Assessment of methyl ester as a green carrier solvent in pesticide emulsifiable concentrate formulation

Nguyen Hoc Tran 1,2,3, Thai Van Trung Hieu 3, Trung Dang-Bao 1,2, Tran Thi Kieu Anh 1,2,*

1Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet Street, District 10, Ho Chi Minh City, Vietnam
2Vietnam National University Ho Chi Minh City, Linh Trung Ward, Thu Duc District, Ho Chi Minh City, Vietnam
3Science Laboratory of Amigos Manufacturing Trading Company Limited, Building A59/I, Vinh Loc Industrial Park, Street No. 7, Binh Hung Hoa B Ward, Binh Tan District, Ho Chi Minh City, Vietnam

Corresponding author’s e-mail: ttkanh@hcmut.edu.vn

Abstract. The conventional pesticide emulsifiable concentrate (EC) formulations usually contain a large amount of aromatic solvents. This causes adverse effects to environment and human health due to the toxicity of such organic solvents. In this study, a cypermethrine 25EC formulation was developed using methyl ester as a green solvent. The physicochemical characterizations, emulsion properties and storage stabilities of the methyl ester EC formulations were investigated and compared with those of the EC formulation using naphtha A100 as a solvent, evidencing excellent emulsion properties and storage stabilities of such methyl ester EC formulations.

1. Introduction

Pesticides are widely used in agricultural areas to increase the yield and quality of crops. In Vietnam, many companies produce pesticide products and the emulsifiable concentrate (EC) formulations of pesticides are the most manufactured because of their simple compositions, easy-handling and good stability. Pesticide EC formulations usually contain active ingredients (pesticides), carrier solvents and adjuvants (surfactants). Surfactants are designed to perform specific functions including buffering, dispersing, emulsifying, spreading, sticking, and wetting properties [1]. In the field, pesticide products (EC formulations) are mixed with water and directly used.

Conventional EC formulations use a large amount of aromatic solvents, which are hazardous to human health. Nowadays, many studies have attempted to develop EC formulations using green carrier solvents such as vegetable oils, animal fats or biodiesels [2–4]. However, these solvents are highly viscous or may be in the solid state at low temperatures. Therefore, it is necessary to explore environmentally friendly alternatives.

Methyl ester or glycol diacetate (colorless and transparent organic solvents with low toxicity) have been increasingly used as green carrier solvents in EC formulations [2]. Study on surfactants (adjuvants) and formulation technology of agrochemical products has recently advanced and resulted in many surfactants and pesticide products in the worldwide market [2, 5]. Choosing the best
surfactant among thousands of surfactants and replacing conventional solvents by using green solvents for the EC formulations are usually challenging.

Pesticides are usually classified into four main groups (organochlorines, organophosphorus, carbamates and pyrethrins). Cypermethrin, a synthetic pyrethroid, is the most widely used pesticide to control various pests of cotton, fruits and vegetable crops. Cypermethrin is easy to dissolve in organic solvents and EC is the main formulation of this pesticide in the market [6].

The objectives of the present study were to evaluate the possibility of replacing aromatic solvents with methyl ester and develop an emulsion system consisting of non-ionic surfactants as an effective emulsifier for some emulsion concentrated pesticides. Cypermethrin, which is widely used in Vietnam for protecting many kinds of crops, was selected as the active ingredient.

2. Materials and methods

2.1. Chemicals and reagents

Active ingredient: Cypermethrin (technical standard, 97% purity) was purchased from Bio Vina Trading Production JSC (Vietnam).

Solvents: D100 (technical standard) was obtained from Amigos Co., Ltd., (Vietnam), and methyl ester was purchased from Wilmar Company (Indonesia).

Surfactants: Studied surfactants are presented in Table 1.

| No. | Surfactant                                    | Abbreviation | Supplier                                | HLB value |
|-----|-----------------------------------------------|--------------|-----------------------------------------|-----------|
| 1   | Aplumul L (anionic non-ionic complex)          | Apl          | Beta Chemical Ltd (Haidian, Beijing, China) | -         |
| 2   | Meranol 775 (cationic surfactant complex)      | 775          | Amigos Co., Ltd (Vietnam)               | 9.0       |
| 3   | Meranol 775 IB (cationic surfactant complex)   | 775IB        | Amigos Co., Ltd (Vietnam)               | 5.3       |
| 4   | TSP 16 (tristyrylphenol ethoxylates)           | TSP 16       | Taiwan surfactant (Taoyuan country, Taiwan) | 13        |
| 5   | TSP 22 (tristyrylphenol ethoxylates)           | TSP 22       | Taiwan surfactant (Taoyuan country, Taiwan) | 14.4      |
| 6   | DB70 (calcium dodecyl benzene sulfonate)       | DB70         | Amigos Co., Ltd (Vietnam)               | 8.6       |
| 7   | Tenomul® AGP – L (cationic non-ionic complex)  | Teno         | Amigos Co., Ltd (Vietnam)               | 7.2       |

HLB refers to the hydrophilic-lipophilic balance of surfactant [7].

2.2. Preparation of cypermethrin EC formulations

Cypermethrin 10% EC (Cyper10EC sample): cypermethrin (10.31 g) was completely dissolved in 84.69 g studied solvents. Subsequently, the studied surfactants (5.0 g) (Table 2 and Table 3) were added and continuously stirred to obtain a homogeneous solution. Finally, the resulting samples were stored in a sealed state for further experiments.

Cypermethrin 25% EC (Cyper25EC sample): cypermethrin (25.77 g) was completely dissolved in 69.23 g studied solvents. Subsequently, the studied surfactants (5.0 g) (Table 4) were added and continuously stirred to obtain a homogeneous solution. Finally, the resulting samples were stored in a sealed state for further experiments.
2.3. The emulsion stability tests
The emulsion stability tests were conducted according to the official CIPAC standard method (CIPAC MT36, 1995) [8]. In brief, 5 mL of the EC samples (Cyper10EC or Cyper25EC) were diluted in 95 mL of deionized water in a 100-mL measuring cylinder. Firstly, the cylinder covered by a stopper was turned upside down ten times, and then the cylinder was allowed to stand undisturbed. The amounts of free oil or cream separated from the top or the bottom of the emulsion were recorded at various intervals (0.5, 2 or 24 h) (Figure 1). The results at 24 h were required only when the results at 2 h were in doubt.

![Figure 1. The emulsion stability at various intervals.](image)

2.4. Replacement of D100 solvent with methyl ester on 10% Cypermethrin EC formulation
The stability of Cyper10EC samples using a mixture of D100 and methyl ester with different ratios as solvents, Apl and Teno as surfactants (Table 2) was examined after 0.5 h fabrication.

2.5. Effect of two surfactants on 10% Cypermethrine EC formulation with 25% methyl ester replacement
The stability of Cyper10EC samples using a mixture of D100 and methyl ester (3:1, w/w) (25% replacement) as the solvent, Apl and Teno as surfactants 1 (Surf 1) and other surfactants (Surf 2) (Table 3) with their different ratios was examined after 0.5 h fabrication.

2.6. Effect of developed surfactants on 10% and 25% Cypermethrin EC formulations with 100 % methyl ester replacement
The stability of Cyper10EC or Cyper25EC samples using methyl ester (100% replacement) as the solvent, Apl and Teno as Surf 1 and 775IB as Surf 2 with their different ratios (Table 4 and Table 5) was examined after 0.5, 2 and 24 h fabrication. Diameter of micelle was measured using a microscope (Microscope, model BB.1153-PL, EUROMEX, Netherlands).

3. Results and Discussion

3.1. Replacement of D100 solvent with methyl ester on 10% Cypermethrin EC formulation
Surfactants play an important role in EC formulations. As shown in Table 2, Apl or Teno was only comparative with conventional D100 solvent, resulting in the homogeneous solutions. In contrast, the samples with methyl ester replacement were separated after 0.5 h mixing (≥ 4 mL oil separated). According to CIPAC standard method, the separated volume must smaller than 2 mL. We then attempted to fabricate EC formulation using a combination of two surfactants to compare with methyl ester replacement.
Table 2. The stability of 10% Cypermethrin EC formulation using D100 and methyl ester as solvents and Apl or Teno as a single surfactant.

| Cyper10 EC | Solvent | Methyl ester (%) | Surfactant (%) | Stability post ½ hr. of mixing |
|------------|---------|------------------|---------------|------------------------------|
| Apl        | 100     | 0                | 5.0           | No creamy or sedimentation   |
| Apl        | 90      | 10               | 5.0           | 2.0 mL oil separation        |
| Apl        | 80      | 20               | 5.0           | 3.0 mL oil separation        |
| Apl        | 75      | 25               | 5.0           | 4.0 mL oil separation        |
| Apl        | 50      | 50               | 5.0           | 5.0 mL oil separation        |
| Teno       | 100     | 0                | 5.0           | No creamy or sedimentation   |

Table 3. The stability of 10% Cypermethrine EC formulations using two surfactants with 25% methyl ester replacement.

| Cyper10 EC | Surf ratio (w/w) (Σsurf = 5%) (a) | Methyl ester in solvent (%) (b) | Stability post ½ hr. of mixing |
|------------|-----------------------------------|---------------------------------|-------------------------------|
| Apl        | TSP 16                            | 25                              | separation                    |
| Apl        | 775                               | 25                              | separation                    |
| Apl        | TSP 22                            | 25                              | separation                    |
| Apl        | 775IB                             | 25                              | 1.5 mL creamy separation      |
| Teno       | 775IB                             | 25                              | 1.0 mL creamy separation      |

(a) Surf ratio = Surf 1 / Surf 2, ΣSurf = Surf 1 + Surf 2.
At any surfactant ratios, the EC formulations were always separated after 0.5 h fabrication.
(b) Methyl ester = 100 – %D100.

3.2. Effect of two surfactants on 10% Cypermethrin EC formulation with 25% methyl ester replacement
Combinations of two surfactants may change HLB values and resulted in the comparative of EC formulations. The first attempt was to examine the stability of 10% cypermethrin EC formulations with 25% methyl ester replacement using Apl or Teno as surfactant 1 (Surf 1) in combination with a surfactant 2 (Surf 2) (Table 3). Apl or Teno combined with 775IB showed good comparative properties of EC formulations (creamy separation < 2 mL). Surfactant 775IB was chosen as Surf 2 for further studies.

3.3. Effect of developed surfactants on 10% Cypermethrin EC formulation with 100% methyl ester replacement
Different ratios of surfactant 1 (Apl or Teno) and surfactant 2 (775IB) were studied to examine the comparative properties of 10% cypermethrin EC formulations with different methyl ester solvent (25, 50 and 100%) replacements. In general, the combination of two surfactants (Apl or Teno with 775IB at different ratios) showed good comparative properties and can be used for fabrication of cypermethrin EC formulations (Table 4).
Table 4. The stability of 10% Cypermethrin EC formulation with different methyl ester replacements in combination with different studied surfactants.

| Cyper10EC | Surf 1 | Surf 2 | Surf ratio(a) | Diameter of micelles (μm) | Stability post ½ hr. of mixing(c) | Stability post 2 hr. of mixing(d) | Stability post 24 hr. of mixing(d) |
|-----------|--------|--------|---------------|----------------------------|----------------------------------|----------------------------------|----------------------------------|
| Methyl ester (%) | Apl | 775IB | 20 | 2–8 | 1 | 1 | 1.5 |
| 25 | Apl | 775IB | 10 | 1–4 | 0 | 0 | 0.5 |
| 50 | Apl | 775IB | ∞ | 5–12 | 6 | 10 | n.d. |
| 50 | Apl | 775IB | 7 | 1–4 | 0 | 0 | 0 |
| 50 | Teno | 775IB | ∞ | n.d. | 4 | n.d. | n.d. |
| 50 | Teno | 775IB | 9 | 5–15 | 4 | n.d. | n.d. |
| 50 | Teno | 775IB | 4,5 | 1–4 | 0 | 0 | 2 |
| 50 | Teno | 775IB | 4 | 1–2 | 0 | 1 | n.d. |
| 50 | Teno | 775IB | 2,6 | 1–2 | 0 | 0 | 0 |
| 100 | Apl | 775IB | 4 | 1–3 | 0 | 1 | n.d. |
| 100 | Teno | 775IB | 3 | 1–3 | 0 | 0.5 | n.d. |

(a) %Methyl ester = 100 – %D100.
(b) Surf ratio = mass of Surf 1 / mass of Surf 2; total surfactant (5%) = Surf 1 + surf 2.
(c) Test after 0.5 h fabrication (volume of separated creamy, mL).
(d) Un-required test if test (c) in doubt (volume of separated creamy, mL).

n.d. = not determined.

3.4. Effect of developed surfactants on 25% Cypermethrin EC formulation with 100% methyl ester replacement

The final attempt of this study was to replace conventional D100 solvent by methyl ester in cypermethrin EC formulations. The high active ingredient (25% cypermethrin) in EC formulations using 100% methyl ester as the solvent with the two investigated surfactants was studied. The combination of two surfactants Apl or Teno (Surf 1) and 775IB (Surf 2) at the different ratios (2.3, 4 for Apl/775IB and 1.5, 2.3 and 3 for Teno/775IB) showed good comparative properties of studied EC formulations (Table 5).

Table 5. The stability of 25% Cypermethrin EC formulations using 100% methyl ester as solvent in combination with two developed surfactants.

| Cyper25EC | Surf 1 | Surf 2 | Surf ratio(b) | Diameter of micelles (μm) | Stability post ½ hr. of mixing(c) | Stability post 2 hr. of mixing(d) | Stability post 24 hr. of mixing(d) |
|-----------|--------|--------|---------------|----------------------------|----------------------------------|----------------------------------|----------------------------------|
| Methyl ester (%) | Apl | 775IB | 1.5 | n.d. | 4 | n.d. | n.d. |
| 100 | Apl | 775IB | 2.3 | 1–3 | 0 | 0.5 | 2 |
| 100 | Apl | 775IB | 4 | 1–2 | 0 | 0.5 | 1.5 |
| 100 | Apl | 775IB | 9 | 3–15 | 4 | n.d. | n.d. |
| 100 | Teno | 775IB | 1.5 | 1–2 | 0 | 0 | 10 |
| 100 | Teno | 775IB | 2.3 | 1–3 | 0 | 0 | 1 |
| 100 | Teno | 775IB | 3 | 2–4 | 1 | 3.5 | 5 |
| 100 | Teno | 775IB | 4 | 1–4 | 0.5 | 2 | 3.5 |

(a) Total surfactant, Σsurf = %Surf 1 + %Surf 2.
(b) Surf ratio = mass of Surf 1 / mass of Surf 2.
(c) Test after 0.5 h fabrication (volume of separated creamy, mL).
(d) Un-required test if test (c) in doubt (volume of separated creamy, mL).
  n.d. = not determined.

4. Conclusions
Carrier solvents play an important role in EC formulations, in which a large amount of hazardous aromatic solvents have been found in mostly conventional EC formulations. In this study, with the use of mixtures of two non-ionic surfactants, environmentally friendly Cypermethrin EC formulations were prepared using methyl ester as a green solvent, achieving excellent emulsion stability. The storage stability, wettability, spreading and adhesion abilities to ensure higher utilization of pesticides are underway.

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