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Formulating a pesticide in microemulsion with three active components-one-hydrophilic and two-lyophilic

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Microemulsion of a mixed pesticide with three active components of imidacloprid, fipronil and monosultap has been formulated and characterized. Pseudoternary phase diagrams and cloud points of microemulsions are drawn and measured with changing mass ratios of surfactant to co-surfactant (*Km*). It was found out that the mixed pesticide microemulsion can be formulated at the *Km* of 1:1 and the manufacturing temperature of 25-55°C. Properties such as density, surface tension, and contact angle of as-prepared microemulsion are characterized.

Keywords: Fipronil, Imidacloprid, Microemulsion, Mixed pesticide, Monosultap

Introduction

Research related to development of eco-friendly pesticides[1-5] and replacement of chemically synthesized pesticides with 'organic pesticides'[6] are areas of immense interest for the scientists nowadays. Scientists have also researched to degrade trace amount of harmful pesticides which had already been spread and occurred in soil[7-9]. Developing a more efficient pesticide is possible when we use a mixed pesticide instead of individuals using synergistic effect and increase efficiency in usage which can be guaranteed by form of a microemulsion. Some scientists have focused on formulating hydrophobic microemulsion pesticides[10-14].

In our agro-practice, insects such as rice water weevil (*Lissorhoptrus oryzophilus Kuschel*) and rice stem borer (*Chilo suppressalis Walker*) are in main problem, and carbosulfan and deltamethrin have been used for controlling them respectively[15-17]. Through a series of experiments for estimating synergistic effects, we found that three components such as monosultap, fipronil and imidacloprid are of synergistic effect, which is much greater than that of abamectin, carbosulfan, and deltamethrin. Imidacloprid and fipronil have structures as shown in Fig. 1. Using a mixed pesticide is also effortlessly advantageous because it can control undesirable insects at the same time. Some difficulty, however, with development of a mixed pesticide arises because of their differences in water-solubility. Imidacloprid and fipronil are oil-soluble, while monosultap is water-soluble. Thus, it is required to formulate stable microemulsion with those three components.

In this work, we investigated to prepare stable microemulsion of a mixed pesticide with three active components by drawing a phase diagram and to characterize properties like viscosity, wettablility, etc.

Experimental Section

Materials

All the main chemicals such as imidacloprid, fipronil and monosultap used in experiment were of analytical grade with the purity of more than 99.5% and purchased from Beijing Chemical Reagent Co. Alcohols such as ethanol methanol and butanol, solvents such as butylacetate, methylacetate, dimethylsulfoxide (DMSO), dimethylformamide (DMF), xylene, toluene, acentone, furfural and water were twice distilled. Nonionic surfactants such as 4-nonylphenyl polyoxyethylene(7) ether or NP-7 and 4-octylphenylpolyoxyethylene(10) ether or OP-10 with purity of 95% were purchased from Xingtai lantian Jingxi Chemical Co. Lt.

Methods

Determining solubility of imidacloprid, fipronil and monosultap in various solvents

The solubilities of imidacloprid, fipronil and monosultap in solvents were measured by static method. Experimental temperatures kept constant by thermostatic water bath. Measurements were carried

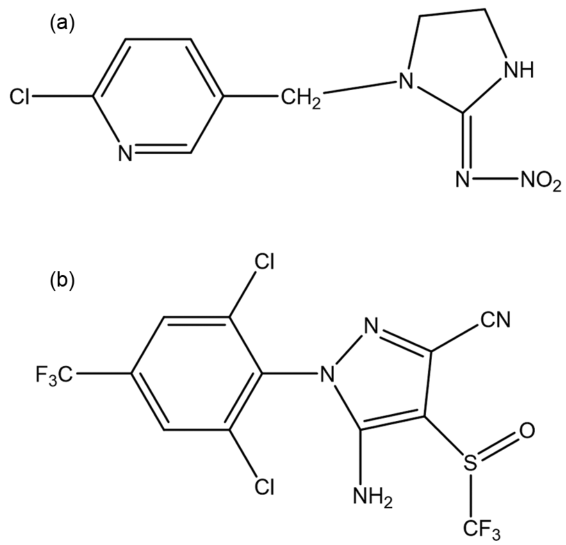

Fig 1 — Structures of (a) imidacloprid and (b) fipronil

out several times until the measuring value is repeated within 2.7%(Ref.18).

Procedure to determine a phase diagram

Calculated amounts of surfactant, alcohol, oil and water were taken in sealed test tubes and shaken vigorously in a vortex shaker for 5-10 min and then kept in a thermostatic water bath (with accuracy of ±0.1°C) at the desired temperature (25°C) more than a week. The oil phase was furfural + imidacloprid + fipronil + OP-10 and the compositions of imidacloprid and fipronil were fixed at 2 wt%, respectively, while the water phase was monosultap and water and the composition of monosultap was fixed at 13wt%. Microemulsion region was decided by pseudo-ternary phase diagrams, which were built at different mass ratios of surfactant to 1-butanol (*Km*). *Km* was set to 1:1, 2:1, 3:1, 4:1,3:2, 4:3, 2:3, 3:4, 1:3, 1:2, respectively, during each experiment. The transparent and cloud state was determined by visual appearance. If any sample remained transparent after further dilution until 500 times, the microemulsion was considered as bicontinuous phase.

Measurements of viscosity and contact angle on the surface of a microemulsion

Viscosity measurements were performed using a LVDV-II+PCP cone and plate type rotoviscometer (Brookfiled Eng.Lab, USA). The temperature was kept constant (25°C) for viscosity measurement within ±0.1°C by circulating thermostatic water, through a jacketed vessel containing the solution. The reproducibility of the viscosity measurement was found to be within ±1%.

The spreading of dilute microemulsions onto leaf substrates was measured through dynamic contact angle measurements using drop shape analyzer DAS-100 (Kruss Company, Germany). Each experiment was repeated as least three times and averaged the results.

Dynamic light scattering (DLS) measurements

The size of the microemulsion droplet was determined by DLS method. The same sets of solutions, as used for viscosity measurements, were employed for droplet sized analysis at 25°C. DLS measurements were carried out using a Zetasizer Nano ZS90 (ZEN3690, Malvern Instruments Ltd, U.K.). A He-Ne laser of 632.8 nm wavelength was used and the measurements were made at a scattering angle of 90°.

Cloud point measurement

Microemulsions comprising of non-ionic surfactants undergo cloud formation during temperature change due to the dehydration of oxyethylene head groups. The cloud point is the temperature at which cloudiness is observed and is determined by heating the microemusions at 1°C intervals. The microemulsion taken in a sealed test tube is heated at a rate of 1°C rise in temperature per min, to observe the cloudiness. Average cloud point for each of the microemulsion were determined by three such separate experiments until an error is less than ±0.5°C

Dynamic surface tension measurement

The dynamic surface tension was measured using a Kruss BP100 bubble-pressure tensiometer (Kruss Company, Germany). Measuring was performed at effective surface ages ranging from 10 to 300000 ms. Measurements were operated at 25±0.1°C.

Results and Discussion

Finding the optimal solvent to dissolve imidacloprid and fipronil

Several solvents were tested to find an appropriate solvent for dissolving imidacloprid, fipronil and monosultap. Table 1 shows solubility data of imidacloprid, fipronil and monosultap in solvents such as butylacetate, methylacetate, DMSO, DMF, xylene, toluene, ethanol, acentone, furfuraland water at 25°C. As shown in Table 1, imidacloprid and fipronil are soluble in DMSO, DMF and furfural. Although furfural is worse in ability to dissolve imidacloprid than DMSO and DMF, it is able to dissolve fipronil in substantial amount and also has a significant importance of industrial application due to its low cost, thus it is determined as a solvent for two active components.

Otherwise monosultap is insoluble in furfural but soluble in water. Thus making a mixed pesticide with three active components such as fipronil, imidacloprid and monosultap requires for preparing a stable microemulsion.

Finding the optimal surfactant to dissolve furfural in water

Solubilizing amount of various surfactants was measured by titration method. The oil phase consists of imidacloprid, fipronil and furfural. The water phase consists of monosultap, surfactant and water. A calculated amount of surfactants such as OP-10, NP-10 and sodium dodecyl sulfonate (SDS) were added to water with monosultap before oil was added. As an agricultural requirement weight mass of imidacloprid, fipronil and monosultap was fixed at 2, 2, 13 wt%, respectively. Fig. 2 shows the solubilizing amount of surfactants versus surfactant concentrations. As shown in this figure, OP-10 is more favourable for preparing microemulsion than any other surfactants. To find the optimum alcohols as a co-surfactant, various alcohols were tested their ability to make a stable microemulsion at 25°C.

Table 2 shows stability of furfural/ surfactant/ co-surfactant/ water emulsions versus amount of co-surfactant added. As shown in Table 2, OP-10 and ethanol was favourable to make furfural/surfactant/co-surfactant/ water microemulsion and was determined to formulate mixed pesticide-microemulsion.

Construction of puseudo-ternary phase diagram

Fig 3 shows the puseudo-ternary phase diagrams of furfural/OP-10/ethanol/ water microemulsions at different ratios of OP-10/ethanol (*Km*) at 25°C. As shown here, bicontinuous phase (BC phase) range changes in emulsions with different *Km* and the microemulsions with *Km* of 3:2, 4:3, 3:4 and 2:1 have a wide range of BC phase, which is more favourable to formulate a mixed pesticide concentrate.

Relation of *Km* with cloud point

Cloud points (CP) of furfural/OP-10/ethanol/water BC mocroemulsions at different *Km* which were prepared for construction of phase diagram were measured and are shown in Table 3. The microemulsions with *Km* of 1:1, 3:4 and 2:3 have the highest cloud point of 55°C, which is significant in practical use. Thus, formulating microemulsions with *Km* of 1:1 is important in both practical and industrial aspects. The micelle particles in BC microemulsion is assumed to behave in a similar way as shown in Fig. 4.

Physical characteristics of prepared microemulsion pesticide

As shown in Fig 5, as-prepared the concentrate and 500 times-diluted micremulsions have similar

Table 1 — Solubility data of imidacloprid, fipronil and monosultap in various solvents

Solvent	imidacloprid/g·100 g^{-1} solvent	fipronil/g·100 g^{-1} solvent	monosultap/g·100 g^{-1} solvent
butylacetate	-	20.3	-
methylacetate	-	38.4	-
DMSO	12.8	32.2	-
DMF	20.6	45.0	-
xylene	-	-	-
toluene	-	-	-
ethanol	-	-	-
acetone	-	-	-
furfural	20.3	19.1	-
water	-	-	68.8

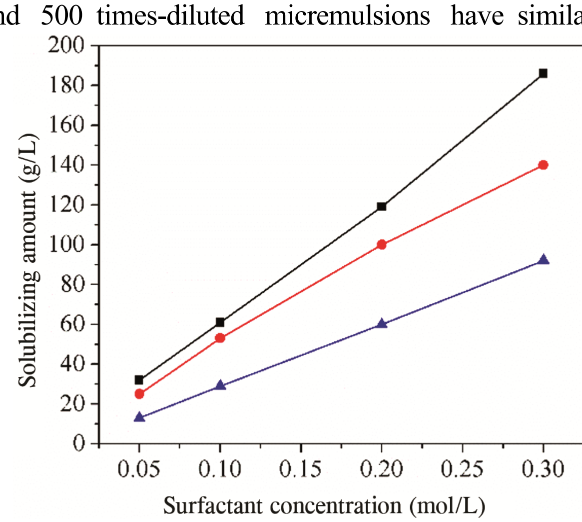

Fig. 2 — Solubilizing amount versus surfactant concentration at 25°C; black: OP-10, red: NP-10, and blue: SDS

Table 2 — Stability of furfural/ surfactant/ co-surfactant/ water emulsions versus co-surfactant amount

Surfactants	Ethanol (%)				n-Butanol (%)				n-Hexanol (%)				n-Octanol (%)			
	5	10	15	20	5	10	15	20	5	10	15	20	5	10	15	20
OP-10	○	○	○	○	-	-	-	-	-	-	-	-	-	-	-	-
NP-10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SDS	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

○: transparent state, -: cloud state

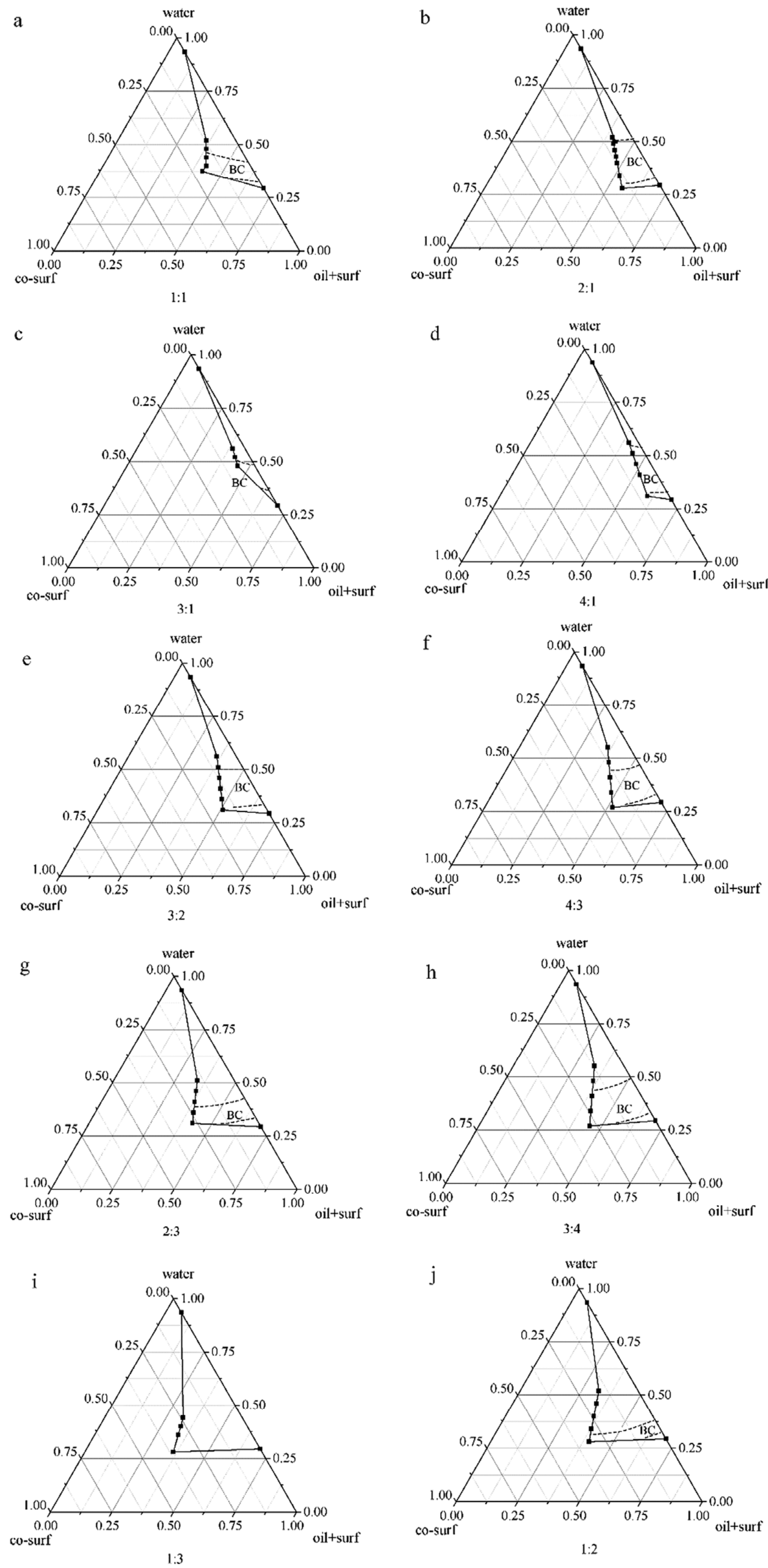

Fig. 3 — Pseudo-ternary phase diagram of microemulsion with different *Km* at 25°C; (a) 1:1, (b) 2:1, (c) 3:1, (d) 4:1, (e) 3:2, (f) 4:3, (g) 2:3, (h) 3:4, (i) 1:3 and (j) 1:2

Table 3 — Cloud points of furfural/OP-10/ethanol/water mocroemulsions at different *Km*

Km	Furfural: OP-10: Ethanol:Water	CP (°C)	*Km*	Furfural: OP-10: Ethanol: Water	CP (°C)
1:1	24/15/15/46	55	4:1	24/20/5/51	30
	24/16/16/44	55		24/24/6/46	30
	24/18/18/40	55	3:2	24/18/12/46	45
	24/20/20/36	55		24/21/14/41	45
2:1	24/18/9/49	35		24/24/16/46	45
	24/20/10/46	40	4:3	24/20/15/41	50
	24/22/11/43	40		24/24/18/34	50
	24/24/12/40	35	3:4	24/15/20/41	55
3:1	24/21/7/48	30	2:3	24/16/24/36	55
	24/24/8/44	30			

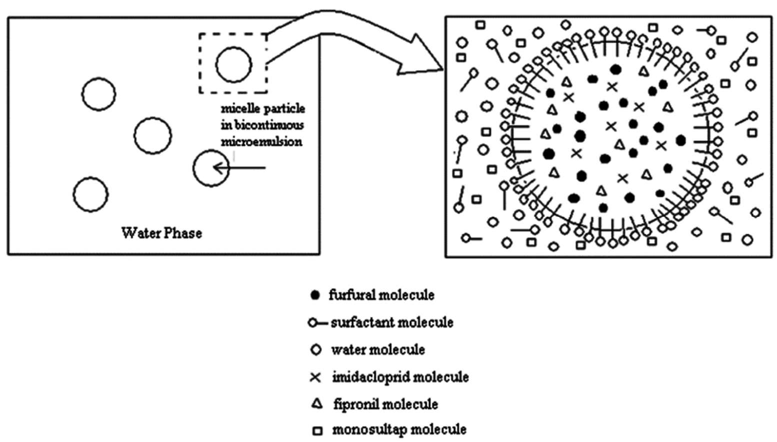

Fig. 4 — Molecular view of BC microemulsion

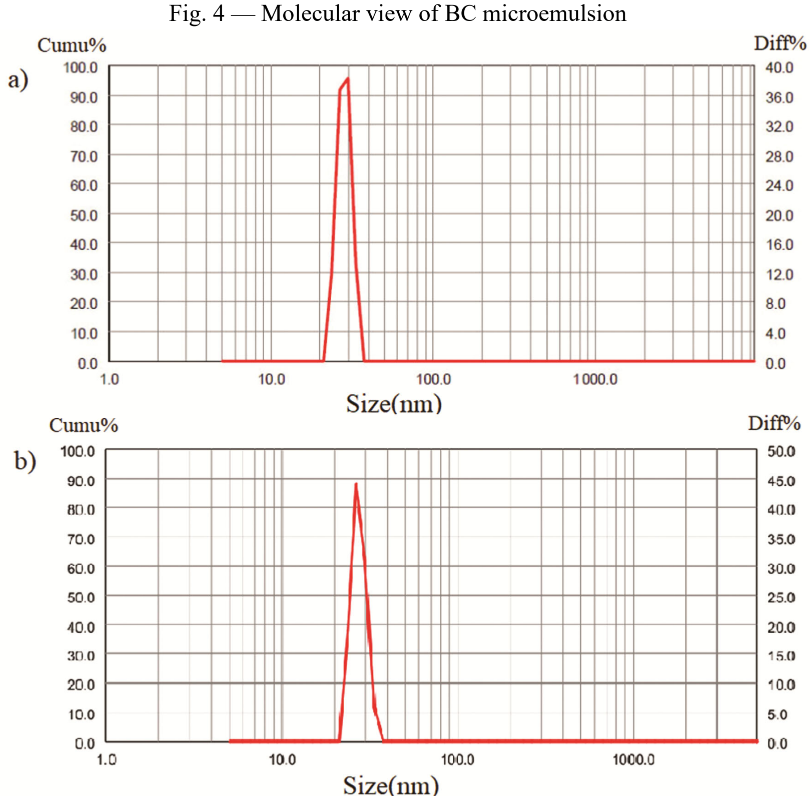

Fig. 5 — Particle size of micelles in as-prepared microemulsion (a) concentrate and (b) 500 times-diluted emulsion

Table 4 — Physical properties of as-prepared microemulsion

Physical properties	Density (g/cm^3)	pH, 1% aqueous liquid	Surface tension (mN/m) 0.2% aqueous liquid	Contact angle
as-prepared microemulsion	1.14	6.16	27.73	21°38′

distribution with the average particle size of 35.3 nm. This implies industrial and practical use of a mixed pesticide microemulsion concentrate. Table 4 shows properties related with as-prepared microemulsion of a mixed pesticide with 3 active components.

Conclusion

Microemulsion concentrate of a mixed pesticide with three active components of imidacloprid (2 wt%), fipronil (2 wt%) and monosultap (13 wt%) with furfural as an oil, OP-10 as a surfactant and ethanol as a co-surfactant was formulated. BC microemulsion was estimated by drawing pseudo-ternary phase diagrams with changing values of *Km*. Taking account to cloud points of BC microemulsions with different *Km*, microemulsion concentrate of mixed pesticide with *Km* of 1:1 is estimated to have an industrial and practical significance. Properties of as-prepared microemulsion were characterized; particle size of 35.3 nm, density of 1.14 g/cm^3, surface tension of 27.73 mN/m (in the case of 0.2% aqueous liquid) and 21°38′of contact angle. As-prepared microemulsion had particle size of 35.3 nm and a similar particle distribution with a concentrate in even 500 times diluted-microemulsion.

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