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Formula Optimization Design of Pesticide Microemulsion

Zhao Feng and Wu Yaqian
Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science & Technology Normal University Nanchang
China

1. Introduction

Water-based pesticide microemulsions have become one of the most potential pesticide formulation instead of the conventional pesticide formulation in recent years, which indeed have been a good insecticidal performance and a minimal impact on the environment. But the commonly organic solvents and cosurfactants such as toluene, xylene and methanol were widely applied in the procession of preparing the formulation. They are detrimental to environment and health of human beings all the same (Knowles., 2008). Therefore, controversy over the nocuous additives added excessively, really did put the production and application of pesticide microemulsion into trouble. But the traditional pesticide formulation can't be compared with the pesticide microemulsion based on excellent properties of microemulsion in some respects. We should prohibit the addition of toxic substances into microemulsion, rather than forbid the pesticide microemulsion formulation itself. The development of pesticide microemulsions need providing more equitable space and rational platform.

The formulation of pesticide microemulsion is an inexact science and eludes prediction for the most part, and largely dependent upon specific and incompletely understood interaction between the molecules of oil, emulsifiers, and water. So that, studies of pesticide microemulsions are limited to the combination of various components(Pratap, A. P.& Bhowmick, D. N.,2008; Narayanan, K. S., 1994; Narayanan, K. S., 1994; Jon, D. I. et al,1999). A considerable number of studies are processes of trial and error, similar to the proverbial "needle in a haystack". Very few works have studied the methodology of pesticide microemulsion preparation (Skelton, P. R. et al, 1988; Hiromoto, B., 2007). Therefore, investigations on the formula design of pesticide microemulsions are worthwhile for more detailed theoretical and technological studies.

In this paper, we reported our methods based on the pseudo-ternary phase diagram and orthogonal design. Although, the pseudo-ternary phase method has been employed to preparation of microemulsion, the combination method of the pseudo-ternary phase diagram and the orthogonal design has rarely been reported. The nearly non-toxic solvent and cosurfactants were employed to prepare pesticide microemulsion, and the optimization formulation of green environmentally friendly chlorpyrifos microemulsion was achieved. The experimental results were expected to provide new ideas and technical methods for the development of microemulsion.

2. Experimental section

2.1 Materials

Chlorpyrifos pesticide (96%) was provided by Jiangxi Agricultural University Plant Protection Chemical industry Co., Ltd. China; Nonionic surfactant (agricultural emulsifier.600) was obtained from local market in jiangxi province, China; Various grease compounds (natural carboxylate) was made present by Shandong University in China; Ethyl acetate, ethanol and ethylene glycol, analytical grade, were purchased from Tianjing Chemistry factory, China; Distilled water was used throughout the experiments.

2.2 Construction of pseudo-ternary phase diagram

The pseudo-ternary phase diagram can be drafted with the water titration method as described in many previous papers (Watnasirichaiku S. et al,2000; Chen H B. et al,2004; Zhang, Q. Z. et al,2004; Boonme, P. et al,2006). Chlorpyrifos pesticide was dissolved in Ethyl acetate as an oil phase (O); natural carboxylate, agricultural emulsifier.600 and mixed alcohol were blended at certain weight ratio to obtain the surfactant mixture (S), then mixture at the given weight ratios as an surfactant phase, the mixture of the oil phase and the surfactant phase at the weight ratios of 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1 were diluted with distilled water which remarked water phase (W) next by the microburst, at various concentrations, respectively. The dosage of water which made the mixture from the clarification to muddle was recorded, and the quality score of each phase point was analyzed. Phase diagrams were drawn based on visual inspection at ambient temperature.

2.3 Arrangement of orthogonal experiment

A standard orthogonal array matrix (L25; 3^5) was constructed with three factors and five levels (Table 1) to select optimum formation conditions in order to obtain the infinite dilute region(M) of pesticide microemulsion in the phase diagrams. The content of pesticide in solvent, the weight ratios of natural carboxylate/AE600 and mixed alcohol quality/S phase quality in total were selected as three impact factors.

Levels	Factors		
	Content of pesticide in solvent A (w/w)	Natural carboxylate/AE600 B (w/w)	Mixed alcohol C (w/w)
1	A_1 (50%)	B_1 (1:1)	C_1 (95%)
2	A_1 (40%)	B_2 (1:2)	C_2 (90%)
3	A_1 (30%)	B_3 (2:1)	C_3 (85%)
4	A_2 (20%)	B_1 (1:1)	C_2 (85%)
5	A_2 (10%)	B_2 (1:2)	C_3 (85%)

Table 1. A standard L25 (3^5) matrix

3. Results and discussion

3.1 Selection of formula components

Firstly, ester is a sort of lowly toxic matter, which has less impact on the environment. The experimental results show that the chlorpyrifos pesticide can be effectively solubilized in ethyl esters analogy to the most solubility of chlorpyrifos pesticide in toluene or xylene.

There was more 90%(weight ratios) chlorpyrifos pesticide to be able to be dissolved in the ethyl esters. So the ethyl ester was regarded as the substitute of tolunene or xylene. Secondly, the nonylphenols and alkylphenol phenoxy poly(ethyleneoxy)ethanol have been employed comprehensively in the commonly microemulsion so far. But they had even been limited to production and application with endangering the ecological environment in many countries. Then the nature carboxylate and AE600 at the weight ratios of 1:3, 1:2, 1:1, 2:1, and 3:1 were mixed and prepared to reach the demands of experiment. And the natural carboxylate is a kind of cheap, efficiency and safe anionic surfactant, because it derived from the oil scraps in green plants. Finally, the glycol and ethanol were regarded as the additives in the procession of preparing the microemulsion and their effectivity were predominant. All those could try to do minimum damage to the environment.

3.2 Choice of the best phase diagram

L_{25} (3^5) orthogonal table and orthogonal experimental data were listed in Table 2. Due to the pesticide microemulsion should be diluted with 200-fold water, the infinite dilute region's area (M) had been chosen as criterion in the pseudo-ternary phase diagram.

Table 2 shows that the order of the three factors' effect on the infinite dilution area with water is $R_A > R_B > R_C$ and the optimal conditions were found to be $A_5B_1C_5$ with the maximum infinite dilution area with water. To confirm the result of the orthogonal experiments,the pseudo-ternary phase diagram determined by $A_5B_1C_5$ (10% original drug phase content in the ethyl esters, natural carboxylate/AE600 = 1:3, Mixed alcohol quality/S phase quality in total = 85%) was illustrated in Fig.1. However, it is considered that the content of organic phase was only 10% and the content of chlorpyrifos also was 3%, the another optimal conditions was the $A_4B_2C_4$(20% original drug phase content, natural carboxylate/agricultural emulsifier.600 = 1:2, Mixed alcohol quality/S phase quality in total = 85%) (Fig.2) which was reasonable as compared with the area of the infinte dilution region (M=30.012) in the 25 group phase diagrams. The most significant reason is that the content of chlorpyrifos pesticide can reach 4%.

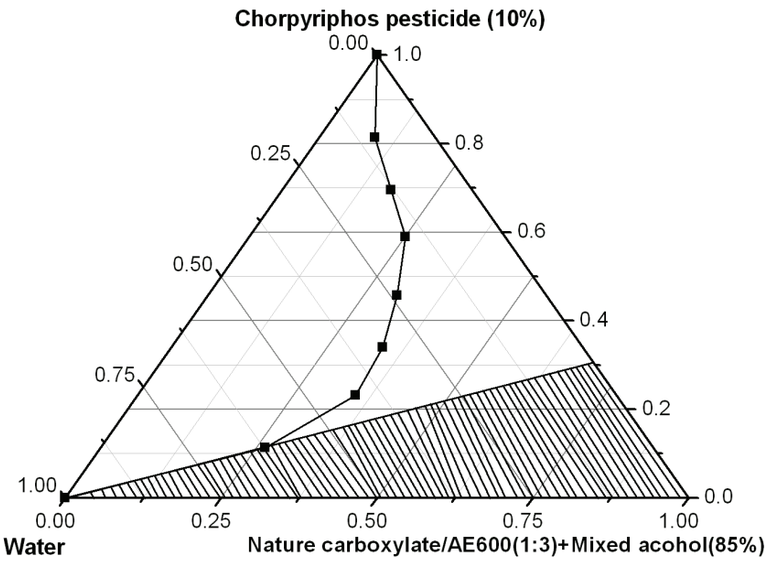

Fig. 1. Pesudo-ternary phase diagram defined by $A_5B_1C_{5[}$

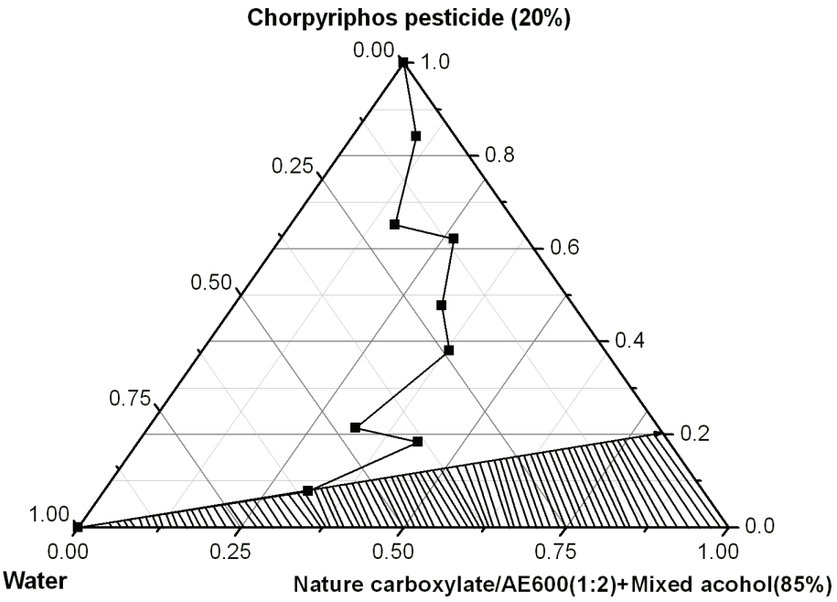

Fig. 2. Pesudo-ternary phase diagram defined by $A_4B_2C_4$

Level	Content of pesticide in solvent	Natural carboxylate/AE600	Mixed alcohol	Level	Content of pesticide in solvent	Natural carboxylate/AE600	Mixed alcohol
1	A1 (50%)	B1 (1:3)	C1 (95%)	14	A3 (30%)	B4 (2:1)	C5 (85%)
2	A1 (50%)	B2 (1:2)	C2 (90%)	15	A3 (30%)	B5 (3:1)	C1 (95%)
3	A1 (50%)	B3 (1:1)	C3 (85%)	16	A4 (20%)	B1 (1:3)	C5 (85%)
4	A1 (50%)	B4 (2:1)	C4 (85%)	17	A4 (20%)	B2 (1:2)	C1 (95%)
5	A1 (50%)	B5 (3:1)	C5 (85%)	18	A4 (20%)	B3 (1:1)	C2 (90%)
6	A2 (40%)	B1 (1:3)	C4 (85%)	19	A4 (20%)	B4 (2:1)	C3 (85%)
7	A2 (40%)	B2 (1:2)	C5 (85%)	20	A4 (20%)	B5 (3:1)	C4 (85%)
8	A2 (40%)	B3 (1:1)	C1 (95%)	21	A5 (10%)	B1 (1:3)	C3 (85%)
9	A2 (40%)	B4 (2:1)	C2 (90%)	22	A5 (10%)	B2 (1:2)	C4 (85%)
10	A2 (40%)	B5 (3:1)	C3 (85%)	23	A5 (10%)	B3 (1:1)	C5 (85%)
11	A3 (30%)	B1 (1:3)	C2 (90%)	24	A5 (10%)	B4 (2:1)	C1 (95%)
12	A3 (30%)	B2 (1:2)	C3 (85%)	25	A5 (10%)	B5 (3:1)	C2 (90%)
13	A3 (30%)	B3 (1:1)	C4 (85%)				
K_1	10.174	16.426	12.544				
K_2	10.022	14.118	10.096				
K_3	11.948	11.674	13.604				
K_4	14.408	10.01	12.024				
K_5	17.906	12.25	14.332				
R	7.884	6.416	5.236				

Table 2. Three factors and five levels orthogonal table and the analysis of experimental results

label	Surfactant phase /%	Oil phase /%	Water phase /%	Surfactant phase/Water phase(m/m)	Exterior	Dispersion into the water	cold storage	Heat storage
1	40.53	9.95	49.52	0.82	Transparent	Filamentous material sank, then mixture became transparent after shaking	Demixing in the 2nd day	Muddy
2	37.32	7.42	55.26	0.68	Transparent	Ibid	Demixing in the 3rd day	Muddy
3	35.15	5.03	59.82	0.59	Transparent	Ibid	Demixing in the 6th day	Muddy
4	32.27	2.41	65.31	0.49	Transparent	Ibid	Demixing in the 3rd day	Muddy
5	42.57	7.42	50.01	0.85	Transparent	Ibid	Demixing in the 2nd day	Transparent
6	44.84	5.07	50.08	0.90	Transparent	Ibid	Demixing in the 6th day	Transparent
7	51.48	2.76	45.77	1.12	Transparent	Ibid	Demixing in the 5th day	Transparent
8	48.02	11.96	40.02	1.20	Transparent	Ibid	Demixing in the 4th day	Transparent
9	48.24	10.10	41.65	1.16	Transparent	Ibid	Demixing in the 4th day	Transparent
10	48.46	7.55	44.00	1.10	Transparent	Ibid	Demixing in the 3rd day	Transparent
11	47.72	5.21	47.07	1.01	Transparent	Ibid	Demixing in the 2nd day	Transparent
12	49.63	2.61	47.76	1.04	Transparent	Ibid	Demixing in the 3rd day	Transparent
13	49.72	10.18	40.09	1.24	Transparent	Ibid	Stable over 7 days	Transparent
14	52.45	7.42	40.13	1.31	Transparent	Ibid	Stable over 7 days	Transparent
15	54.89	5.07	40.04	1.37	Transparent	Ibid	Stable over 7 days	Transparent
16	57.49	2.53	39.98	1.44	Transparent	Ibid	Demixing in the 2nd day	Transparent

Table 3. The composition of the points in the microemulsion and the result of stability text

3.3 The research of physical stability

The 16 points were selected in the best phase diagram($A_4B_2C_4$) and according to concentrations of the 16 points, the 16 experimental samples were prepared and then each experimental sample was divided into two parts. The one was examined in heat storage condition [(55 ± 2) degrees, 15d], and the other was examined in cold storage condition [(0 ± 1) degree, 7d]. Experimental results were listed in Table 3.

It is showed that the thirteenth, fourteenth and fifteenth group was raised above the sixteen groups experiment after heat treatment and cold storage in Table 3. Because the consumption of the surfactant was the lowest in the 13th group, and the concentration of the chorpyriphos pesticide content was the highest in the 13th group. So the composition of the

13th group was the best formula, which was listed as follows: chlorpyrifos (2.036%), ethyl acetate (8.154%), agricultural emulsifier.600(4.972%), natural carboxylate(2.486%, glycol (21.131%), ethanol (21.131%), water (40.090%).

4. Conclusions

The organic solvent, surfactant and kinds of additives were researched in the procession of preparing the chlorpyrifos microemulsion based on the method of pseudo-ternary phase diagram and orthogonal experiment in detail. The more green environment-friendly and extremely development potential chlorpyrifos microemulsion formulation was obtained. The optimized formula was composed of chlorpyrifos (2.036%), ethyl acetate (8.154%), agricultural emulsifier 600(4.972%), natural carboxylate(2.486%), glycol (21.131%), ethanol (21.131%), water (40.090%). Experimental results supported the foundation of the development in search of more green environmental protection chlorpyrifos microemulsion, and had a strong practical value on the principal of green environmental protection of chlorpyrifos microemulsion.

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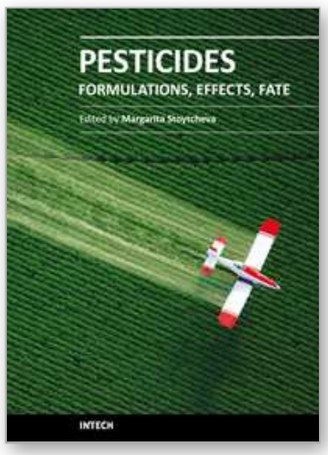

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This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.

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Slavka Krautzeka 83/A
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