

Preparation and Characterization of O/W Emulsion Formulation of Deltamethrin

Abstract

The purpose of this study was to prepare a stable o/w emulsion formulation of deltamethrin. O/w emulsion was prepared 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 pint, effect of centrifugation, persistent foam 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.

Key words

Formulation, O/w, emulsion, deltamethrin.

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 (Knowles, 2008 and Gašić et al., 2012).

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 (Mulquen, 2003). 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 (Hess and Foy, 2000).

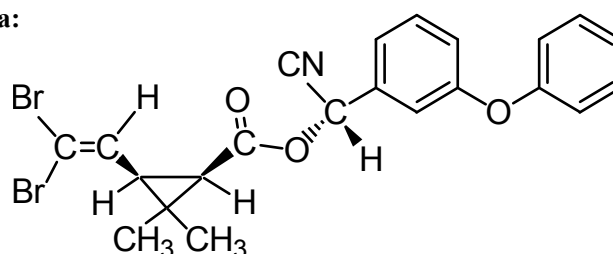
The aim of the present study was to formulate oil-in-water (EW) emulsion of deltamethrin and check shelf life stability by measuring a number of physical parameters before and after storage tests to be sure that the formulation was stable.

2. Materials and methods.

2.1. Materials

Deltamethrin (technical grade, Purity 98 %)

Structural formula:



Empirical formula: $C_{22}H_{19}Br_2NO_3$

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, calcium, sodium hydroxide and hydrochloric acid were purchased

from ADWIC, Egypt. Cyclohexanone was purchased from Taiwan. Butylated hydroxytoluene (BHT) and **Pine Oil** (PO173) were purchased from China, while the propionic acid was purchased from Chem-Lab, Belgium, Magnesium oxide and Methyl red were purchased from Qualikems fine chemicals Pvt.Ltd. New Delhi, Ammonia solution was purchased from Prolabo. Water used in all preparations obtained from Water distiller LABCONCO water PRO^{T.M} PS LABCONCO Corporation, KANSAS City, Missouri 64132-USA. All reagents used were of analytical grade.

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 finally 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-water emulsion.

2.2.2.1. Emulsion particle size distribution.

The mean particle size of oil-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. [MT 75.3].

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. [ASTM, 2005].

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. [MT 12].

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 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 [MT 36.1], stability at 0°C [MT39.3], accelerated storage procedure [MT46.3], and persistent foaming [MT47.2]. All test methods followed the official CIPAC standard method outlined in the CIPAC handbook, Volume F (1995) and Volume J (2000).

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,

$\text{Ca}^{2+} : \text{Mg}^{2+} = 1:1$ and CIPAC D, 342 ppm hardness, pH 6.00-7.00, $\text{Ca}^{2+} : \text{Mg}^{2+} = 4:1$) MT 18 (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 24 h 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 Handbook, Volumes 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. [MT 47.2].

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.

Data in Table (1) demonstrated that the active ingredient content of deltamethrin in the prepared formulation at different storage conditions 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, 4.86 and 4.51 %, which was in the acceptable range of defined specification (FAO specifications and evaluations for deltamethrin, 2006). 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).

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 (Knowles, 2005). 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.

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 (Khan et al., 2010). No phase separation after centrifugation was seen in oil-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 (Abdurahman and Rosli, 2006).

The formulation exhibited acidic pH value, the pH ranged from (4.17-4.77) according to FAO Specifications (2006).

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) and are quite safe. The formulation displayed low viscosity value of 2.84-3.10 mPas at 214 s⁻¹ shear rate.

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 are 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 stability of the product on initial emulsification and re-emulsification were good.

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 $\pm$ 2 and 14 days at 54 $\pm$ 2°C). Such signs are good preliminary indicators of physical stability.

Results are given in table (3). The prepared formulation passed the recommended rat of foam.

4. Conclusion

From the above mentioned data, characterization of the emulsion for its active ingredient content, mean particle size distribution, pH, viscosity, flash pint, 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.

Table1. Physicochemical properties of o/w 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	4.86	4.51
Ave rage Particle Size Distribution (d.nm)	605.8	595.5	593.2
pH (1%)	4.71	4.77	4.17
Viscosity at Shear rate of 214 S-1 (mPas)	2.84	3.10	3.04
Flash Point	Over 70 °C	Over 70 °C	Over 70 °C

Table2. Emulsion stability of o/w emulsion formulation of deltamethrin before and after storage test.

Time		Fresh Formulation	After 7 days	After 14 days
Temperature		room temperature	0°C	54°C
Stability of Emulsion	0.5h	0/0	0/0	0/0
	2h	0/0	0/0	0/0
	24h	0/0	0/0	0/0
Reemulsification	REE	0/0	0/0	0/0

Table 3. Persistent Foam (ml) o/w emulsion formulation of deltamethrin before and after storage test.

Sample Code	CIPAC Water A			CIPAC Water D		
	1 min	5 min	12 min	1 min	5 min	12 min
Fresh formulation At 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

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