# 3. Physico-chemical properties of spray solutions and their impact on penetration

The absorption of foliar-applied nutrients by the plant surface involves a series of complex processes and events. The main processes involved include formulation of the nutrient solution; the atomization of the spray solution and transport of the spray droplets to the plant surface; the wetting, spreading and retention of the solution by the plant surface; the formation of a spray residue onto the surface; and the penetration and distribution of the nutrient to a (metabolic) reaction site (Young, 1979). The above events are interrelated and overlap in that a change in one usually has an effect on the others, and each process is affected by plant growth stage factors, environmental conditions and application parameters (Bukovac, 1985).

The properties of the spray formulations are crucial in determining the performance of foliar fertilizers, especially since most of the conditions at the time of treatment cannot be fully controlled. Foliar nutrient sprays are generally aqueous solutions containing mineral element compoundss as active ingredients. The physico-chemical characteristics of the specific nutrient compound in aqueous solution, such as its solubility, pH, point of deliquescence (POD) and molecular weight will have a major influence on the rate of absorption of the element by the leaf. However, an array of additives that may modify the properties of the fertilizer solution are often included in the formulations with the aim of improving the performance of nutrient sprays. The rate of retention, wetting, spreading and rainfastness of a nutrient foliar spray is governed by the physico-chemical properties of the formulation which can contain chemical compounds with different characteristics that may interact with each other when they are together in aqueous solution.

When an aqueous solution is applied to a leaf, initially there is a high rate of penetration which decreases with time resukting from the drying of the applied solution (Sargent and Blackman, 1962). This drying is influenced by the prevailing environmental conditions and by the formulation of the applied foliar spray solution.

In the following sections, the principal physico-chemical properties of a fertilizer formulation that may affect and improve its performance will be described in theoretical and applied terms.

- Water is the usual matrix of foliar nutrient sprays.
- Plant surfaces are hydrophobic to a greater or lesser degree and the contact area of pure water drops can be limited depending on the characteristics of the surface.
- The prevailing environment will affect the physico-chemical properties and performance of the formulations on the leaf surfaces.

## 3.1. Factors determining spray retention, leaf wetting, spreading and rate of penetration

Plant responses to foliar fertilizers may be affected by the properties of the spray solution, which determine the success in achieving the absorption and translocation of the applied nutrients into plant organs. While the process of absorption of leaf-applied solutions is complex and currently remains unclear (Chapter 2), the properties of the formulations are associated with strict chemical principles well as by the prevailing environmental conditions (e.g. relative humidity and ambient temperature) at the time of treatment. An account of the principal physico-chemical factors in relation to the foliar application of nutrient solutions will be provided in the following sections.

### 3.1.1. Concentration

In Chapter 2 it was shown that the current cuticular diffusion models are based on Fick´s first law and relate the diffusive flux to the concentration gradient between the outer and the inner parts of the plant surface. The concentration of a nutrient present in a foliar spray will always be significantly higher than the concentration found within the plant organ. Therefore, a concentration gradient will be established when a nutrient solution is applied onto the plant surface and this will potentially lead to the diffusion of the nutrient across the surface. Higher penetration rates in association with increased concentrations of several applied mineral elements have been reported in studies performed with isolated cuticles (Schönherr, 2001) and intact leaves (Zhang and Brown, 1999a; Zhang and Brown, 1999b). However, the relationship between concentration of the applied solution and foliar penetration rates is currently not fully understood. A negative correlation between increasing Fe-chelate concentrations and the penetration rate through isolated cuticles and intact leaves, expressed as a percentage of the amount applied, has been observed (Schlegel *et al.*, 2006; Schönherr *et al.*, 2005). A similar negative correlation has been reported for foliar-applied K (Ferrandon and Chamel, 1988) and other elements (Tukey *et al.*, 1961). It is hypothesized that the decrease in relative penetration rates with higher K concentrations may be due to a progressive saturation of the uptake sites (Chamel, 1988). As an alternative hypothesis, Fe-salts and chelates may reduce the size of the hydrophilic pathway by inducing the partial dehydration of the pores in the cuticle (Schönherr *et al.*, 2005; Weichert and Knoche, 2006a; Weichert and Knoche, 2006b).

The ideal concentration range of mineral nutrient solutions for foliar application should be selected according to factors such as the kind of nutrient (e.g. macro- or micro-nutrient), plant species, plant age, nutritional status and weather conditions (Kannan, 2010; Wittwer and Teubner, 1959; Wojcik, 2004), and all of these will ultimately be limited by the need to avoid phyto-toxicity.

### 3.1.2. Solubility

Before applying a foliar spray formulation, it is crucial that the compounds it contains are appropriately dissolved or suspended. Foliar fertilizers are commonly dissolved or suspended in water and contain as active ingredients chemical compounds as salts, chelates or complexes of mineral nutrients. The solubility of a chemical compound in a specific solvent (usually water) at a given temperature is a physical property which can be altered through use of additives. The highest limit of the solubility of a substance in a solvent is referred to as the saturation concentration where adding more solute does not increase solution concentration. Water solubility of the applied substance is a key factor for foliar uptake, since absorption will occur only when the applied compound is dissolved in a liquid phase on the plant surface that will subsequently diffuse into the plant organs.

### 3.1.3. Molecular weight

The size of the nutrient molecule in solution will affect the rate of penetration of a foliar fertilizer as a consequence of the mechanism of cuticular absorption. It has been suggested that water and solutes cross the cuticle *via* aqueous pores (Schönherr, 2006) or in an aqueous continuum (Beyer *et al.*, 2005), and a few studies have estimated the *radii* of such pores by indirect means. The *radii* of cuticular aqueous pores has been estimated at approximately 0.3 to 0.5 nm in leaves and 0.7 to 1.2 nm in fruits of some species (Beyer *et al.*, 2005; Luque *et al.*, 1995; Popp *et al.*, 2005; Schönherr, 2006). However, larger pore radii between 2 and 2.4 nm have been calculated for the cuticle of coffee and poplar leaves by Eichert and Goldbach (2008). Several experiments with different solutes and cuticular membranes have shown that the process of cuticular permeability is size-selective with high molecular weight (larger) compounds being discriminated against low molecular weight molecules (Schreiber and Schönherr, 2009).

Recent evidence (Eichert and Goldbach, 2008) suggests that the foliar uptake pathway is less size selective than would be predicted by the cuticular penetration route of entry which may indicate that there is a stomatal pathway (Chapter 2). However the process of stomatal uptake is also size-selective since particles with a diameter of 1 μm did not enter the stomatal pore whereas particles of 43 nm diameter did penetrate into the stomata (Eichert and Goldbach, 2008).

### 3.1.4. Electric charge

Salts are electrolytes and will dissociate into free ions when dissolved in water with the final solution being electrically neutral. Anions and cations present in aqueous solution will be hydrated or solvated to different degrees depending upon their physico-chemical characteristics. The same phenomena will apply for nutrients supplied as chelates or complexes since with few exceptions most of these compounds are not neutral and will therefore be ionized when dissolved in water. For example, many of the Fe-chelates available on the market are negatively charged (Fernandez and Ebert, 2005). At a $\text{pH} > 3$ plant cuticles are negatively charged (Schönherr and Huber, 1977) and cell walls have charges corresponding to dissociated weak acids (Grignon and Sentenac, 1991). Consequently uncharged or electron-charged compounds and anions can penetrate the leaf and are translocated in the apoplast[8] easier than positively-charged complexes or cations.

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[8] Non-living, extracellular space surrounding the living cells (i.e. the symplast).

However, when applying salts or chelates or complexes, the latter two being formed by mixing metal salts with ligands accompanied with their own corresponding ions, the anions and cations present in solution can penetrate into the leaves. The nature of the anions and cations in the foliar applied solution will have physiological significance and must be considered when designing a foliar spray formulation.

### 3.1.5. Solution pH

Since plant cuticles are poly-electrolytes, their ion exchange capacity will be altered with pH fluctuations (Chamel and Vitton, 1996). Cuticles were shown to have iso-electric points around pH 3 and when solution pH values are higher than this they will render the cuticle negatively charged and the cuticular carboxyl groups will then readily bind positively charged cations (Schönherr and Bukovac, 1972; Schönherr and Huber, 1977).

While it is clear that the pH of the spray solution alters penetration there is no consistency in plant response and it appears that the pH of the solution alone is not that predictive of penetration and is influenced more significantly by the nutrient being applied and the plant species being treated. In most of the scientific reports on foliar fertilization usually no reference is made to the pH of the nutrient spray solution applied to the foliage which is a critical oversight particularly in the case of pH unstable mineral elements such as Fe. Cook and Boynton (1952) recorded the greatest absorption of urea by apple leaves in the pH range 5.4 to 6.6. Furthermore the highest uptake rates by citrus leaves after foliar urea treatment were recorded when the pH of the solution was kept between 5.5 to 6.0 (El-Otmani *et al.*, 2000). Working with Fe compounds, Fernandez *et al.* (2006) and Fernandez and Ebert (2005) observed that pH values around 5 were optimal for foliar uptake of Fe-containing solutions. Blanpied (1979) showed that maximum Ca absorption by apple leaves occurred when the solution pH ranged from 3.3 to 5.2. However, Lidster *et al.* (1977) reported the highest Ca absorption rates by sweet cherry (*Prunus avium* L.) fruits when $CaCl_2$ solution of pH 7 was applied. Reed and Tukey (1978) observed maximum P absorption by chrysanthemum leaves when the solution pH was between 3 to 6 for Na-phosphate and between 7 to 10 pH for K-phosphate.

Frequently foliar spray salts dissolved in pure water will alter spray solution pH and some formulations may have extreme pH values and hence will affect the uptake process of by the foliage. For instance the majority of Fe(III)-salts are very acidic while 1% $CaCl_2$ or 8% $K_2SO_4$ have pH values above 9.

### 3.1.6. Point of deliquescence

The processes of hydration and dissolution of a salt are determined by its point of deliquescence (POD) which is a physical property associated with a compound at a given temperature (Schönherr, 2001). Deliquescent salts are hygroscopic substances (i.e. capable of trapping water from the surrounding environment) and will dissolve once a critical relative humidity threshold has been attained. The point of deliquescence is defined as the relative humidity value at which the salt becomes a solute. Thereby, the lower the point of deliquescence of a salt is, the sooner it will dissolve upon exposure to ambient relative humidity (Fernandez and Eichert, 2009). When ambient relative humidity is higher than the point of deliquescence of the foliar applied compound, the substance will dissolve and will be available for absorption by the leaf. The effect of relative humidity on the solution or crystallization of salts has been assessed in studies carried out with cuticular membranes and intact leaves and could be better explored following the experimental practices used in aerosol research (Fernandez and Eichert, 2009). Similarly, the physiological effects associated with the deposition of hygroscopic aerosol particles onto plant surfaces are currently not fully understood, but it is considered that such particless may either act as leaf desiccants or promote increased uptake rates (Burkhardt, 2010).

## 3.2. Environment

Environmental factors such as relative humidity and temperature will play a role with regard to the performance of a foliar sprays and the uptake of leaf-applied solutions. Environment can also alter foliar spray efficacy through its influence on the biology of the plant - a process that will be discussed in Chapter 4.

The most relevant environmental factors affecting the performance of solutions when sprayed to the foliage will be described, considering that under field conditions, continuous interaction between such factors will result in different physiological and physico-chemical responses and effects. The effect of the environment on foliar uptake-related phenomena will be discussed in more detail when describing the biological factors affecting the efficacy of foliar fertilization in Chapter 4. Here the two environmental factors that most directly affect the performance of foliar nutrient sprays are temperature and relative humidity.

Relative humidity is a major factor influencing foliar uptake of nutrient sprays since it affects the permeability of the plant surface and the physico-chemical responses to applied compounds. At high relative humidity permeability may be increased due to cuticular hydration and the delayed drying of the salts deposited onto the plant surface following the application of a foliar spray. Salts with points of deliquescence above the prevailing relative humidity in the phyllosphere[9] will theoretically remain as solutes and leaf penetration will be prolonged.

Temperature will affect various physico-chemical parameters of the foliar spray formulation such as its surface tension, solubility, viscosity or point of deliquescence. In general, increasing temperature range (e.g. from 0 to 40°C) under any field conditions will increase solubility of the active ingredients and adjuvants, but will decrease viscosity, surface tension and the point of deliquescence. In addition, high temperatures will speed the rate of evaporation from the spray solutions deposited onto the foliage reducing the time until solution dryness occurs when leaf penetration can no longer occur.

Other environmental factors such as light intensity or precipitation may also affect the performance of foliar nutrient sprays. For instance, several Fe(III)-chelates are known to be degraded by exposure to sun-light. On the other hand, the occurrence

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[9] The aerial part of plants that can serve as a habitat for microorganisms.

of precipitation shortly after the application of a foliar spray may rapidly wash-off the treatment. As a consequence, weather forecasts should be taken into consideration prior to foliar spray applications to avoid conditions that can reduce humidity or increase drying speed such as high winds, heavy rain or extremes of temperature at the time of foliar application.

## 3.3. Formulations and adjuvants

Commercial foliar nutrient sprays are generally composed of at least two major components, namely: the active ingredient(s) and the inert material(s) or adjuvant(s). Adjuvants help to improve the spreading (wetting) and persistence (sticking) of the active ingredient(s) or mineral element(s) on the leaf surface as well as promote the rate of uptake and bioactivity of the mineral element(s) applied. Limitations to the foliar uptake of applied mineral elements has led to the widespread use and continuous search for adjuvants that improve the performance of spray treatments. In the following paragraphs information on the active ingredients and adjuvants will be provided.

### 3.3.1. Mineral compounds applied as foliar sprays

A preliminary distinction should be made concerning the application of either macro- or micro-nutrients, the latter being supplied at lower rates and concentrations and often being unstable when applied as inorganic salts. An account of the most common mineral element carriers according to recent articles is shown in Tables 3.1 and 3.2. The foliar fertilizer industry is characterized by a large number of proprietary products that are frequently derived from common salts which can be occasionally mixed in novel ratios and/or with addition of compounds that serve to ‘complex, chelate or bind’ and/or adjuvants that can ‘enhance’ efficiency of uptake.

**Table 3.1.** Macro-nutrient carriers normally used in foliar spray formulations.

| Macronutrient | Common element compounds | References |
|---|---|---|
| N | Urea, ammonium sulphate, ammonium nitrate | Zhang *et al.* (2009); Fageria *et al.* (2009) |
| P | $H_3PO_4$, $KH_2PO_4$, $NH_4H_2PO_4$, $Ca(H_2PO_4)_2$, phosphites | Noack *et al.* (2011); Schreiner (2010); Hossain and Ryu (2009) |
| K | $K_2SO_4$, KCl, $KNO_3$, $K_2CO_3$, $KH_2PO_4$ | Lester *et al.* (2010), Restrepo-Díaz *et al.* (2008) |
| Mg | $MgSO_4$, $MgCl_2$, $Mg(NO_3)_2$ | Dordas (2009a), Allen (1960) |
| S | $MgSO_4$ | Orlovius (2001), Borowski and Michalek, (2010) |
| Ca | $CaCl_2$, Ca-propionate, Ca-acetate | Val and Fernández (2011); Wojcik *et al.* (2010); Kraemer *et al.* (2009a,b). |

**Table 3.2.** Micro-nutrient carriers normally used in foliar spray formulations.

| Micronutrient | Common element compounds | References |
|---|---|---|
| B | Boric acid ($B(OH)_3$), Borax ($Na_2B_4O_7$), Na-octoborate ($Na_2B_8O_{13}$), B-polyols | Will *et al.* (2011); Sarkar *et al.* (2007), Nyomora *et al.* (1999) |
| Fe | $FeSO_4$, Fe(III)-chelates, Fe-complexes (lignosulphonates, glucoheptonates, etc.) | Rodríguez-Lucena *et al.* (2010a, 2000b); Fernández *et al.* (2008b); Fernández and Ebert (2005); Moran (2004) |
| Mn | $MnSO_4$, Mn(II)-chelates | Moosavi and Ronaghi (2010), Dordas (2009a), Papadakis *et al.* (2007), Moran (2004) |
| Zn | $ZnSO_4$, Zn(II)-chelates, ZnO, Zn-organic 'complexes' | Amiri *et al.* (2008); Haslett *et al.* (2001), Moran (2004); Zhang and Brown (1999). |

Until the 1970´s, the foliar micronutrient fertilizer market was dominated by products based on inorganic compounds particularly sulphates (Moran, 2004). During the 1980´s a wide variety of micronutrient 'chelates' and 'complexes' (e.g. synthetic chelates using EDTA, glucoheptonates, polyols, amino-acids, or lignosulphonates, among many other types) were offered as an alternative to the application of inorganic compounds.

The recommended rates at which foliar fertilizers are used are highly variable and are usually based on the specific plant species being treated. As previously described the physico-chemical properties of the active ingredients, e.g. molecular size, solubility or point of deliquescence, will influence the rate of uptake by foliage. In general, synthetic chelates are much larger and have higher points of deliquescence than the inorganic mineral salts commonly used as active ingredient carriers. While some materials are recommended on the basis of rigorous controlled environment and extensive field trials, many frequently utilize rates designed to merely ensure safety and satisfy cost concerns. Optimal concentration rates for the many and varied foliar fertilizers available for different crops are currently lacking and future research efforts should focus on trials to establish clear concentration thresholds for foliar-applied nutrient solutions.

Foliar-applied nutrient solutions could be phytotoxic due to their high osmotic potential and pH by affecting important physiological processes such as photosynthesis and/or stomatal opening (Bai *et al.*, 2008; Elattal *et al.*, 1984; Fageria *et al.*, 2009; Kluge, 1990; Swietlik *et al.*, 1984; Weinbaum, 1988). These effects can be a critical factor for consideration when spraying macro-nutrient fertilizers to the foliage.

## 3.3.2. Formulation additives: adjuvants

### *General information*

As described in Chapter 2, plant surface topography may vary between plant species and varieties, organs and growing conditions. The presence, chemistry and topography of epicuticular waxes and epidermal structures such as trichomes may render the surface difficult to wet. Under such circumstances, the proper wetting, spreading and penetration of foliar fertilizers may require the addition of co-formulants such as surface-active agents (adjuvants) that modify the properties of the spray solution. Numerous foliar and cuticular uptake studies have shown the improved efficacy of formulations containing adjuvants that act by enhancing the wetting, spreading, retention, penetration and humectant properties of foliar sprays as compared to pure mineral element solutions applied alone. Therefore the formulation of mineral element solutions with adjuvants can have a significant effect on the uptake and bioactivity of the nutrients supplied to the foliage though this may also decrease or increase the phytotoxicity risk associated with the nutrient active ingredients applied. This implies a fine-tuning of the nutrient active ingredients and the adjuvant compounds and their relative concentration which is necessary to develop a foliar nutrient formulation that provides reproducible plant uptake responses without plant damage.

Adjuvants can be defined as any substance included in a formulation or which is added to the spray tank that modifies the nutrient active ingredient activity or the spray solution characteristics (Hazen, 2000). They are generally classified as; (i) activator adjuvants (e.g. surface active agents) which increase the activity, penetration, spreading and retention of the active ingredient or; (ii) utility adjuvants (e.g. acidifiers) that modify the properties of the solution without directly affecting the efficacy of the formulation (Penner, 2000).

Although there are many commercially adjuvant co-formulants on the market (Table 3.3) there is considerable confusion concerning the classification of such compounds and their purported mode of action (Green and Foy, 2000).

Adjuvant names are usually related to the major properties they confer upon the spray formulations to which they are added. However the categorization and distinction between activator and utility adjuvants is rather subjective and currently lacks standardization. For instance, adjuvants described as ‘penetrators’, ‘synergists’ or ‘activators’ may increase the rate of foliar uptake through different chemical or physical mechanisms though the general principle of enhanced spray absorption is the same. Adjuvants described as “buffering agents” or “neutralizers” are generally chemical systems that adjust and stabilize spray solution pH; while other surfactants may be refered to as “detergents”, “wetting agents”, or “spreaders”; but again for both types the general principles are the same. There are several adjuvants types usually refered to as stickers that increase solution retention and rainfastness and some of these may also prolong or retard the process of solution drying when included in foliar sprays.

Humectants are compounds with water-binding properties which can be either organic, such as carboxy-methyl cellulose (Val and Fernandez, 2011), or inorganic, such as $CaCl_2$. Their presence in the formulation lowers the point of deliquescence (POD) and prolongs the process of solution drying which is especially important to increase the efficacy of foliar sprays in arid and semi-arid growing regions. Some typess of “surface-active” agents or “utility” adjuvants such as stickers or humectants can also act to increase the rate of retention and rain fastness of foliar applied formulations (Blanco *et al.*, 2010; Kraemer *et al.*, 2009b; Schmitz-Eiberger *et al.*, 2002) which can be particularly important in regions of high rainfall or where frequent overhead irrigation is employed. Typical examples of stickers and humectants are latex and soy lecithin

**Table 3.3.** Example of adjuvants available on the market classified according to their purported mode of action.

| Adjuvant name on label | Proposed mode of action |
|---|---|
| *surfactant* | lowering surface tension |
| *wetting agent* | equivalent to "surfactant" |
| *detergent* | equivalent to "surfactant" |
| *spreader* | equivalent to "surfactant" |
| *sticker* | increasing solution retention; rainfastness |
| *retention aid* | increasing solution retention; rainfastness |
| *buffering agent* | pH buffering |
| *neutraliser* | pH buffering |
| *acidifier* | lowering pH |
| *penetrator* | increasing the rate of foliar penetration (e.g. by 'solubilizing' cuticular components) |
| *synergist* | increasing the rate of foliar penetration |
| *activator* | increasing the rate of foliar penetration |
| *compatibility agent* | improving formulation compatibility |
| *humectant* | retarding solution drying by lowering the formulation's point of deliquescene (POD) on the leaf |
| *drift retardant* | better spray targeting and deposition on foliage |
| *bounce and shatter minimizer* | better spray targeting and deposition on foliage |

both of which can significantly improve the retention of foliar sprays on leaves and are frequently included in commercial formulations of many plant protection products although there is an apparent lack of sound information concerning the effectiveness of such adjuvants when used with foliar fertilisers.

The reasons underlying this are that considerable research efforts have been made in recent decades to develop adjuvants for foliar spray formulations which enhance the performance of pesticides and herbicides while less attention has been paid to developing products specific for foliar nutrient sprays. Adjuvants are usually marketed separately and may contain single compounds (e.g. "surface-active" agents alone) or are sold as mixtures of surfactants, lecithin, synthetic latex, vegetable oils, tallow amines or fatty acid esters that confer a spectrum of the desired properties outlined previously when included in a foliar-applied solution.

As a consequence since most commercial adjuvant products have been devised for their application in combination with plant protection products to facilitate their performance when applied to the foliage, their suitability for combination with foliar nutrient sprays, which are normally hydrophilic solutes, cannot be *a priori* assumed and should therefore always be empirically tested. For foliar nutrient sprays it is critical that the treatments are not phytotoxic to leaves and plants since their value and marketability can be compromised by crop damage caused by such treatments. Unfortunately it is not currently possible to predict theoretically the performance of any active ingredient whether a herbicide, a pesticide or a mineral nutrient element in combination with a particular adjuvant (Fernandez *et al.*, 2008a; Liu, 2004).

### *Surfactants*

Surface-active agents or surfactants are the most widely-used type of adjuvant in foliar spray formulations. One of the first examples of these compounds being added to foliar nutrient sprays was in the first half of the 20th century with the use of the ionic surfactant Vatsol in combination with Fe compounds (Guest and Chapman, 1949).

One method used to assess the effect of a surfactant is to measure the contact angle with a paraffined microscope slide and the drop shape by the pending drop method comparing the surface tensions of pure water (A and B) with a 0.1% organosilicon surfactant solution (C and D) as shown in Figure 3.1.

These measurements were carried out at 25°C and the contact angles (Figure 3.1 A and C) for water and a 0.1% organosilicon surfactant solutions were approximately 95° and 45° respectively giving calculated surface tensions of approximately 72 and 22 mN

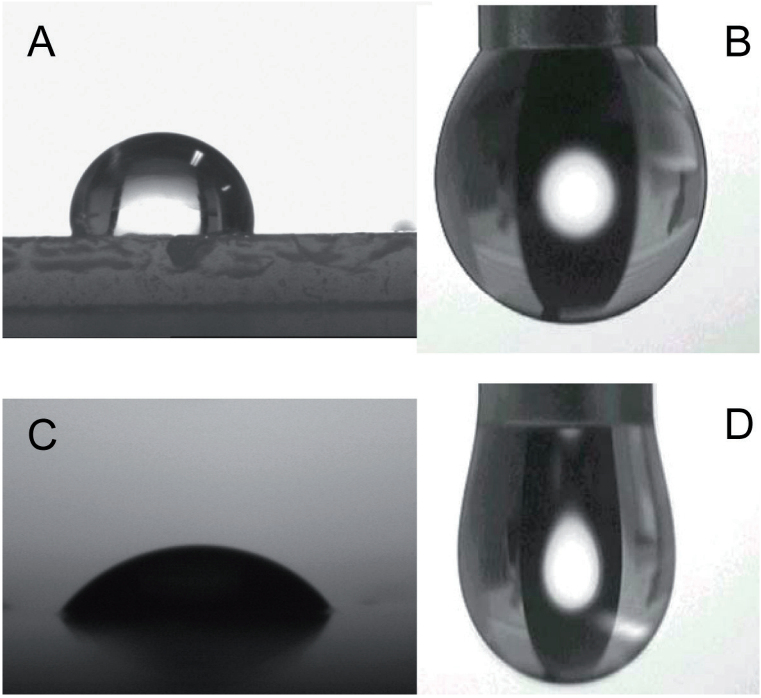

**Figure 3.1.** Contact angles (A and C) and pending drops used to calculate the surface tension (B and D) of distilled water (A and B) and a 0.1% organosilicon (C and D) distilled water solution (V. Fernández, 2011).

respectively. This experimental system demonstrates how the addition of a surfactant to a pure water solution lowers its surface tension and increases dramatically the area of contact between the liquid and the solid (in this case a paraffined surface) by lowering the contact angle.

Surfactants are large molecules consisting of a non-polar, hydrophobic portion attached to a polar, hydrophilic group (Cross, 1998; Tadros, 1995). It is important that the ends of the hydrophobic and the hydrophilic parts of the surfactant molecule are far away from each other so that they can react independently of each other with surfaces and solvent molecules (Cross, 1998). The hydrophobic part of the surfactant interacts weakly with water molecules while the polar or ionic head group interacts strongly with these so rendering the surfactant molecule water soluble.

Surface active agents are characterized by the abrupt change in their physical properties they undergo once a certain concentration has been reached. These changes in solubility, surface tension, equivalent conductivity or osmotic pressure are due to the association of surfactant ions or molecules in solution to form larger units. These associated units are called micelles and the concentration at which this association takes place is known as the critical micelle concentration. Each particular surfactant molecule has a characteristic critical micelle concentration value for a given temperature and concentration.

The mechanisms of action of surfactants when applied to the foliage are very complex and are only partially understood (Wang and Liu, 2007) although possible modes of surfactant action have been suggested by Stock and Holloway (1993) and include: increasing the effective contact area of deposits; dissolving or disrupting epicuticular waxes; solubilizing agrochemicals in deposits; preventing or delaying crystal formation in deposits; retaining moisture in deposits; and promoting stomatal infiltration. However, it is now known that surfactants can also alter the diffusion of substances *via* cuticular solubilization or hydration and that they can also affect the permeability of the plasma membrane. Therefore surfactant composition and concentration are key factors influencing the performance of foliar sprays (Stock and Holloway, 1993).

The hydrophilic portion of a surfactant can be non-ionic, ionic or zwitterionic, accompanied by counter-ions in the last two cases. When present in a foliar spray formulation the polarity of the hydrophilic part of a surfactant may determine factors such as the occurrence of interactions between the surfactant and the active ingredients or the contact properties between the spray solution and each particular plant surface.

### Non-ionic surfactants

Non-ionic surfactants are widely used in foliar sprays as they are theoretically less prone to interact with other polar components of the formulation. The most common hydrophilic polar group in non-ionic surfactants is that based on ethylene oxide (Tadros, 1995) with the organosilicons, alkyl phenol ethoxylates, alkyl-polyglucosides, fatty alcohol ethoxylates, polyethoxylated fatty acids, ethoxylated fatty amines, alkanolamides or sorbitan esters belonging to this group of surfactants.

An example of a non-ionic surfactant molecule is shown in Figure 3.2.

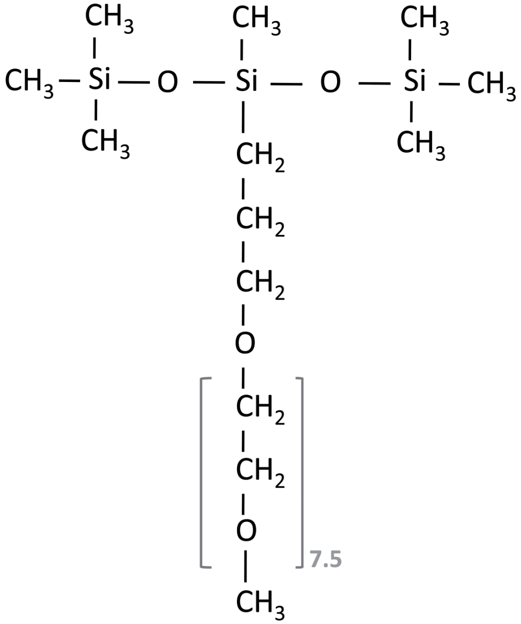

**Figure 3.2.** Molecular structure of the non-ionic surfactant, Silwet® L-77.

According to Stock and Holloway (1993) the addition of non-ionic surfactants with low ethylene oxide contents, which are good spreaders with their low surface tensions, will favour the uptake of lipophilic pesticides; while conversely uptake of hydrophilic pesticides is improved by surfactants with higher ethylene oxide units and therefore poor spreading properties. However, conflicting evidence concerning the effect of high and low ethylene oxide containing surfactants suggests that ethoxylated surfactants may enhance the uptake of both hydrophilic and lipophilic compounds by different mechanisms as yet not fully clarified (Haefs *et al.*, 2002; Kirkwood, 1993; Ramsey R. J. L., 2005). For example, low ethylene oxide-content surfactants that enhance uptake of lipophilic compoundss were found to alter the physical properties of cuticles and to be more phytotoxic. By contrast, surfactants with higher ethylene oxide contents appear to increase cuticular hydration and to be less phytotoxic (Coret and Chamel, 1993; Ramsey, 2005; Uhlig and Wissemeier, 2000). Surfactants with either large hydrophobic groups or long hydrophilic chains, or both, have been reported to be less phyto-toxic because of their lower water solubility and hence, slower rate of foliar uptake (Parr, 1982). Studies performed with Ca-containing compounds ($CaCl_2$ and Ca-acetate) in combination with ethoxylated rapeseed oil surfactants with different ethylene oxide contents (Kraemer *et al.*, 2009a; Kraemer *et al.*, 2009b; Schmitz-Eiberger *et al.*, 2002) showed that they can affect the rate of cuticular permeability of Ca *via* the distribution of the active ingredient in the droplet and the rain-fastness of the formulations. Organosilicon, non-ionic surfactants, also known as super-spreaders, are a group of chemicals containing alkylsiloxane groups as the hydrophobic moiety (Knoche, 1994). Owing to their low surface tension (well below 30 mN $m^{-1}$ and generally between 20 to 25 mN $m^{-1}$) such surfactants are known to promote stomatal infiltration (Knoche, 1994; Schönherr *et al.*, 2005; Stevens, 1993) and increase leaf wetting and spreading that reduces solution retention by the foliage due to the formation of a thin liquid film and increased run-off by the spray solution. The effect of nutrient foliar sprays containing organosilicon surfactants has been assessed in several foliar uptake studies (Fernandez *et al.*, 2008a {Horesh, 1981 #1568}; Horesh and Levy, 1981; Neumann and Prinz, 1975; Neumann and Prinz, 1974) and a high phytotoxicity-risk due to increased penetration rates has often been observed suggesting that such compounds should be used with caution (i.e. at lower concentrations and/or by reducing the active ingredient dose) to avoid leaf burn and potential defoliation.

In spite of being non-ionic, several investigations showed that this type of surfactant (e.g. containing organosilicons, alcohol ethoxylates or triglyceride ethoxylates) can interact with mineral element ions present in foliar nutrient solutions and alter their performance by salting-in or salting-out of surfactant molecules or resulting in the formation of polymers (Fernandez and Eichert, 2009; Knoche, 1994; Uhlig and Wissemeier, 2000). The interaction of mineral nutrient compounds with surfactants may lead to the loss of surface tension as has been observed for the organosilicon surfactant Silwet® L-77 in the presence of ferric-citrate (Knoche *et al.*, 1991; Neumann and Prinz, 1975). On the other hand, the interaction between the divalent cations $Ca^{2+}$ and $Mg^{2+}$ (supplied as $CaCl_2$ and $MgSO_4$) and surfactant molecules reduced the phytotoxicity of 0.1% Triton® X-100 and Genapol® C-80 when applied to *Euphorbia pulcherrima* leaves and bracts (Uhlig and Wissemeier, 2000).

### Ionic surfactants

Ionic surface-active agents are widely used in formulations devised for cleaning purposes such as detergents, shampoos or washing powders but they are of limited relevance in agriculture since most nutrients are delivered as ionized compounds (e.g. nutrient salts) which may interact and bind to the ionic surfactant molecules and thereby alter their surface-active performance.

The hydrophilic portion of an ionic surfactant can be either anionic or cationic. Anionic surfactants may possess one or more functional groups which become(s) ionized in solution and generate the negatively-charged organic ions responsible for lowering surface tension. This group of surfactants is probably the most widely used and includes various chemical compound groups such as alkyl-sulphates, alkyl-phosphates and alkyl-polyether sulphates and also paraffin-, olefin- and alkylbenzene-sulphonates and sulphate esters. The sulphate ester groups (C-O-S) attaching the hydrophilic head to the surfactant is easily hydrolysed to the corresponding alcohol and sulphate ion by dilute acids while the stronger C-S bond of sulphonate groups is much more stable and will be broken only under extreme chemical conditions (Cross, 1998).

Cationic surfactants have one or more functional groups which becomes ionized in solution to generate positively-charged organic ions and therefore they are incompatible with anionic surfactants. The most representative cationic surfactants are based on quaternary ammonium, alkyl-ethoxylate-ammonium or alkyl pyridinium compounds which have been found to have anti-microbial properties (Badawi *et al.*, 2007).

**Zwitterionic or amphoteric surfactants**

This kind of surface-active agents contains both anionic and cationic head groups and can be anionic, cationic or non-ionic depending on the pH of the solution. These surface-active agents are milder as compared to other surfactants and are often used in cosmetics and 'soft' household chemicals in combination with other additives. Examples of commonly used zwitterionic surfactants are alkyl-betaines and lecithin and there are a number of commercially available adjuvant mixtures which use soya lecithin as the major ingredient.

- Mineral element carriers can be applied alone or in combination with a variety of adjuvants that may improve the contact properties, rate of absorption and surface distribution of the active ingredient(s) when applied to the foliage. Surfactants are an important and widely used group of adjuvants that reduce the surface tension of nutrient solutions as well as generally improve their wetting and spreading onto the plant surface.
- Some adjuvants like surfactants, penetration synergists, stickers and humectants may increase the rate of uptake, retention and retard the rate of drying of foliar nutrient sprays.

## 3.4. Conclusions

In this chapter the current state of knowledge about the physico-chemical properties of foliar nutrient spray formulations and of the factors which can affect such properties has been provided. Since plant surfaces are hydrophobic to a lesser or greaterer degree depending on the plant species, organ and growing conditions, pure water (un-formulated) solutions are limited in their uptake by the foliage. Therefore it is important to formulate foliar sprays with appropriate forms of nutrients and adjuvants to take into account these physico-chemical properties and limitations so that the overall efficacy of foliar fertilizers can be optimized.

With this current knowledge base, the following certainties, uncertainties and opportunities for the application of foliar fertilizers can be addressed.

### *Certainties*

- There is abundant empirical and scientific evidence to demonstrate that to varying degrees pure water and formulated nutrient solutions can be taken up by plant foliage.

- The hydrophobic character of plant surfaces impairs the rate of uptake of pure water nutrient solutions compared to formulations containing additives that reduce surface tension, increase retention and humectancy.
- While higher nutrient concentration solutions can be supplied without adjuvants their efficacy will be lower compared to foliar spray treatments co-formulated with adjuvants and furthermore they may also be more phytotoxic to leaves.
- Environmental factors such as relative humidity and/or ambient temperature will affect the physical properties and performance of a foliar fertilizer formulation and these should be taken into consideration before applying spray treatments under field conditions.

### *Uncertainties*

- The physico-chemical parameters that govern foliar uptake are poorly understood.
- Interactions between nutrients and adjuvants occur and are not fully understood.
- While the performance of a particular nutrient carrier can be improved by addition of surfactants and/or other additives, it is currently not possible to determine accurately which adjuvant or additive will be most effective, or to determine the optimum rates of their addition, without empirical testing.

### *Opportunities*

- Increased understanding of the mechanisms of nutrient penetration into leaves will provide better targets for the development of foliar fertilizer formulations with improved efficacy and safety.
- Improved understanding of the properties of formulation additives, their interactions with nutrients and their effects on leaf structure and chemistry will also help improve the efficacy and reproducibility in performance of foliar sprays.
- The addition of humectants to foliar fertilizer formulations helps to prolong the process of solution drying which can improve the efficacy of the spray treatments especially in arid and semi-arid regions.