

Preparation and Characterization of Alternative Oil-in-Water Emulsion Formulation of Deltamethrin

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Authors' contributions

This work was carried out in collaboration between all authors. Author WE designed the study, provided the chemicals used in the preparation of the formulation and managed the analyses of the study. Author TGMM assisted in the design of the study, searched, reviewed literature and wrote the first draft of the manuscript. All authors read and approved the final manuscript before submission.

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ABSTRACT

The purpose of this study was to prepare a stable oil-in-water emulsion formulation of deltamethrin. Oil-in-water emulsion was prepared by using a two-step procedure. Stability studies were performed at different accelerated conditions (0°C and 54°C) to predict the stability of the formulation. Different parameters, namely, active ingredient content, mean particle size distribution, pH, viscosity, flash point, effect of centrifugation, persistent foaming and emulsion stability were determined during stability studies. The formulation exhibited good stability after preparation at different temperatures. No phase separation was observed during stability testing.

Keywords: Formulation; oil-in-water; emulsion; deltamethrin.

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1. INTRODUCTION

The importance of pesticide use in increasing agricultural production is well established, however, pesticides can cause damage to the environment and sometimes to users. Recently the pesticide industry has made a good progress in terms of development and production of low risk, environmentally friendly pesticide formulations, although pesticides are still mainly available in conventional formulations such as dust powders, wettable powders, emulsifiable concentrates, solutions, etc. Such conventional formulations could cause problems related to environmental protection, leaving residues in the ecosystem, food, final produce, etc. Hence, there is a growing demand for use of environmentally friendly water based formulations as oil-in-water emulsions, aqueous suspension concentrates, aqueous capsule suspensions and so on instead of conventional pesticide formulations. These formulations tend not only to replace toxic, non-degradable ingredients with safer ones, but also to increase the efficacy of products through proper choice and balance of all the components in the formulation [1,2].

Emulsifiable concentrates (EC) conventionally contain one or more active ingredients, one or more emulsifiers and a water-immiscible solvent. Typical solvents used in conventional EC formulations are aromatic hydrocarbons. They have very low solubility in water and a high capability of dissolving a wide range of active ingredients. However, the solvents used in the conventional EC formulations could damage the environment or may cause toxicity problems.

Oil-in-water emulsions (EW) consist of an active ingredient dissolved in a water-immiscible solvent, which is dispersed as fine oil-phase droplets in water in the presence of surfactants. However, they still contain the solvent but in smaller quantities than EC formulations. This type of formulation is important in agriculture as a mean of formulating oil based systems in a more environmentally convenient form than the conventional emulsifiable concentrate (EC). Such EW formulations tend to have lower skin and eye toxicity compared to corresponding EC products as well as higher flash point. Also, EW formulations are safer in transport and storage and they are more compatible with water based SC formulations for blends of active ingredients [3]. Finally, oil-in-water emulsions are now receiving considerable attention because water based formulations hydrate hydrophilic pesticides and prevent crystal formation which increases the pesticide uptake [4].

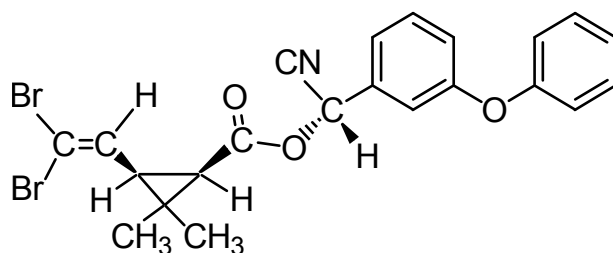
The aim of the present study was to formulate oil-in-water (EW) or (OW) emulsion of deltamethrin and check shelf life stability by measuring a number of physical parameters before and after storage tests to be sure that the formulation was stable.

2. MATERIALS AND METHODS

2.1 MATERIALS

Deltamethrin (Technical grade, Purity 98%)

Structural formula:



Empirical formula: C₂₂H₁₉Br₂NO₃

IUPAC name: (S)-α-cyano-3-phenoxybenzyl (1R,3R)-3-(2,2-dibromovinyl) 2,2-dimethylcyclopropane carboxylate was purchased from China. Non-ionic surfactant, Ethoxylated Castor oil HLB 14.9 (ALKAMULS 14/R) was kindly supplied by Rhodia-Home, Personal Care & industrial Ingredients, Milano, Italy. Propylene glycol and sodium hydroxide were purchased from ADWIC; El Nasr Pharmaceutical Chemical Co., Egypt, Cyclohexanone was purchased from Taiwan. Butylated hydroxytoluene (BHT) and Pine Oil (PO173) were purchased from China, calcium carbonate was purchased from Sigma- Aldrich Chemie GmbH Steinheim, Germany, Magnesium oxide and methyl red were purchased from Qualikems Fine Chemicals. PVT.Ltd.India. Ammonia Solution was purchased from Prolabo, while the propionic acid was purchased from Chem-Lab, Belgium. Water used in all preparations obtained from Water distiller LABCONCO water PROT.M PS LABCONCO Corporation, KANSAS City, Missouri 64132-USA.

2.2 METHODS

2.2.1 Emulsion Preparation

The oil-in-water emulsion (EW) was formed by incorporating progressively the oil phase into the water phase. First, deltamethrin technical grade (5.10 wt %) was dissolved in cyclohexanone completely, then the oil solution was mixed together with the surfactant by stirring (using a magnetic stirrer with hot plate “Terrey Pines Scientific”, USA), and then dissolving the BHT to form the oil phase. The water phase was prepared with deionized water, propionic acid, PO173 and propylene glycol. Finally, the oil phase was added into the water phase under high shear mixing using a homogenizer (X120 GmbH, Germany).

2.2.2 Characterization of oil-in-water emulsion formulation

2.2.2.1 Emulsion mean particle size distribution

The mean particle size of oil-in-water emulsions was determined by light scattering, using Zetasizer Ver.6.20 (Malvern Instruments Ltd., Worcestershire, England). Sample analysis was carried out after sample preparation and on day 7 and 14. The concentrated emulsion was diluted with deionized water (1:100) to avoid multiple scattering effects, and placed directly into a metal jar that circulated the sample through the measuring-glass cuvette.

2.2.2.2 Active Ingredient Content

The content of active ingredient in technical material and formulation was detected by Gas liquid chromatography (Unicam pro GC with FID) equipped with Electron Capture Detector (ECD) programmed for external standardization using peak area, was used. The capillary column was Capillary Column 5% polysiloxane column 0.25i, dx30m by SGE – Australia.

2.2.3 Physicochemical characterization

2.2.3.1 pH Measurement

The pH value of the prepared formulation was measured by using a pH Meter “Model: Hanna Instruments pH 211 Microprocessor and Hanna pH electrode. [5].

2.2.3.2 Viscosity Measurement

Viscosity of the prepared formulation was measured with a “Brookfield DV II+ PRO” digital Viscometer (Brookfield, USA). The temperature was kept at 25°C during the measurement using a water bath TC-502, USA and each reading was taken after equilibrating the sample. [6].

2.2.3.3 Flash point

Flash point is an important property of the formulation, because it is used in various ways to control the conditions under which substances are stored and transported especially when they can be potentially dangerous and constitute a fire hazard. Measurement of flash point of the prepared formulation was carried out by Fisher/Tag Cleveland open cup Flash Tester, USA. The sample was gently heated and a flame was passed across the center of the open cup. The flash point was recorded as the temperature of the thermometer when a flash appeared. [7].

2.2.4 Stability of emulsion

2.2.4.1 Centrifugation

The centrifugation is a relatively simple method and allows one to accumulate a large set of data for a relatively short period of time. Formulation was subjected immediately after preparation to centrifugation at speeds up to 5400 rpm for 10 minutes by using a Laboratory Centrifuge REMI Centrifuge REMI Equipment, Bombay-India- R32A. 4000002. The formulation was centrifuged at 25°C.

2.2.4.2 Formulation Stability Test

The formulation stability tests included emulsion stability and re-emulsification [8], stability at 0°C [9], accelerated storage procedure [10], and persistent foam [11]. All test methods followed the official CIPAC standard method outlined in the CIPAC handbook, Volume F (1995), Volume J (2000) and volume K (2003).

In the emulsion characteristics experiment, 5 ml of the formulation sample was separately mixed with standard water: (CIPAC A, 20 ppm hardness, pH 5.00-6.00, Ca²⁺: Mg²⁺=1:1 and

CIPAC D, 342 ppm hardness, pH 6.00-7.00, $\text{Ca}^{2+}:\text{Mg}^{2+} = 4:1$ [12] (defined in the CIPAC handbook, Volume F) in a 100 ml measuring cylinder to produce 100 ml of aqueous emulsion. The stopper was placed on the cylinder, which was subsequently turned upside down 10 times. Subsequently, the amount of free oil or cream that separated at the top or the bottom of the emulsion was observed after the emulsion was allowed to stand undisturbed for various time intervals (0.5, 2 and 24h and (24.5h: 30 min after re-emulsification).

For the stability test at low temperature (0°C), 100 ml of each sample was transferred to a glass tube. For cooling, the tube and its contents were placed in a refrigerator and remained at $0 \pm 1^{\circ}\text{C}$ for 7 days. At the end of day 7, the tube was removed from the refrigerator, and allowed to remain undisturbed at room temperature for 3 hours. The volume of any separated material at the bottom of the tube was subsequently recorded. Accelerated storage procedure was executed by placing the sample (about 50 ml) in a bottle and placing the capped bottle and its contents in an oven at $54 \pm 2^{\circ}\text{C}$ for 14 days.

Persistent foam is a measure of the amount of foam likely to be present in a spray tank or other application equipment following dilution of the product with water. Specified amount of the material is added to standard water (CIPAC water A& D) (95ml) in the measuring cylinder and made up to the mark. The cylinder was stoppered and inverted 30 times. The cylinder was left to stand undisturbed on the bench for the specified time (1 min, 5 min and 12 min). The volume of foam was recorded. [11].

3. RESULTS AND DISCUSSION

The formulations of agrochemicals cover a wide range of systems that are prepared to suit specific applications. 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. An important criterion for any agrochemical is its safety, both to the crop and to the agrochemical workers.

3.1 Active Ingredient Content

The data in Table 1 shows the active ingredient content of deltamethrin in the prepared formulation at different storage conditions as detected by GC chromatogram. The deltamethrin content in freshly prepared and accelerated storage (0°C for 7 days and 54°C for 14 days) samples were 5.00, 4.86 and 4.51 %, which was in the acceptable range of defined specification (FAO specifications and evaluations for deltamethrin [13].The chromatograms demonstrated no degradation or interface in the determination of deltamethrin, and the peak for deltamethrin was independent with excellent sharpness (Data not Shown).

Table 1. Physicochemical properties of oil-in-water emulsion formulation of deltamethrin before and after storage test

| Time | Fresh formulation | After 7 days | After 14 days |
|-----------------------------------------|--------------------------|---------------------|----------------------|
| Temperature | Room temp. | 0°C | 54°C |
| Active ingredient Content (%) | 5.00 | 4.86 | 4.51 |
| Mean Particle Size Distribution (d.n.m) | 605.8 | 595.5 | 593.2 |
| pH (1%) | 4.71 | 4.77 | 4.17 |
| Viscosity (mPas) | 2.84 | 3.10 | 3.04 |
| Flash Point | Over 70 °C | Over 70 °C | Over 70 °C |

3.2 Mean Particle Size

It is known that droplet size is one of the most important factors governing its stability in emulsions, and reduction of droplet size usually leads to formation of stable emulsions. Usually finer droplets give better long term stability in the formulation provided they can be prevented from flocculating, coalescing or growing by Ostwald ripening [14]. Also, the small droplet size may also improve overall efficacy by enhancing the speed of the formulation over the plant foliar surface. The changes in droplet size as a prediction of time become more important to the stability of the emulsion, because the o/w emulsion possess the stability against sedimentation or creaming. The value of particle size was slightly differed in storage formulation than the fresh prepared formulation.

3.3 Centrifugation Test

The centrifugation test is based on the principle of using centrifugal force to separate two or more substances of varied densities, such as two different liquids or a liquid and a solid, and is a useful tool for assessing and predicting the shelf life of emulsions [15]. No phase separation after centrifugation was seen in oil-in-water emulsion samples kept at different storage conditions. This was presumably due to the proper homogenization speed during emulsion formulation which might have prevented the breakage of the formulations during testing [16].

3.4 pH Test

The most important parts of chemical stability are performances on accelerated testing and kinetics of pH profiles [17]. The formulation exhibited acidic pH value, the pH ranged from (4.17-4.77) according to FAO Specifications [13].

The manufacturer proposed that the acceptable pH range should be 4.1 to 7.5. The Meeting questioned the suitability of a minimum pH of 4.1, because a rounded value of 4.0 or 4.5 appeared to be more appropriate. The manufacturer stated that the minimum pH of 4.1 arose from an EU registration requirement to perform a test for acidity if the pH range extended to ≤ 4 . The Meeting considered this to be a regulatory issue, not directly related to the quality of the product and the stability of deltamethrin to hydrolysis and epimerization under acidic conditions acceptable. FAO Specifications [18].

Hydrolysis half life time of deltamethrin stable at pH 5 and 7 at 25°C, but at pH 8 and pH 9 at 25°C the half life time of deltamethrin was 31 and 2.5 days, respectively [19].

3.5 Flash Point

The flash point is a measure of the tendency of a sample to form flammable mixtures with air in controlled laboratory conditions and is parameter for storage and handling consideration of flammable materials [20]. The liquid formulations must obtained in this study, was much higher than the prescribed minimum limit of 24.5°C [21] and WHO specification, According to WHO specifications, the liquid formulations must have a flash point not less than 22.8°C. The prepared formulations had high flash point (more than 70°C) make it safer to transport and handle.

3.6 Viscosity

The viscosity of a fluid is the property that determines the resistance offered to a shearing force under laminar flow conditions, e.g. resistance to slow stirring, or to flow through a capillary or narrow channel [22].

The formulation displayed low viscosity value of 2.84-3.10 mPas at 214 s⁻¹ shear rate.

3.7 Stability of Formulated Emulsion

“Oil in water” (O/W) or “water in oil” (W/O) emulsions, are thermodynamically unstable, usually splitting into two distinct phases. This instability could be manifested at different time rates and through a variety of physicochemical destabilizing processes, for example, creaming (or sedimentation), flocculation, coalescence, or phase inversion [23].

The results are presented in Table 2 controlling the stability and aging of an emulsion is important because of application perspectives. The stability of a product at low and high temperatures is one of the technical indices of product quality. The major factors affecting the stability of formulation are concentration and the hydrophilic-lipophilic balance of added surfactants (HLB). The stability of oil-in-water emulsions can be predicted by measuring some physical parameters before and after accelerated tests. Storage at 0°C and 54°C has been used to control physical and chemical stability. It has been generally accepted that two weeks at 54°C represent 2 years in normal conditions. There is no evidence to indicate that a product has a satisfactory shelf life (of at least 2 years) in different temperature zones. The test thus provides a useful guide for performance after storage in warm or continental temperature climates. However, it is not quite sure that the product which passes these tests will be satisfactory in field conditions. Also, the stabilities of the product on initial emulsification and re-emulsification were good.

Table 2. Emulsion characteristics of oi-in-water emulsion formulation of eltamethrin before and after storage test at different time intervals

| Time | | Fresh formulation | After 7 days | After 14 days |
|-----------------------|--------|-------------------|--------------|---------------|
| Temperature | | Room temp. | 0°C | 54°C |
| Stability of Emulsion | 0.5h | nil | nil | nil |
| | 2h | nil | nil | nil |
| | 24h | nil | nil | nil |
| | 24.5 h | nil | nil | nil |

nil: no creamy or oily layer was observed.

24.5 h: 30 minutes after reemulsification

The experimental results demonstrated that the prepared formulation was physically and chemically stable. The formulation produced a white emulsion and showed no change in color or appearance through the storage period. (7 days at 0°C ± 2 and 14 days at 54 ± 2°C). Such signs are good preliminary indicators of physical stability.

3.8 Persistent Foam

Persistent foam is a measure of the amount of foam likely to be present in a spray tank or other application equipment following dilution of the product with water.

Results are given in Table 3. The volume of foam from the samples in CIPAC water A and D is low and passed through the recommended rat of foam.

Table 3. Volume of foam Persistence (ml) observed in oi-in-water emulsion formulation of deltamethrin before and after storage test in CIPAC Water A and D

| Sample code | CIPAC water A | | | CIPAC water D | | |
|------------------------------------|---------------|-------|--------|---------------|-------|--------|
| | 1 min | 5 min | 12 min | 1 min | 5 min | 12 min |
| Fresh formulation room temperature | 6 | 4 | 3 | 7 | 5 | 4 |
| After 7 days 0°C | 7 | 5 | 4 | 7 | 5 | 5 |
| After 14 days 54°C | 7 | 5 | 4 | 7 | 5 | 5 |

4. CONCLUSION

From the above mentioned data, characterization of the emulsion for its active ingredient content, mean particle size distribution, pH, viscosity, flash point, effect of centrifugation and emulsion stability were determined during storage studies. It was noted that deltamethrin could be successfully formulated in the form of a stable oil-in-water emulsion. Further studies could be performed to evaluate the pesticidal activity of the prepared formulation and also to find a more stable emulsion with other emulsifying agents.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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