1
General Introduction

The formulations of agrochemicals cover a wide range of systems that are prepared to suit a specific application. Agrochemicals are usually effective at levels from several grams to hundreds of grams of active ingredient per 1000 m^2. It is therefore difficult to apply such a small amount uniformly to the crop. In all cases, the active ingredient is first formulated in a suitable diluent such as water or an organic solvent, and when the formulation is applied it is further diluted in the spray tank to ensure uniform deposition on spraying. In some cases, an agrochemical is a water-soluble compound, of which paraquat and glyphosate (both are herbicides) are probably the most familiar. Paraquat is a 4,4′-bypyridinium salt and the counterions are normally chloride. It is formulated as a 20% aqueous solution, which on application is simply diluted into water at various ratios (1 : 50 up to 1 : 200 depending on the application). To such an aqueous solution, surface-active agents (also called surfactants, and sometimes referred to as wetters) are added, which are essential for a number of reasons. The most obvious reason for adding surfactants is to enable the spray solution to adhere to the target surface and spread over it to cover a large area. However, such a picture is an over-simplification since the surfactant plays a more subtle role in the optimization of the biological efficacy. Thus, the choice of the surfactant system in an agrochemical formulation is crucial since it has to perform a number of functions. To date, such a choice is made by a trial-and-error procedure, due to the complex nature of application and a lack of understanding of the mode of action of the chemical. It is the objective of this book to apply the basic principle of colloid and interface science in agrochemical formulations, subsequent application and optimization of biological efficacy.

The main purpose of any agrochemical formulation is to make handling and application of the active ingredient as easy as possible. An important function of the formulation is to optimize the biological efficacy. This is achieved in most cases by controlling the physical characteristics of the formulation and the use of adjuvants. An important criterion for any agrochemical is its safety, both to the crop and to the agrochemical worker. This requires adequate control of the spray droplet spectrum, reduction of any drift and removal of any toxic effect on contact with the individual. These stringent requirements can be achieved by careful analysis of all the interfacial phenomena that are involved on application. The concept of a 'pesticide delivery system' (PDS) must be applied, whereby the

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active ingredients are made available to a specified target at a concentration and duration designed to accomplish an intended effect, i.e. obtain the fullest biological efficacy while minimizing the various harmful effects.

Most agrochemicals are water-insoluble compounds with various physical properties, which have first to be determined in order to decide on the type of formulation. One of the earliest types of formulations were wettable powders (WPs), which are suitable for formulating solid water-insoluble compounds that can be produced in a powder form. The chemical (which may be micronized) is mixed with a filler such as china clay and a solid surfactant, such as sodium alkyl or alkyl aryl sulfate or sulfonate, is added. When the powder is added to water, the particles are spontaneously wetted by the medium and on agitation dispersion of the particles takes place. It is clear that the particles should remain suspended in the continuous medium for a period of time depending on the application. Some physical testing methods are available to evaluate the suspensibility of the WP. Clearly, the surfactant system plays a crucial role in wettable powders. First, it allows spontaneous wetting and dispersion of the particles. Second, by adsorption on the particle surface, it provides a repulsive force that prevents aggregation of the particles. Such a process of aggregation will enhance the settling of the particles and may also cause problems on application, such as nozzle blockage.

The second and most familiar type of agrochemical formulations is emulsifiable concentrates (ECs). These are produced by mixing an agrochemical oil with another one such as xylene or trimethylbenzene or a mixture of various hydrocarbon solvents. Alternatively, a solid pesticide could be dissolved in a specific oil to produce a concentrated solution. In some cases, the pesticide oil may be used without any extra addition of oils. In all cases, a surfactant system (usually a mixture of two or three components) is added, for a number of purposes. First, the surfactant permits self-emulsification of the oil on addition to water. This occurs by a complex mechanism that involves a number of physical changes, such as lowering of the interfacial tension at the oil/water interface or enhancement of turbulence at that interface, with the result of spontaneous production of droplets. Second, the surfactant film that adsorbs at the oil/water interface stabilizes the emulsion produced against flocculation and/or coalescence. As we will see in later chapters, emulsion breakdown must be prevented, otherwise excessive creaming or sedimentation or oil separation might take place during application. This results in an inhomogeneous application of the agrochemical on the one hand and possible losses on the other. The third role of the surfactant system in agrochemicals is in enhancement of biological efficacy. As we will see in subsequent chapters, it is essential to arrive at optimum conditions for effective use of the agrochemicals. In this case, the surfactant system will help in spreading of the pesticide on the target surface and may enhance its penetration.

In recent years, there has been a great demand to replace ECs with concentrated aqueous oil-in-water (O/W) emulsions. Several advantages may be envisaged for such replacements. First, one is able to replace the added oil with water, which is of course much cheaper and environmentally acceptable. Second, removal of the oil could help in reducing undesirable effects such as phytotoxicity and skin irritation. Third, by formulating the pesticide as an O/W emulsion one is able to control the droplet size to an optimum value which may be crucial for biological efficacy. Fourth, water-soluble surfactants, which may be desirable for biological optimization, can be added to the aqueous continuous phase. As we will see later, the choice of a surfactant or a mixed surfactant system is crucial for the preparation of a stable O/W emulsion. In recent years, macromolecular surfactants have been designed to produce very stable O/W emulsions which could be easily diluted into water and applied without any detrimental effects to the emulsion droplets.

A similar concept has been applied to replace wettable powders, namely with aqueous suspension concentrates (SCs). These systems are more familiar than ECs and they have been in use for several decades. Indeed, SCs are probably the most widely used systems in agrochemical formulations. Again, SCs are much more convenient to apply than WPs. Dust hazards are absent and the formulation can be simply diluted in the spray tanks, without the need for any vigorous agitation. As we will see later, SCs are produced by a two- or three-stage process. The pesticide powder is first dispersed in an aqueous solution of a surfactant or a macromolecule (usually referred to as the dispersing agent) using a high-speed mixer. The resulting suspension is then subjected to a wet milling process (usually bead milling) to break any remaining aggregates or agglomerates and reduce the particle size. One usually aims at a particle size distribution ranging from 0.1 to 5 μm, with an average of 1–2 μm. The surfactant or polymer added adsorbs on the particle surface, resulting in colloidal stability. The particles need to be maintained stable over a long period of time, since any strong aggregation in the system may cause various problems. First, the aggregates, being larger than the primary particles, tend to settle faster. Second, any gross aggregation may result in a lack of dispersion on dilution. The large aggregates can block the spray nozzles and may reduce biological efficacy as a result of the inhomogeneous distribution of the particles on the target surface. Apart from their role in ensuring the colloidal stability of the suspension, surfactants are added to many SCs to enhance their biological efficacy. This is usually achieved by solubilization of the insoluble compound in the surfactant micelles. This will be discussed in later chapters. Another role that a surfactant may play in SCs is in the reduction of crystal growth (Ostwald ripening). This process may occur when the solubility of the agrochemical is appreciable (say greater than 100 ppm) and when the SC is polydisperse. The smaller particles will have a higher solubility than the larger particles. With time, the small particles dissolve and become deposited on the larger particles. Surfactants may reduce this Ostwald ripening by adsorption on the crystal surfaces, thus preventing deposition of the molecules on the surface. This will be described in detail in Chapter 7 on SCs.

Recently, microemulsions have been considered as potential systems for formulating agrochemicals. Microemulsions are isotropic, thermodynamically stable systems consisting of oil, water and surfactant(s), whereby the free energy of formation of the system is zero or negative. It is obvious why such systems, if they can be formulated, are very attractive, since they will have an indefinite shelf-life (within a certain temperature range). Since the droplet size of microemulsions is very small (usually less than 50 nm), they appear transparent. As we will see in later chapters, the microemulsion droplets may be considered as swollen micelles and hence they will solubilize the agrochemical. This may result in considerable enhancement of the biological efficacy. Hence microemulsions may offer several advantages over the commonly used macroemulsions. Unfortunately, formulating the agrochemical as a microemulsion is not straightforward since one usually uses two or more surfactants, an oil and the agrochemical. These tertiary systems produce various complex phases and it is essential to investigate the phase diagram before arriving at the optimum composition of microemulsion formation. As we will see in Chapter 10 on microemulsions, a high concentration of surfactant (10–20%) is needed to produce such a formulation. This makes such systems relatively more expensive to produce compared with macroemulsions. However, the extra cost incurred could be offset by an enhancement of biological efficacy, which means that a lower agrochemical application rate could be achieved.

An important application in agrochemicals is that of controlled-release formulations. Several methods are used for controlled release, of which microcapsules are probably the most widely used. These are small particles with a size range of 1–1000 μm consisting of a core material and an outer wall. The latter isolates the core material from the environment and protects it from degradation and interaction with other materials. The core active ingredient is designed to be released in a controlled manner as required. Microencapsulation of agrochemicals is usually carried out by interfacial condensation, *in situ* polymerization or coacervation. Interfacial condensation whereby two monomers, one oil soluble (placed, say, in an emulsion droplet) and one water soluble placed in the continuous medium, undergo interfacial polycondensation, producing a capsule wall of polyurea or polyurethane. The polymer wall must have appropriate molecular weight, glass transition temperature and thickness to achieve the desirable controlled release. The polymer wall should not interact with the agrochemical. This polymer wall must not cause any environmental damage on degradation after application and hence a biodegradable polymer is preferred. The polymer wall, which must be easily manufactured, should also be stable on storage and usage. The main advantages of microcapsule formulations are controlled or slow release of the core active ingredients, thus improving residual activity, reduction of application dosage, stabilization of the core active ingredient against environmental degradation, reduction of mammalian and fish toxicity, reduction of phytotoxicity and reduction of environmental pollution.

It can be seen from the above short discussion that agrochemical formulations are complex multi-phase systems and their preparation, stabilization and subsequent application require the application of the basic principles of colloid and interface science, and this is the objective of the present book. Chapter 2 gives a brief description of surfactants and dispersants that are commonly used in agrochemical formulations. This is followed by Chapter 3 on the solution properties of surfactants, in particular describing the phenomenon of micellization, Krafft temperature and phase behavior of surfactants. Chapter 4 deals with the interfacial aspects of agrochemical formulations. In this respect, the adsorption of surfactants at the air/water interface that is essential for spray application is described, with particular reference to the dynamics of adsorption. This is then followed by a description of the adsorption isotherms at the oil/water interface. A section is devoted to the adsorption of surfactants and polymeric surfactants at the solid/liquid interface. Chapter 5 considers the interaction forces between particles or droplets in disperse systems. The main interaction forces, namely van der Waals attraction and electrostatic and steric repulsion, are described at a fundamental level. Combination of these interaction forces gives the general trends of the energy–distance curves between particles or droplets in disperse systems. These curves can describe the stability/instability of dispersions. Chapter 6 deals with liquid/liquid dispersions (emulsions) that are referred to as EWs. The various breakdown processes that occur on storage are described and the methods that can be applied to overcome them are discussed. Chapter 7 is concerned with suspension concentrates (SCs) that are used to formulate solid agrochemicals with high melting points. The problem of sedimentation and its prevention are discussed. In particular, the use of rheology modifiers for the prevention of sedimentation is described. Chapter 8 deals with oil-based suspensions, which have recently been introduced, allowing one to formulate agrochemical solids that are chemically unstable in aqueous media. In addition, such oil-based suspensions allow one to incorporate water-insoluble adjuvants, thus enhancing the biological efficacy. Chapter 9 considers suspoemulsions (mixtures of suspensions and emulsions). The various interactions that may occur between the particles and droplets are analyzed at a fundamental level. Chapter 10 describes the use of microemulsions for the formulation of agrochemicals and their main advantages. Chapter 11 gives a short summary of the potential application of multiple emulsions in agrochemical formulations. Controlled-release formulations are discussed in Chapter 12. Finally, Chapter 13 describes the basic principles for the selection of adjuvants in agrochemical formulations.

Further Reading

1 Th.F. Tadros, *Surfactants in Agrochemicals*, Marcel Dekker, New York (1994).

2 Th.F. Tadros, *Applied Surfactants*, Wiley-VCH, Weinheim (2005).