PHYSICOCHEMICAL PROPERTIES OF ADJUVANTS AS PREDICTED KEY FOR AGROCHEMICAL BEHAVIOUR

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Abstract

The physicochemical properties of adjuvants determine their function and impact upon biological activity. Various physicochemical parameters are key to modifying both the pre-retention events and post-retention consequences of adjuvant usage, irrespective of whether the adjuvants are tank-mix additives or built into formulation. This paper discusses the relationship between physicochemical properties of adjuvants and their functions in agrochemical applications. From a more coherent understanding of the parameters involved, it can be shown that there are ways of predicting the required properties of an adjuvant to solve specific problems. The recognition that different problems often require quite different approaches illustrates that universal adjuvant do not exist per se, so it is essential to know each of their features in order to make correct selection of the appropriate adjuvant depending of diagnosed problem.

1. INTRODUCTION

Increasing population and reducing availability of arable land has boosted the use of agrochemicals to improve productivity, crop protection and storage. The global agrochemicals market is expected to grow from $134 billion in 2010 to $223 billion in 2015, registering a high Compound Annual Growth Rate (CAGR) of 10.6% from 2010 to 2015[1]. Market growth is also driven by the use of agrochemicals in the production of biofuels, which are rapidly gaining in importance over traditional petroleum-based fuel.

Agrochemicals (fertilizers, fungicides, herbicides, and insecticides) contain besides the active ingredients many other compounds called adjuvants (Fig.1).

Fig.1: Functionality of adjuvants used in agrochemical industry.

In general sense, adjuvants can define as *"Any substance that helps and enhances the performance of a process while improving the characteristics of the finished product"*. They can be built into the formulation during manufacture or used separately for tank mixing with the formulation just before spraying.

To understand the mode of action and behavior of the diverse chemical range of adjuvants currently available, a full understanding of their physicochemical characteristics is critical. Some adjuvants fulfill a number of important functions, including: imparting shelf-life stability to agrochemical formulations; dispersing, solubilizing, wetting or emulsifying the active ingredients; and binding granules.

The choice of adjuvant(s) varies according to the properties of active ingredient (herbicide, bacteria or enzyme) and its mode of action (residual, contact or systemic), type of formulation, (solution, emulsion or suspension), the nature of plant barriers (trichomes, leaf, stem, root), as well as the intended target (weed, fungus, insect). Also, spray application of agrochemical formulation involves a number of discrete processes that occur consecutively and, initially, in first seconds where adjuvants play their part.

Many studies have been discussed the role of adjuvants in agrochemical formulations[2-5], or their effect on sprays nozzles types[6-8], or their consequence on foliar deposition[9] and uptake of pesticides[10] or herbicides[11-13], or even their wetting effect on leaf surfaces[14-15]. However, no studies addressing in detail the relationship between the own functions of adjuvant alone and its physicochemical properties. In this review, mainly physicochemical properties of adjuvants will be discussed, with examples illustrating how a fuller understanding of key parameters can be benefit to workers within the agrochemical industry. It is not possible to cover all physicochemical properties of adjuvants, however it is hoped that this investigation will serve to highlight the selection of right adjuvant for use.

2. Classification of adjuvants: value and application

Some research indicates that up to 70 percent of the effectiveness of a pesticide depends on a proper spray application. However, the weakest link in the pesticide development process is the actual spray application. Therefore, using adjuvants to minimize or eliminate many spray application problems will help boost the pesticide's effectiveness. Adjuvants are designed to perform specific functions, including buffering, dispersing, emulsifying, spreading, sticking, reducing evaporation, foaming, spray drift, and volatilization (Figure 1).

Also, adjuvants allow crossing the barriers of plants (membranes and hair of leaves and Roots) thanks to their wetting, retention and penetration effect (Figure 2).

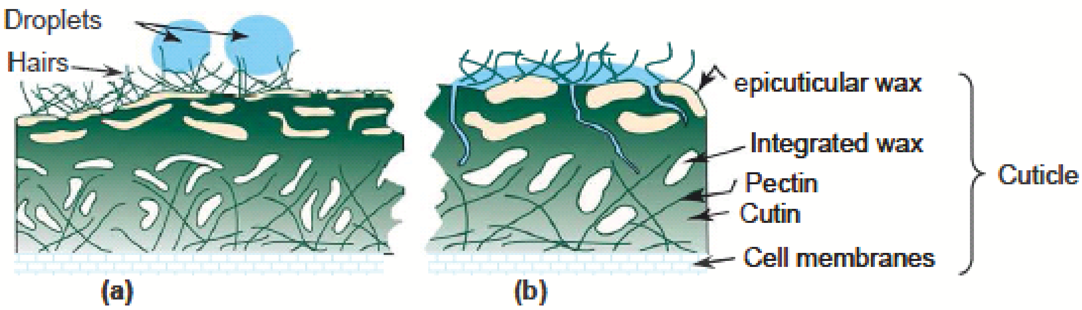

Fig.2: Schematic illustration of spray droplet behavior on plant leaf surface: (a) without adjuvant; (b) with adjuvant.

No single adjuvant can perform all these functions, but different compatible adjuvants often can be combined to perform multiple functions at the same time.

The agricultural and horticultural industries are being overwhelmed by adjuvant choices. With so many products to choose from, how do you make an informed decision about which adjuvant to use for a particular situation? A good place to start is to understand the physicochemical characteristics of this diverse group of chemicals.

Generally, adjuvants can be classified in four principal families on the basis of their chemical composition.

2.1. Surfactants

Surfactants (surface acting agents), also called wetting agents and spreaders, physically change the surface tension of a spray droplet. For a pesticide to perform its function properly on a plant, the spray droplet must be able to wet the foliage and spread out evenly. Surfactants make the area of pesticide coverage larger, which increases the pest's exposure to the chemical. Surfactants are particularly useful when applying a pesticide to a plant with waxy or hairy leaves (Fig.2). Without proper wetting and spreading, spray droplets often run off or fail to provide good coverage to the surfaces. Too much surfactant, however, can cause excessive runoff, which may make the pesticide less effective.

Surfactants are classified by the way they ionize, or split apart, into electrically charged atoms or molecules called ions.

1)Anionic surfactants: they have a negative charge and are most effective when used with contact pesticides.

2)Cationic surfactants: they have a positive charge and should never be used as standalone surfactants because they are usually phytotoxic (poisonous to plants).

3)Nonionic surfactants: they ave no electrical charge. Pesticidal activity in the presence of a nonionic surfactant can be quite different from activity in the presence of a cationic or anionic surfactant. Nonionic surfactants are often used with systemic pesticides and help pesticide sprays penetrate plant cuticles. Also, nonionic surfactants are compatible with most pesticides and most EPA-registered pesticides that require a surfactant recommend a nonionic type. Keep in mind that selecting the wrong surfactant can reduce the effectiveness of a pesticide product and increase the risk of plant injury.

Organo-silicone surfactants are a newer group of surfactants that are taking the place of the more traditional nonionic surfactants.

They reduce surface tension, increase spreading ability, and improve rainfastness (the amount of time between a pesticide application and rainfall). Rainfastness can be improved when more pesticide is absorbed into the plant (fig.3).

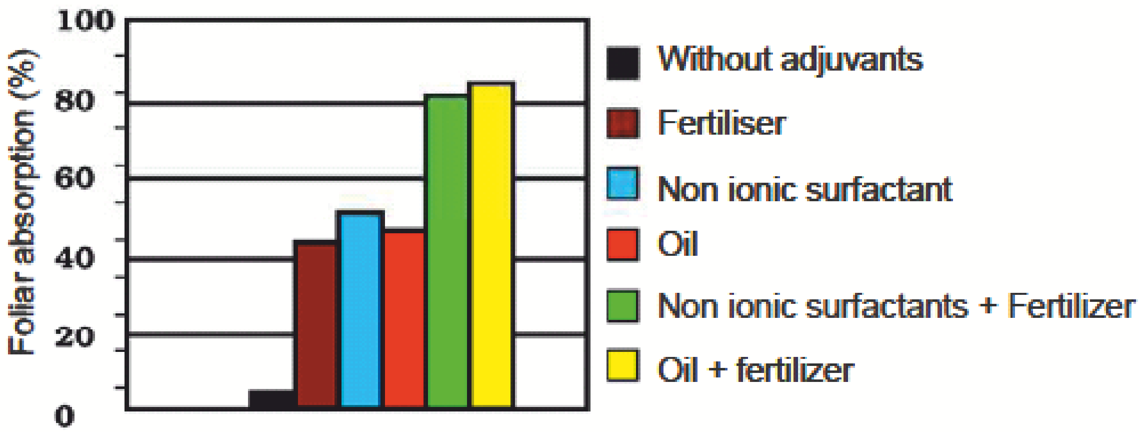

Fig.3: Percentage of foliar uptake according to the adjuvant family.

2.2. Oils

Oils are being used to control grassy weeds. The three types of oil-based adjuvants include crop oils, crop oil concentrates, and vegetable oil concentrates.

1) *Crop oil:* is generally 95 to 98 percent paraffin or naptha-based petroleum oil with 1 to 2 percent surfactant/emulsifier. Crop oils promote the penetration of a pesticide spray either througha plant's waxy cuticle or through an insect's tough, chitinous shell. Traditional crop oils are more commonly used for insect and disease control and rarely with herbicides.

2) *Crop oil concentrates (COCs):* are made up of 80 to 85 percent emulsifiable petroleum-based oil and 15 to 20 percent nonionic surfactant. Crop oil concentrates have the penetration properties of oil and the spreading properties of a surfactant. COCs are often used with post emergence herbicides.

3) *Vegetable oil concentrates (VOCs):* are made up of 80 to 85 percent crop derived seed oil (usually cotton, linseed, soybean, or sunflower oil) and 15 to 20 percent nonionic surfactant.

To improve their performance, many VOCs have undergone a process called esterification, which increases the oil-loving characteristics of the seed oil and results in methylated seed oil (MSO). MSOs work the same as traditional crop oil concentrates to increase penetration of the pesticide into the target pest.

2.3. Nitrogen-based fertilizers

They improved herbicide activity has been shown by adding ammonium sulfate or urea ammonium nitrate to the spray mixture. Nitrogen fertilizers may replace some adjuvants but are usually included in addition to a surfactant and a crop oil concentrate for use with systemic pesticide products. Many fertilizer-based adjuvants are available in liquid forms, which are easier to mix and provide more consistent results.

2.4. Utilities

As the name suggests, this class of adjuvants is used to fix specific physical or chemical conditions that can affect the formulation, spray solution or the application of the pesticide. Utilities adjuvants can be classed in five groups:

1) Compatibility agents: pesticides are commonly mixed with liquid fertilizers or other ingredients. However, some combinations can be physically or chemically incompatible, causing clumps and uneven distribution in the spray tank. Occasionally, the incompatible mixture will clog the pump and hoses, resulting in expensive cleanup and repairs. Using a compatibility agent may eliminate these problems.

2) Buffering and conditioning agents: most formulation, solutions or suspensions are stable between pH 5.5 and pH 7.0 (slightly acidic to neutral). Pesticide solutions above pH 7.0 are at greater risk of degrading or breaking down. Acidifiers are adjuvants that lower the pH of the water in the spray tank, although they do not necessarily maintain a constant pH level. Buffers tend to stabilize the pH at a relatively constant level. Conditioning or water-softening agents reduce problems caused by hard water. Hard water minerals, especially calcium and magnesium ions, bind with active ingredients of some pesticides, which may decrease pesticide performance. Before using a buffer or conditioning agent, consider the specific active ingredients requirements and test the water for pH and hardness.

3) Defoaming agents: some agrochemical formulations create foam or a frothy head in some spray tanks. This is often the result of the type of surfactant used in the formulation and the type of spray tank agitation system. The foam usually can be reduced or eliminated by adding a small amount of a defoaming agent.

4) Deposition agents: these adjuvants, which are often referred to as "stickers," increase the ability of solid particles to stick to the target surface. These adjuvants can decrease the amount of active ingredients that washes off during irrigation or rain. Deposition agents can also reduce evaporation of the active ingredients and some can slow degradation of active ingredients by ultraviolet rays. Many deposition agents also include a wetting agent to make a general purpose product that both spreads and sticks to the target surface.

5) Drift control agents and thickeners: drift is a function of droplet size, wind speed, and height of the spray boom. Small droplets (with diameters of 100 microns or less) tend to drift away from targeted areas. Drift retardants or deposition aids improve on-target placement of the pesticide spray by increasing the average droplet size. Drift reduction is a priority near sensitive sites, and using a spray drift agent may be well worth the small reduction in the effectiveness of the application that can result from the change in droplet size. Thickeners, as the name suggests, increase the viscosity of spray mixtures. These adjuvants are used to control drift or slow evaporation after the spray has been deposited on the target area. Slowing evaporation is important when using systemic pesticides because they can penetrate the plant cuticle only as long as they remain in solution. Once the water has evaporated, any unabsorbed pesticide will remain on the leaf surface and can only be taken up by the plant if it returns to solution by rewetting.

In recent years, the use of dry adjuvants has received greater attention. These tend to be based upon surfactants adsorbed onto carriers, such as silica, clays, zeolites, or in complexes such as urea clathrates. In the latter situation, physical compatibility for producing a dispersible product can be an issue, as can the physical space available within a product of acceptable volume.

3. Agrochemical events modified by adjuvants

Next to their role as physical and chemical stabilizers of agrochemical formulation, adjuvants may be used to modify the following sequence of foliar or soil events (Tab.1) leading to improve the efficiency of formulated product. This list of foliar or soil events is clearly not exhaustive but is representing the major sequence of events modifying by adjuvants. Because adjuvants can acts on more than one step simultaneously, it is not practical to discuss the events outlined above, as there is significant overlap with regard to the physicochemical parameters indicators in operation.

Foliar events	Soil events
Spray droplet formation	Ensure good water retention
Spray droplet trajectory	Ensure good wetting of the soil
Droplet impaction on the leaf surface	Ensure the penetration of water and lateral movement
Spray retention on the leaf surface	Maximize absorption of water and irrigation efficiency
Spreading, wetting and coverage	Improve rooting
Deposit character and adsorption rate	Ensure good mixing with solid fertilizers
Volatilization and Humectancy	Erosion Control

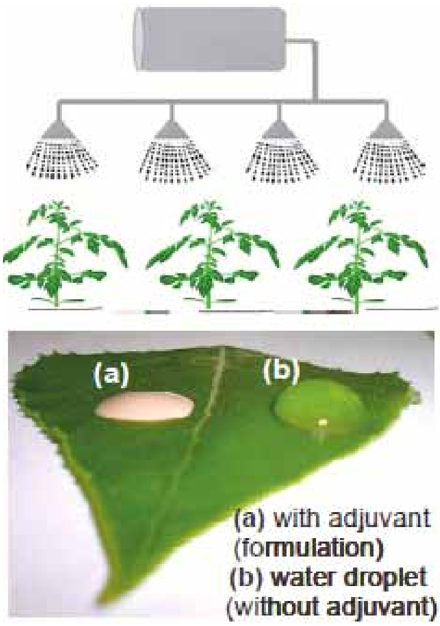

Photo showing erosion control by using adjuvant.

Tab.1: Major sequences of foliar and soil events modified by adjuvants.

Table 2 gives the mainly physicochemical parameters predictors for foliar events. In the following paper, the impact of each physicochemical parameter listed in table 2 will be discussed in detail and the processes that are influenced will be outlined.

Physicochemical parameters of Adjuvants	Modified agrochemical behavior and foliar events
Chemical structure	wettability, adsorption, diffusion, pesticide synergy, pesticide efficiency (activity, uptake, delivery)
Molecular weight	Deposition, diffusion, penetration, surface coating
Viscosity	Spray atomization, deposition, anti-evaporation, adhesion, drift control,
Hydrophobicity/Lipophilicity (solubility)	wettability, diffusion, carrying, delivery, anti-volatilization, deposition, surface coating
Surface tension	Retention, adhesion, deposition, speading, recovery, wettability, penetration
Vapor pressure	Volatilization, uptake, penetration
heating/cooling temperature	Volatilization, crystallization, uptake, penetration

Tab.2: Relationship between some physicochemical parameters of adjuvant and agrochemicals behavior.

Conclusion

After this brief screening on the categorization of adjuvants and their value, it is clear that it is possible to make some form of rational judgment about the mode of action of an adjuvant on the basis of its physicochemical properties (data not shown). Also, it is clear that adjuvants have a considerable influence on the efficiency of herbicides, agrochemical formulation, or water sprays. However, the magnitude of this effect is depend on the composition of the additive, the way in which it is formulated and the amount present in the spray liquid. This, in turn, affects the physicochemical properties of spray droplets in terms of their size and velocity, and governs their ultimate impaction and spreading behavior. Surfactant adjuvants represent the simplest situation because coformulants are not normally used; retention enhancing performance of water-soluble products is superior to water-dispersible ones and vice versa for spreading[16].

Predicting the behaviour of commercial complex blends is more delicate, because most of them contain more than one adjuvant. However, it would appear that their spray performance is influenced greatly by the amounts of these coformulants present in the spray liquid after dilution of the corresponding EC; in some cases, applications using the emulsifier alone have been shown to provide retention enhancement similar to the adjuvant oil-in-water emulsion itself[17].

Suspension concentrate and wettable powder formulations containing different proportions of active ingredient, adjuvant and coformulants, is a more complicated situation where predicting behaviour is more difficult to judge from physicochemical properties, because this system can contains more subsystem e.g. (emulsion system, colloid system, etc…).

Finally, more than one physicochemical function or adjuvancy mechanism may reside in a particular molecule (adjuvant). This relative importance of particular modes of action will depend upon the nature of active ingredient that is being delivered.

As active ingredient (e.g. herbicides, fungicides, etc...) vary widely in their physicochemical properties, from highly water soluble to extremely water insoluble, with significant variations in molecular weight and melting point, it would be naïve to expect one particular adjuvant to solve all active ingredient delivery problems.

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