

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

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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.

Key words

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

43 pesticides are still mainly available in conventional formulations
44 such as dust powders, wettable powders, emulsifiable
45 concentrates, solutions, etc. Such conventional formulations
46 could cause problems related to environmental protection,
47 leaving residues in the ecosystem, food, final produce, etc.
48 Hence, there is a growing demand for use of environmentally
49 friendly water based formulations as oil-in-water emulsions,
50 aqueous suspension concentrates, aqueous capsule
51 suspensions and so on instead of conventional pesticide
52 formulations. These formulations tend not only to replace toxic,
53 non-degradable ingredients with safer ones, but also to
54 increase the efficacy of products through proper choice and
55 balance of all the components in the formulation (Knowles,
56 2008 and Gašić et al., 2012).

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

65 Oil-in-water emulsions (EW) consist of an active ingredient
66 dissolved in a water-immiscible solvent, which is dispersed as
67 fine oil-phase droplets in water in the presence of surfactants.
68 However, they still contain the solvent but in smaller quantities
69 than EC formulations. This type of formulation is important in
70 agriculture as a mean of formulating oil based systems in a
71 more environmentally convenient form than the conventional
72 emulsifiable concentrate (EC). Such EW formulations tend to
73 have lower skin and eye toxicity compared to corresponding
74 EC products as well as higher flash point. Also, EW
75 formulations are safer in transport and storage and they are
76 more compatible with water based SC formulations for blends
77 of active ingredients (Mulquen, 2003). Finally, oil-in-water
78 emulsions are now receiving considerable attention because
79 water based formulations hydrate hydrophilic pesticides and
80 prevent crystal formation which increases the pesticide uptake
81 (Hess and Foy, 2000).

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

87

88 2. MATERIALS AND METHODS

89 2.1 MATERIALS

90 Deltamethrin (technical grade, Purity 98 %)

91 Structural formula:

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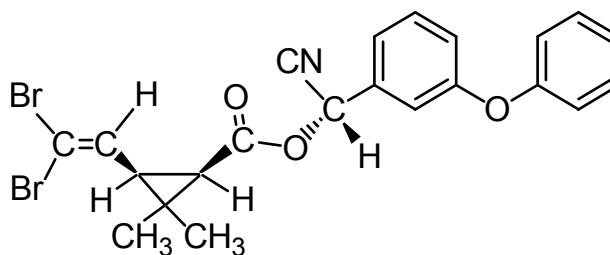
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99 Empirical formula: C₂₂H₁₉Br₂NO₃

100 IUPAC name:

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

118 2.2 METHODS

119 2.2.1 Emulsion Preparation

120 The oil-in-water emulsion (EW) was formed by
121 incorporating progressively the oil phase into the water phase.

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

131 **2.2.2 Characterization of oil-in-water emulsion** 132 **formulation.**

133 **2.2.2.1 Emulsion mean particle size distribution**

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

142 **2.2.2.2 Active Ingredient Content**

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

150 **2.2.3 Physicochemical characterization**

151 **2.2.3.1 pH Measurement**

152 The pH value of the prepared formulation was measured by
153 using a pH Meter “Model: Hanna Instruments pH 211
154 Microprocessor and Hanna pH electrode. [MT 75.3].

155 **2.2.3.2 Viscosity Measurement**

156 Viscosity of the prepared formulation was measured with a
157 “Brookfield DV II+ PRO” digital Viscometer (Brookfield, USA).
158 The temperature was kept at 25°C during the measurement
159 using a water bath TC-502, USA and each reading was taken
160 after equilibrating the sample. [ASTM, 2005].

161

162

163 **2.2.3.3 Flash point**

164 Flash point is an important property of the formulation,
165 because it is used in various ways to control the conditions
166 under which substances are stored and transported especially
167 when they can be potentially dangerous and constitute a fire
168 hazard. Measurement of flash point of the prepared formulation
169 was carried out by Fisher/Tag Cleveland open cup Flash
170 Tester, USA. The sample was gently heated and a flame was
171 passed across the center of the open cup. The flash point was
172 recorded as the temperature of the thermometer when a flash
173 appeared. [MT 12].

174 **2.2.4 Stability of emulsion.**

175 **2.2.4.1 Centrifugation.**

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

182 **2.2.4.2 Formulation Stability Test.**

183 The formulation stability tests included emulsion stability
184 and re-emulsification [MT 36.3], stability at 0°C [MT39.3],
185 accelerated storage procedure [MT46.3], and persistent foam
186 [MT47.2]. All test methods followed the official CIPAC standard
187 method outlined in the CIPAC handbook, Volume F (1995),
188 Volume J (2000) and volume K (2003).

189 In the emulsion characteristics experiment, 5 ml of the
190 formulation sample was separately mixed with standard water:
191 (CIPAC A, 20 ppm hardness, pH 5.00-6.00, Ca²⁺: Mg²⁺ = 1:1
192 and CIPAC D, 342 ppm hardness, pH 6.00-7.00, Ca²⁺: Mg²⁺ =
193 4:1) MT 18 (defined in the CIPAC handbook, Volume F) in a
194 100 ml measuring cylinder to produce 100 ml of aqueous
195 emulsion. The stopper was placed on the cylinder, which was
196 subsequently turned upside down 10 times. Subsequently, the
197 amount of free oil or cream that separated at the top or the
198 bottom of the emulsion was observed after the emulsion was
199 allowed to stand undisturbed for various time intervals (0.5, 2

200 and 24 h and (24.5h: 30 min after re-emulsification).

201 For the stability test at low temperature (0°C), 100 ml of
202 each sample was transferred to a glass tube. For cooling, the
203 tube and its contents were placed in a refrigerator and
204 remained at $0 \pm 1^\circ\text{C}$ for 7 days. At the end of day 7, the tube
205 was removed from the refrigerator, and allowed to remain
206 undisturbed at room temperature for 3 hours. The volume of
207 any separated material at the bottom of the tube was
208 subsequently recorded. Accelerated storage procedure was
209 executed by placing the sample (about 50 ml) in a bottle and
210 placing the capped bottle and its contents in an oven at $54 \pm$
211 2°C for 14 days.

212 Persistent foam is a measure of the amount of foam likely
213 to be present in a spray tank or other application equipment
214 following dilution of the product with water. Specified amount of
215 the material is added to standard water (CIPAC water A& D)
216 (95ml) in the measuring cylinder and made up to the mark. The
217 cylinder was stoppered and inverted 30 times. The cylinder
218 was left to stand undisturbed on the bench for the specified
219 time (1 min, 5 min and 12 min). The volume of foam was
220 recorded. [MT 47.2].

221 **3. RESULTS AND DISCUSSION.**

222 The formulations of agrochemicals cover a wide range of
223 systems that are prepared to suit specific applications. The
224 main purpose of any agrochemical formulation is to make
225 handling and application of the active ingredient as easy as
226 possible. An important function of the formulation is to optimize
227 the biological efficacy. This is achieved in most cases by
228 controlling the physical characteristics of the formulation. An
229 important criterion for any agrochemical is its safety, both to the
230 crop and to the agrochemical workers.

231 **Active Ingredient Content**

232 Data in Table (1) demonstrated that the active ingredient
233 content of deltamethrin in the prepared formulation at different
234 storage conditions by GC chromatogram. The deltamethrin
235 content in freshly prepared and accelerated storage (0°C for 7
236 days and 54°C for 14 days) samples were 5.00, 4.86 and 4.51
237 %, which was in the acceptable range of defined specification
238 (FAO specifications and evaluations for deltamethrin, 2006).
239 The chromatograms demonstrated no degradation or interface

240 in the determination of deltamethrin, and the peak for
241 deltamethrin was independent with excellent sharpness (Data
242 not Shown).

243 **Mean Particle Size.**

244 It is known that droplet size is one of the most important
245 factors governing its stability in emulsions, and reduction of
246 droplet size usually leads to formation of stable emulsions.
247 Usually finer droplets give better long term stability in the
248 formulation provided they can be prevented from flocculating,
249 coalescing or growing by Ostwald ripening (Knowles, 2005).
250 Also, the small droplet size may also improve overall efficacy
251 by enhancing the speed of the formulation over the plant foliar
252 surface. The changes in droplet size as a prediction of time
253 become more important to the stability of the emulsion,
254 because the o/w emulsion possess the stability against
255 sedimentation or creaming. The value of particle size was
256 slightly differed in storage formulation than the fresh prepared
257 formulation.

258

259 **Centrifugation test**

260 The centrifugation test is based on the principle of using
261 centrifugal force to separate two or more substances of varied
262 densities, such as two different liquids or a liquid and a solid,
263 and is a useful tool for assessing and predicting the shelf life of
264 emulsions (Khan et al., 2010). No phase separation after
265 centrifugation was seen in oil-in-water emulsion samples kept
266 at different storage conditions. This was presumably due to the
267 proper homogenization speed during emulsion formulation
268 which might have prevented the breakage of the formulations
269 during testing (Abdurahman and Rosli, 2006).

270 **pH test**

271 The most important parts of chemical stability are
272 performances on accelerated testing and kinetics of pH profiles
273 (Issa et al., 2000). The formulation exhibited acidic pH value,
274 the pH ranged from (4.17-4.77) according to FAO
275 Specifications (2006).

276 The manufacturer proposed that the acceptable pH range
277 should be 4.1 to 7.5. The Meeting questioned the suitability of
278 a minimum pH of 4.1, because a rounded value of 4.0 or 4.5
279 appeared to be more appropriate. The manufacturer stated

280 that the minimum pH of 4.1 arose from an EU registration
281 requirement to perform a test for acidity if the pH range
282 extended to ≤ 4 . The Meeting considered this to be a regulatory
283 issue, not directly related to the quality of the product and the
284 stability of deltamethrin to hydrolysis and epimerization under
285 acidic conditions acceptable. FAO Specifications (2012).

286 Hydrolysis half life time of deltamethrin stable at pH 5 and 7
287 at 25°C, but at pH 8 and pH 9 at 25°C the half life time of
288 deltamethrin was 31 and 2.5 days, respectively. (RIVM Letter
289 report, 2008).

290 **Flash Point**

291 The flash point is a measure of the tendency of a sample
292 to form flammable mixtures with air in controlled laboratory
293 conditions and is parameter for storage and handling
294 consideration of flammable materials (Encinar et al., 2005).
295 The liquid formulations must obtained in this study, was much
296 higher than the prescribed minimum limit of 24.5°C (Kumar and
297 Parmar, 2000) and WHO specification, According to WHO
298 specifications, the liquid formulations must have a flash point
299 not less than 22.8°C. The prepared formulations had high flash
300 point (more than 70°C) make it safer to transport and handle.

301 **Viscosity**

302 The viscosity of a fluid is the property that determines the
303 resistance offered to a shearing force under laminar flow
304 conditions, e.g. resistance to slow stirring, or to flow through a
305 capillary or narrow channel. (APVMA, 2005)

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

308 **Stability of formulated emulsion**

309
310 "Oil in water" (O/W) or "water in oil" (W/O) emulsions, are
311 thermodynamically unstable, usually splitting into two distinct
312 phases. This instability could be manifested at different time
313 rates and through a variety of physicochemical destabilizing
314 processes, for example, creaming (or sedimentation),
315 flocculation, coalescence, or phase inversion (Masmoudi et al.,
316 2005).

317 The results are presented in Table (2) controlling the
318 stability and aging of an emulsion is important because of
319 application perspectives. The stability of a product at low and

320 high temperatures are one of the technical indices of product
321 quality. The major factors affecting the stability of formulation
322 are concentration and the hydrophilic-lipophilic balance of
323 added surfactants (HLB). The stability of oil-in-water emulsions
324 can be predicted by measuring some physical parameters
325 before and after accelerated tests. Storage at 0°C and 54°C
326 has been used to control physical and chemical stability. It has
327 been generally accepted that two weeks at 54°C represent 2
328 years in normal conditions. There is no evidence to indicate
329 that a product has a satisfactory shelf life (of at least 2 years) in
330 different temperature zones. The test thus provides a useful
331 guide for performance after storage in warm or continental
332 temperature climates. However, it is not quite sure that the
333 product which passes these tests will be satisfactory in field
334 conditions. Also, the stabilities of the product on initial
335 emulsification and re-emulsification were good.

336 The experimental results demonstrated that the prepared
337 formulation was physically and chemically stable. The
338 formulation produced a white emulsion and showed no change
339 in color or appearance through the storage period. (7 days at
340 0°C ± 2 and 14 days at 54 ± 2°C). Such signs are good
341 preliminary indicators of physical stability.

342 **Persistent Foam**

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

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

349

350

351 **Table 1** here

352

353 **Table 2** here

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355 **Table 3** here

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359 **4. Conclusion**

360 From the above mentioned data, characterization of the
361 emulsion for its active ingredient content, mean particle size

362 distribution, pH, viscosity, flash point, effect of centrifugation
363 and emulsion stability were determined during storage studies.
364 It was noted that deltamethrin could be successfully formulated
365 in the form of a stable oil-in-water emulsion. Further studies
366 could be performed to evaluate the pesticidal activity of the
367 prepared formulation and also to find a more stable emulsion
368 with other emulsifying agents.

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