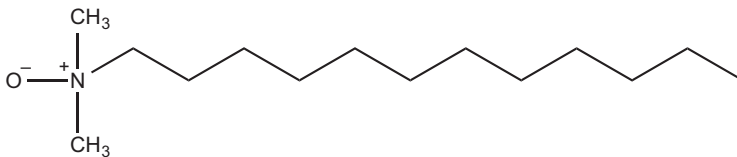


Figure 9.39 Chemical structure of a coco alkyl dimethyl amine oxide, where the alkyl chain has 12 carbon atoms.

To the authors' knowledge lauramine oxide and decyldimethylamine oxide are used in addition to the previously mentioned surfactants found in commercial products.

9.5.7 Non-ionic surfactants

Non-ionic surfactants are mostly based on EO, and are usually referred to as ethoxylated surfactants. [Tadros \(2005\)](#) distinguishes the following classes:

- alcohol ethoxylates
- alkyl phenol ethoxylates
- fatty acid ethoxylates
- monoalkaolamide ethoxylates
- sorbitan ester ethoxylates
- fatty amine ethoxylates
- ethylene oxide–propylene oxide copolymers (also known as polymeric surfactants).

There are also multihydroxy products, such as:

- glycol esters
- glycerol and polyglycerol esters
- glucosides and polyglucosides
- sucrose esters.

Considering their application in concrete, non-ionic surfactants have the advantage of good compatibility with all other types of surfactants. Because of their non-ionic nature these surfactants do not show strong adsorption onto charged surfaces. In terms of undesired loss of surfactant at the solid–liquid interface, this means that more surfactant remains available to saturate the liquid–vapour interface of the air bubbles created through mixing, and less surfactant is needed compared to their analogous ionic surfactants for a given air void surface to be created in concrete.

The main disadvantage of non-ionic surfactants is their inability to properly stabilize the air system they are creating, mitigating coalescence and bubble coarsening. In particular, unlike anionic surfactants, they cannot directly form salts with electrolytes of the cement pore solution at the liquid–vapour interface, while charged heads of ionic surfactants form a shell-like structure with increased rigidity through precipitation (for example lime soap).

This may be the reason why non-ionic surfactants are rarely used as a single compound in AEAs ([Ziche and Schweizer, 1982](#)) and are mostly found in mixtures with surfactants of different natures ([Bour and Childs, 1992](#); [Hill et al., 2002](#); [Budiansky et al., 1999, 2001a,b](#); [Wombacher et al., 2014](#); [Berke et al., 2002](#)). In this sense they can be considered as having mainly a supporting function in formulated admixtures, as discussed in Chapter 15 ([Mantellato et al., 2016](#)).

In this role of cosurfactants they increase the solubility of ionic surfactants and reduce the tendency of the ionic surfactant to adsorb at the solid–liquid interface. In the case of contamination with unburnt carbon in blended cements containing fly

ash, some non-ionic surfactants may serve as sacrifice material because they are good carbon dispersers.

Ethoxylated fatty acids and their amines are referred to as single-component air entrainers (Ziche and Schweizer, 1982). Their application is in cementitious material with rather high stiffness (plaster). Air entrainment in concrete for pavers is another field of application for non-ionic surfactants as a single component.

An example of a commercially available surfactant is coconut fatty amine with a number of EO units between 2 and 20.

In Berke et al. (2002) a triblock polyoxyalkylene copolymer surfactant has been claimed for use in AEAs. This has the general formula:



where,

R_1 ; R_2 : C1–C7 alkyl group, C5–C6 cycloalkyl group or aryl group
 x : 42–133
 y : 21–68.

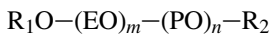
More preferred is:



with a molar mass between 8000 and 12,000 g/mol and an HLB between 20 and 30.

This polymeric surfactant is claimed to show good performance in concrete that contains a surfactant of the same nature used as an SRA.

In Budiansky et al. (1999, 2001a,b) a polymeric surfactant with explicit compatibility with an oxyalkylated SRA is introduced. In particular, the surfactant has a di-block structure:



with preferences on:

R_1 ; R_2	H or CH_3
m ; n	30–60

and a molar mass of $M > 2000$ g/mol. The SRA used in combination is dipropylene-tert-butyl ether (DPTB).

This preferred structure results in a range of $14.2 < HLB < 19.6$ and roughly between 3000 and 6000 g/mol.

In fact, formulators' experience shows that the compatibility issue between SRAs and AEAs is a real problem where a combination of an ethoxylated SRA with a common

air entrainer either consistently reduces air entrainment or requires disproportional high dosages. In [Berke et al. \(2002\)](#) this compatibility issue was solved using a polymeric non-ionic surfactant alone. However, the AEA of [Budiansky et al. \(1999, 2001a,b\)](#) contains not only a di-block polymeric surfactant but also a betaine-based surfactant.

Non-ionic polymeric surfactants have a major advantage with respect to other non-ionic surfactants, that is having a high degree of freedom for tailoring the overall size and HLB of the molecule, as well as the location of the hydrophilic/hydrophobic groups and their distribution.

A good example of this flexibility is provided by the above mentioned block copolymers. The triblock copolymer surfactant can be seen as an amphiphile containing two hydrophilic portions (EO units) and a hydrophobic group (propylene oxide-PO-units) between them, whereas the di-block polymeric surfactant has one hydrophilic block and one hydrophobic.

9.6 Shrinkage-reducing admixtures

9.6.1 Introduction

In this section the chemistry of SRAs is presented as an authorized excerpt of the authors' contribution to the subject ([Eberhardt, 2011](#)), with some additions.

First, an overview on general features of SRAs and their historical background is given. Like air entrainers, SRAs are mainly composed of surfactants, and basic information on this type of molecules was introduced in the section on AEAs. In this section we focus on non-ionic surfactants and/or hydrotropes that are more specifically used in SRAs. This serves to explain and distinguish the modes of action of both these admixture types on the basis of their molecular architecture.

The last section lists compounds present in commercially available SRAs, as well as compounds mentioned in patent literature.

9.6.2 History and working mechanism of SRAs

SRAs are composed of surfactants that decrease the surface tension of pore solution and of the water films that cover the solid surfaces exposed in the course of drying of cementitious porous material. They were introduced in a study by [Sato et al. \(1983\)](#), in which shrinkage reduction due to SRAs was suggested to come from reduced surface tension of the cement pore solution. There, the capillary force theory of drying shrinkage was explicitly referred to because of a more or less good correlation between shrinkage reduction, SRA dosage in cement paste and the dependence of surface tension on SRA concentration in its aqueous solutions.

Moreover, well before SRAs were introduced in 1983, [Ostrikov et al. \(1965\)](#) obtained similar results with shrinkage of cement paste subjected to solvent replacement prior to drying. This study focused on the mechanism of drying shrinkage rather than on shrinkage reduction of concrete; by coincidence, however, it revealed some very interesting results. Ostrikov et al. tried to eliminate capillary forces by osmotically

replacing the pore solution with several organic liquids with substantially lower surface tension. With hexane having a surface tension of about 25% of that of water ($\gamma_{\text{hexane}} \sim 18 \text{ mN/m}$, $\gamma_{\text{water}} \sim 73 \text{ mN/m}$), drying shrinkage deformation surprisingly was reduced to about 25%. At that point in time, however, it was not clear if this proportionality between the reduction of surface tension of the pore fluid and reduction of drying shrinkage deformation was of broader relevance.

It is possible to derive from thermodynamics how the reduction of the surface tension of the liquid–air interface (menisci and water films) leads to shrinkage reduction (Eberhardt, 2011). In particular, it can be shown that the reduction of surface tension coming from SRAs enables the cementitious matrix to reduce its free energy substantially, as it contains a large liquid–vapour interfacial area owing to its fine porosity. More specifically, this is done by increasing the portion of free energy used in the creation of the exposed liquid–air interfacial area, while at the same time reducing the free energy utilized in deformation. This mechanism is shown to be active as long as the surface tension can be maintained sufficiently low. The working mechanism of SRA is discussed more in detail in Chapter 13 (Eberhardt and Flatt, 2016).

9.6.3 General features and overview of surfactants used in SRAs

Regarding the nature of SRAs, a patent search on materials used as SRAs was conducted by Eberhardt (2011). It revealed that two main groups of admixtures can be discriminated:

- SRAs containing one type of non-ionic surfactant or hydrotrope
- SRAs containing mixtures of non-ionic surfactants, cosolvents and hydrotropes.

In both cases there are similarities between SRAs and AEAs, as both contain amphiphilic compounds. However, SRAs distinguish themselves from AEAs in their mode of action. While AEA adsorption onto solids does in part support stabilization of air bubbles (anchoring), SRA surfactants are efficient only by adsorbing at the liquid–vapour interface.

Therefore, surfactants used in SRAs are non-ionic so they do not strongly adsorb onto the charged surfaces of cement or its hydrates. The adsorption of surfactants onto cement is discussed in more detail in Chapter 10 (Marchon et al., 2016). Moreover, non-ionic surfactants used in SRAs are generally less hydrophobic and smaller than surfactants used in air entrainers. This also comes from their different mode of action. In Table 9.5 the actual interfacial area or workspace of an AEA and an SRA is estimated using a standard concrete with 300 kg of Portland cement and an air volume of 50 L/m^3 entrained through $100 \mu\text{m}$ large spherical air bubbles.

One can see that the interface to be theoretically covered with surfactants is higher by a factor of 1000 to 2000 in the case of SRA. This is also the reason why AEAs are used at such low dosages (a few grams per kilo of binder), and why SRA dosages can be 1–2% per weight of binder. More importantly, this requires a significantly higher solubility of the non-ionic surfactants used as SRAs in the strong aqueous electrolyte cement solution.

The use of non-ionic cosolvents and hydrotropes results from the abovementioned need to solubilize non-ionic surfactants efficiently in cement pore solution. For this it is

Table 9.5 Considerations on interfacial area/workspace of an SRA compared to an AEA in 1 m³ concrete

Workspace of air entrainer	Interfacial area created by air bubbles	
Assumptions		
Volume of air bubbles in 1 m ³ concrete	0.05	m ³
Assumed bubble diameter	100	μm
Bubble volume	5.2×10^{-13}	m ³
Number of bubbles	9.5×10^{10}	—
Bubble surface per 1 m³ concrete	3×10^3	m²
Workspace of SRA	Area exposed during drying	
Assumptions		
Surface of 1 cubic metre of fresh concrete (cube)	6	m ²
Cement hydrates content (300 kg cement) reacted	378	kg
Range-specific surface of cement hydrates (BET method)	8–150	m ² /g
Interface (I-v) exposed during drying of 1 m³ concrete	$3 \times 10^6 - 57 \times 10^6$	m²

necessary to close undesired miscibility gaps between the surfactant and the aqueous phase, and to reduce the surfactants' tendency to coprecipitation with electrolytes of the cement aqueous phase.

The previous section on AEAs introduced the HLB concept. Equation (9.3) can be used to calculate the HLB of non-ionic surfactants using the method of individual contributions (group numbers) of hydrophilic and hydrophobic portions or groups in the molecular structure of the surfactant. For mixtures of surfactants, as SRAs often are, an overall HLB of the mixture can be calculated by additivity, according to Tadros (2005), using this equation:

$$\text{HLB} = \sum_{i=1}^n (x_i \text{HLB}_i) \quad (9.4)$$

where,

i : integer, number of surfactants in the mixture

x_i : weight fraction of surfactant i

HLB_i : HLB of surfactant i .

In fact, several SRAs contain additional components like dispersing agents, accelerators and/or air entrainers, indicating that surfactants may influence hydration as well as the mechanical performance of the cementitious material.

Regarding mixtures of surfactants, it is explicitly pointed out that there is a synergistic effect that enhances drying shrinkage reduction (Wombacher et al., 2000, 2002, 2012; Gartner, 2008; Shawl and Kesling, 1995). This is because surfactants with different HLBs can serve each other as cosolvents. The cosolvent increases the surfactant solubility and reduces undesired phenomena such as surface aggregation (hydrates), salting out (coprecipitation with electrolytes from pore solutions) and self-aggregation (liquid crystals).

This is also true when surfactants of different admixture categories are combined in concrete, in particular in the case of air entrainers compatible with SRAs: the more soluble surfactants from an SRA (or the cosolvents and hydrotropes used therein) serve the AEA's rather large and less soluble surfactants as cosolvents, and can sometimes compromise the performance of the AEA. To maintain AEA performance a surfactant of a different nature – amphoteric, according to Berke et al. (2002), Budiansky et al. (1999, 2001a,b) and Kerker and Dallaire (1997) – can be used to establish compatibility between the SRA and the AEA (see the previous section on AEAs).

It is important to note that the molecular design of several surfactants claimed as SRAs limits their applicability in mortar and concrete. Some materials turn out to be too expensive to be used in concrete. Other components have to be excluded because their low molecular weight causes issues regarding low saturation vapour pressure (highly explosive) and/or low flaming points (Wombacher et al., 2000, 2002, 2012; Gartner, 2008).

Several other important material characteristics concerning the use of surfactants in cementitious systems, as well as basic working mechanisms, can be derived from general knowledge on non-ionic surfactants, which is in part outlined in the previous section on the chemistry of air entrainers.

In the next section the chemistry of non-ionic surfactants used in commercial SRAs, as well as surfactants mentioned in patent literature on SRAs, is given.

9.6.4 Classes of compounds used in SRAs

This section covers the molecular architecture of non-ionic surfactants and hydrotropes used in SRAs.

The compounds used in SRAs can be classified as:

- monoalcohols
- glycols
- polyoxyalkylene glycol alkyl ethers
- polymeric surfactants.

Besides these compounds, others can be used as SRAs.

9.6.4.1 Monoalcohols

Monoalcohols are organic compounds characterized by the presence of a hydroxyl functional group, and can be represented by the generic chemical formula $R-OH$, where R is an alkyl radical (linear, branched or cyclic).

Umaki et al. (1993) claimed alcohols with a small number of carbon atoms, also called lower alcohols, to be efficient in shrinkage reduction. In particular, tert-butyl alcohol is considered to be the most efficient SRA.

The solubility of monoalcohols in water depends on the chemistry of the alkyl group. The C4–6 straight alcohols would have limited solubility in water, except tertiary butanol that shows complete miscibility in water. Compared to surfactants used in air entrainers, the HLB application range is rather of a wetting agent (HLB 7–9) than of an oil in water emulsifier (HLB 8–18).

Monoalcohols can be found in formulated SRAs in combination with polyoxyalkylene glycols, polyoxyalkylene glycol alkyl ethers or polymeric surfactants (Shaw and Kesling, 1995, 1997, 2001) (see below).

9.6.4.2 Glycols

The term glycols strictly refers to a class of alcohols that possess two hydroxyl functional groups attached to two adjacent carbon atoms. However, it can be used more generally as a synonym for diol.

Glycols of interest for SRAs are alkandiol (or alkylene glycol) and polyoxyalkylene glycols. The general chemical structure of alkandiol is given in Figure 9.40.

Schulze and Baumgartl (1989, 1993) claim that alkandiol with n between 5 and 10, in particular 2,2-dimethyl-1,3-propanediol (neopentyl glycol), shown in Figure 9.41, are good for reducing shrinkage. Lunkenheimer et al. (2004) classify this type of surface-active molecules as solvo-surfactants or hydrotropic detergents, because they combine properties of solvents and surfactants.

2,2-Dimethyl-1,3-propanediol has good solubility in water (830 g/L at 20 °C), and finds application as single-component SRA, but can also be used as a cosolvent in formulated SRAs containing non-ionic surfactants with lower HLB.

As an example of these multicomponent SRAs, alkane diols have been used in combination with a non-ionic fluorinated polyester (Gartner, 2008) capable of reducing the surface tension of water down to below 30 mN/m. The synergistic effect on enhancing shrinkage reduction by combining glycol and surfactant was explicitly pointed out.

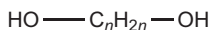


Figure 9.40 Chemical structure of alkane diols.

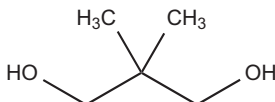


Figure 9.41 Chemical structure of 2,2-dimethyl-1,3-propanediol.

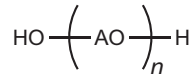


Figure 9.42 Chemical structure of polyoxyalkylene glycols.

The other class of compounds belonging to glycols are polyoxyalkylene glycols, whose chemical structure is shown in [Figure 9.42](#). In the adopted notation, AO represents an oxyalkylene unit.

The number of oxyalkylene units in the molecule can vary, but it is small ($1 < n < 8$).

[Berke and Dallaire \(1997\)](#) claimed a cement admixture able to counteract drying shrinkage by use of alkylene glycol, that is 2-methyl 2,4 pentanediol, or polyoxyalkylene glycols, and maintain compressive strength of concrete using silica fume and a stabilizer as a second component.

The combination of glycols and polyoxyalkylene glycol alkyl ethers has been shown to have a synergistic effect on shrinkage reduction efficiency ([Wombacher et al., 2000, 2002, 2012; Gartner, 2008](#)).

9.6.4.3 Polyoxyalkylene glycol alkyl ethers

The general formula of polyoxyalkylene glycol alkyl ethers is shown in [Figure 9.43](#).

The R group is a linear, branched or cyclic alkyl radical, and represents the hydrophobic tail of the surfactant. The hydrophilic head consists of the hydrated oxyalkylene chain (AO).

Polyoxyalkylene glycol alkyl ethers were claimed to be good SRAs by [Sato et al. \(1983\)](#). A reduction of drying shrinkage of up to 50% was derived theoretically using the capillary force shrinkage model and the reduction of surface tension. In 1985, a US patent ([Goto et al., 1985](#)) was granted to this group of authors.

According to patent literature, the alkyl radical R can vary, but it has a small number of carbon atoms ($C < 20$) and the alkylene group can be EO, PO or a block or random copolymer containing both, in the same proportions. The number of oxyalkylene units in the molecule (n) can be between 1 and 10 ([Sato et al., 1983; Goto et al., 1985](#)) or more ([Sakuta et al., 1990, 1992, 1993](#)).

It has been reported that cyclohexyl radicals are preferred for the shrinkage reduction effect, and that the random configuration of EO and PO units in the polar portion of the molecule is to be preferred for low foamability ([Goto et al., 1985](#)).

In commercial admixtures one representative of this class of compounds is dipropylene glycol tert-butyl ether (DPTB) ([Figure 9.44](#)), with an HLB of 7.05.

The HLB of 7.05 means that DPTB is a wetting agent ([Table 9.2](#)), and would be dispersed in water only by vigorous agitation. The relation between HLB and

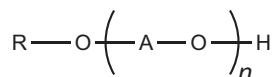


Figure 9.43 Chemical structure of polyoxyalkylene glycol alkyl ethers.

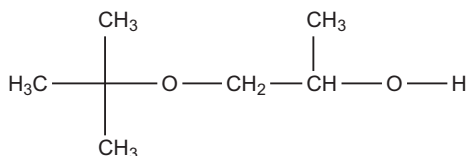


Figure 9.44 Chemical structure of dipropylene glycol tert-butyl ether.

solubility helps us to understand combinations of substances, as for example in the commercial SRA (Eberhardt, 2011). In that case the mix of compounds with very different HLBs (11.2 and 2.9) leads to a sufficient solubility that can be assessed on the basis of the average HLB value of this mix (10.1).

Multicomponent SRAs have been made that include polyoxyalkylene glycol alkyl ethers and other conventional cement admixtures, such as polycarboxylate-based SPs (Colleparidi, 2006), naphthalene sulphonate formaldehyde condensate and melamine sulphonate formaldehyde condensate (Berke et al., 2000).

Because of the defoaming property of shrinkage-reducing compounds and to provide proper air entrainment for concrete, Berke et al. (1997) and Kerkar et al. (2000) combined a shrinkage-reducing compound based on polyoxyalkylene glycol alkyl ethers and an organic amine salt of tall oil fatty acid or an AEA, respectively.

9.6.4.4 Polymeric surfactants

Starting from 1988, Akimoto et al. (1988, 1990a, 1992) proposed a cement admixture efficient in shrinkage reduction obtained by copolymerization of a polyoxyalkylene derivative and maleic anhydride, a hydrolyzed product of the copolymer or a salt of the hydrolyzed product. Akimoto et al. (1990b) filed another US patent, claiming a dispersing compound with a component similar to the structure given in Figure 9.45.

In Figure 9.45, B is a residue carrying two to eight hydroxyl groups, and X and R are hydrocarbon chains of different length and chemistry. The number of oxyalkylene groups can vary from 1 to 1000. The indexes l and n are between 1 and 7, whereas m can be between 0 and 2.

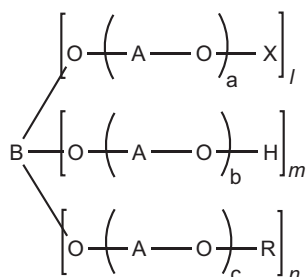


Figure 9.45 Chemical structure of a polymeric surfactant used in SRAs. According to Akimoto et al. (1990b).

The polymer can be classified as a polymeric non-ionic surfactant. In comparison to monoalcohols and polyoxyalkylene glycols alkyl ethers, the surfactant can be rendered two- or three-headed. To prevent slump loss and provide drying shrinkage reduction, a copolymer that is to some extent soluble in water exhibits the best performance (Akimoto et al., 1990b).

As mentioned previously, the efficiency of some molecules as SRAs needs to be enhanced by the presence of a cosurfactant. This is probably for use of compounds with the general formula given in Figure 9.46, which are claimed for use in mixtures with other surfactants already known to be individually effective as SRAs (Shawl and Kesling, 2001).

In this molecule, the oxyalkylene groups have preferably two to four carbon atoms and R is either hydrogen or an alkyl group (C1–16). This surfactant can be classified as polyol ($n = 0$), or a two-headed and three-headed polymeric surfactant.

Starting in 1997, several patents were issued (Berke and Dallaire, 1997; Berke et al., 1997, 1998, 2000, 2001; Kerkar et al., 1997, 2000; Kerkar and Gilbert, 1997) claiming bi-component admixtures containing a shrinkage-reducing component A and a second component B, that is a dispersing admixture.

Berke et al. (2001) described a mixture of different SRAs (polyoxyalkylene glycols, polyoxyalkylene glycols alkyl ether, polyols) and a comb-shaped polymeric dispersant with free carboxylic acid groups and side chains containing oxyalkylene units. This molecule is shown in Figure 9.47, which basically is just a more generic expression of the structure shown in Figure 9.12. The claims in the mentioned patent indicate that the B group is a carboxylic acid ester, an amide, an alkylene ether or an ether

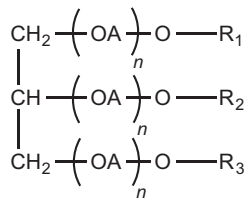


Figure 9.46 Chemical structure of a polymeric surfactant used in SRAs. Adapted from Shawl and Kesling (2001).

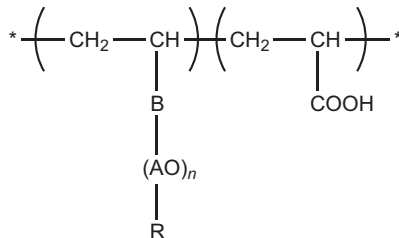


Figure 9.47 Chemical structure of a comb-shaped polymer dispersant used in SRAs (Berke et al., 2001).

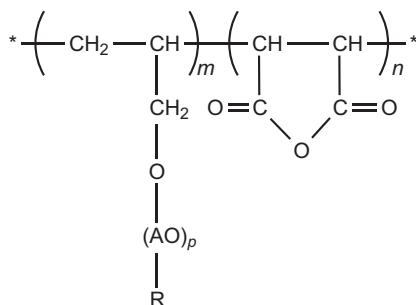


Figure 9.48 Chemical structure of a comb-shaped polymer dispersant used in SRAs (Kerkar and Gilbert, 1997).

group. The radical R can have from 1 to 10 carbon atoms, and the number of oxalyl-ylene units can vary from 25 to 100. A similar comb-shaped copolymer was proposed by Kerkar and Gilbert (1997) (Figure 9.48).

These structures are typical for comb-copolymer dispersants (see Section 9.2.4), but can also be classified as a polymeric macro-surfactant, in which the hydrophilic heads are formed by the grafted chains and the maleic unit serves as a hydrophobic ‘head spacer’.

9.6.4.5 Other SRAs

Other SRAs include amino alcohols, whose chemical structure is shown in Figure 9.49. According to Abdelrazig et al. (1995), amino alcohols where the R groups are short linear or branched alkyl radicals or hydrogen atoms show good shrinkage-reducing properties.

The preferred amino alcohols are 2-amino-butanol and 2-amino-2-methyl-propanol. An estimate of the HLB of such compounds is complicated because of the pH dependence. In cement pore solution (pH > 12.5) the amine group is not protonated, and thus the surfactant will resemble a non-ionic nature. The hydrophilic main contribution comes from the free hydroxyl of the alcohol portion, and the HLB is about 8.

Amino alcohols have been used in formulation together with diols, glycols or alkyl ether glycols or neopentyl glycol (Wombacher et al., 2000, 2002, 2012). The chemical structure of the amino alcohol surfactant claimed is shown in Figure 9.50.

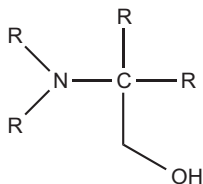


Figure 9.49 Chemical structure of an amino alcohol.

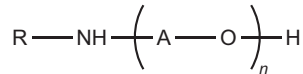


Figure 9.50 Chemical structure of an amino alcohol surfactant.

According to [Wombacher et al. \(2000, 2002, 2012\)](#), the radical R is a C1–6 alkyl group (linear, branched or cyclic) and the alkylene group is either an ethyl (C₂H₄) or a propyl (C₃H₆) group.

The structure of an amino alcohol surfactant is similar to that of polyoxyalkylene glycol alkyl ether, except that here the ether bond is substituted by a secondary amine group.

Shrinkage measurements on mortars modified by using different compositions of amino alcohols, glycols and/or alkyl ether glycols, alone and in combination, reveal a synergistic effect on the enhancement of shrinkage reduction. A similar phenomenon was shown by [Shawl and Kesling \(1995\)](#) for polyoxyalkylene glycol alkyl ethers and glycols or diols.

[Abdelrazig et al. \(1994, 1995\)](#) developed admixtures containing amides or formyl compounds whose general chemical structure is shown in [Figure 9.51](#).

In [Figure 9.51](#) R₁ is a C4–6 alkyl alcohol or alkanoyl radicals, X is either an oxygen atom or a secondary nitrogen group and R₂ is either a primary nitrogen group or a –CH₂C–(O)–CH₃ group if X is an oxygen atom.

According to [Abdelrazig et al. \(1994, 1995\)](#), the preferred SRAs are *n*-butyl urea ([Figure 9.52\(a\)](#)) and *n*-butyl acetoacetate ([Figure 9.52\(b\)](#)).

As for amino alcohols, the estimation of the HLB value of butyl urea is a delicate task because of the deprotonation of the amine group at its isoelectric point. Considering the high pH of cement pore solution, the hydrophilic contribution will mainly come from oxygen. For butyl acetoacetate the HLB is also hard to calculate because of missing group numbers. An estimate would be a range of HLB 7–9.

[Engstrand and Sjogreen \(2001\)](#) claimed a powdered SRA made of a cyclic acetal of a tri- or polyfunctional alcohol and amorphous silica, such as a silicic acid. For further

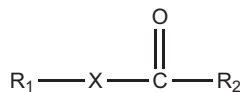


Figure 9.51 Chemical structure of amides or formyl compounds.

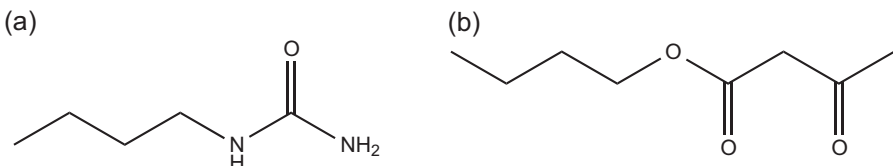


Figure 9.52 Chemical structures of (a) *n*-butyl urea and (b) *n*-butyl acetoacetate.

specification the acetal is a 1,3 dioxane of a trihydric alcohol, trimethylol-C1-8-alkane or trihydric alcoxylated alcohol.

9.7 Conclusions

Chemical admixtures include many types of compounds. In this chapter we have focussed on organic molecules, ranging from small organic compounds to large polymers with a certain polydispersity, of both natural origin and synthetic. The chapter provided an overview of the chemical characteristics of the different organic chemical admixtures.

We have done this because they offer the greatest possibility to chemists to modify properties and target improved performance by specific exploitation of structure–property relationships. This very important aspect of chemical admixtures is illustrated in more detail in the following chapters, where the working mechanisms of the chemical admixtures are discussed. Chapters 11 (Gelardi and Flatt, 2016), 13 (Eberhardt and Flatt, 2016) and 20 (Palacios and Flatt, 2016) deal respectively with the working mechanisms of dispersants, SRAs and VMAs, while Chapter 12 explains the impact that admixtures may have on cement hydration (Marchon and Flatt, 2016b).

Finally, it is important to recall that other aspects concerning the use of chemical admixtures, such as the cost of production, availability of raw materials and performance, are very important in practice and have also been mentioned in this chapter. Aspects relating to the formulation of commercial products are addressed separately in Chapter 15 (Mantellato et al., 2016).

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