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Study of Tannery Phase Diagram of Rotenone *Derris elliptica* (Fabales: Fabaceae): A Novel Approach of Insecticide Formulation

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The present study was conducted for evaluating the tannery phase diagram of microemulsion formulation of rotenone. In this paper, oil-in-water microemulsions were obtained by the titration method through ternary phase diagram study. The widest oil-in-water microemulsion region (48 % isotropic area) in phase diagram system was obtained in Tween 20/Agnique BL 7001/water system compared with others, while the narrowest oil-in-water microemulsion region (6 % isotropic area) was obtained in Agnique PG 9116/Edenor ME/water system. This novel approach for insecticide formulation of rotenone might be useful for the control of insect. This study will provide the maximum utilization of botanical insecticide concerning environmental friendly strategy.

Key Words: Microemulsion, *Derris elliptica*, Insecticide formulation, Isotropic area, Titration.

INTRODUCTION

Rotenone is a bio-active compound that has a strong paralysis action (knock-down effect) on cold-blooded animals and used as an insecticide to combat pests[1]. Pest species controlled by rotenone include aphids, caterpillars, beetles and various aquatic larvae. The use of agro-based materials in the pesticide formulation has become more important, because, they are relatively biodegradable, low toxicity and renewable resources than those from mineral oil derived commodities[2]. Currently, the most studies on pesticide formulation are more focused on herbicides and not much information is available on insecticide formulations and their efficacy study. The use of biodegradable insecticides in crop protection is a practical sustainable alternative to the synthetic organic-based insecticides and they could maintain biological diversity of predators, reduces environmental contamination and human health hazards[3].

As a new environment-friendly pesticide formulation to replace the traditional ones like emulsifiable concentrate and to decrease the content of the organic solvent in the formulation, the content of surfactants will be reduced and the dosage of pesticide active ingredient will be increased as much as possible in the new formula design. Beside this, it is also a basic requirement for the design of pesticide formulation to form a thermodynamic stabilized microemulsion when diluted with water at practice use[4]. Despite the significance of agrochemicals use for pest control, the environmental problems caused by over use of agrochemicals have brought scientists and publics much concern in recent years[5]. Thus, formulation scientists now are facing the challenge to explore novel green or environmental friendly agrochemical formulation to improve the biological efficacy and develop technique that can be employed to reduce pesticide use while maintaining plant protection.

Microemulsions are currently the subject of many investigations because of their wide range of potentiality and utilization[6]. It is composed of oil phase, surfactant and aqueous phase at appropriate ratios[7]. It has several specific physicochemical properties such as transparency, optical isotropy, low viscosity and thermodynamic stability[8,9]. There has been considerable interest in many applications of microemulsion in a variety of chemical and industrial processes, such as pharmaceutics, cosmetics, especially agrochemicals. Therefore, for successful establishment of microemulsion formulation of rotenone and to reduce insecticidal load in the environment, the role of this plant extract is very important. Keeping this view, the present study was conducted for evaluating the tannery phase diagram of microemulsion formulations of rotenone.

EXPERIMENTAL

The experiment was conducted in the Laboratory of Toxicology, Department of Plant Protection, Faculty of Agriculture, University Putra Malaysia. The present study was

TABLE-1
COMPOUND USED IN TERNARY PHASE DIAGRAM STUDY

Compounds	Trade name	% a.i.[1]	Class
Surfactant-			
Alkyl polyglycoside	Agnique PG 8107-U	68-72	Surfactant
Alkyl polyglycoside	Agnique PG 9116	48-52	Surfactant
Polyoxyethylene sorbitan monolaurate	Tween 20	N.A.	Surfactant
Oil/Carrier-			
Palmitic acid-oleic acid Methyl ester	Edenor ME (ME C18-70U MY)	N.A.	Adjuvant
Methyl ester and fatty alcohol (blended)	Agnique BL 7001	N.A.	Adjuvant
Methyl ester and fatty alcohol (blended)	Agnique BL 7002	N.A.	Adjuvant
Xylene	Xylene	99.8	Solvent
Rotenone (CLCE)	N.A.	1.15	Insecticide

[1]a.i = Active ingredient and N. A. = Not available

carried out under laboratory conditions (temperature 26 ± 2 ºC, RH 65 ± 5 % and photoperiod 12 h L: 12 h D). Two alkyl polyglycoside surfactants, Agnique PG 8107-U and Agnique PG 9116 were obtained from Cognis Oleochemical (M) Sdn. Bhd, Tween 20 was purchased from Sigma-Aldrich Inc., USA. Palm oil based carrier, Edenor ME, Agnique BL 7001 and Agnique BL 7002 were obtained from Cognis Oleochemical (M) Sdn. Bhd, while xylene was purchased from Merck KGaA, Germany.

The rotenone was concentrated liquid crude extract from *Derris elliptica* (Fabales: Fabaceae) and supplied by Chemical Engineering Pilot Plant, University Technology of Malaysia. The brief description, characteristic and source on inert and active materials were showed in Table-1. The microemulsions were prepared at room temperature (26 ± 1 ºC) using aqueous titration method[10]. The ratio of surfactant and oil in experimental mixture was fixed as 9 combinations; 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20 and 90:10. Appropriate amounts of surfactant and oil were weighed for a total of 0.5 g into 10 mL culture glass tube with cap. Sample was shaken for sufficient time to attain equilibrium. Water was added by titrating into the oil and surfactant mixture at which transition occurred were used to determine the phase domains. Each sample was assessed visually for spontaneous emulsification through clarity, stability and transparency. The ratio of water, oil and surfactant obtained was mark on three axis ternary phase diagram and similar procedure was repeated to other oil and surfactant ratios (Table-2). Those point which joint together indicated the isotropic area of microemulsion in the 3 component phase diagram systems. Samples which retained transparent one-phase appearance were kept at room temperature for 4 weeks to indicate the stability of a microemulsion[11]. The results obtained from the experiment were used to plot ternary phase diagram. The phase diagram consisted of water phase, second presenting surfactant and third representing oil.

TABLE-2
SURFACTANTS, OILS AND AQUEOUS PHASE GROUPED IN DIFFERENT COMBINATIONS FOR PHASE DIAGRAM CONSTRUCTION

Group	Surfactant phase	Oil phase	Aqueous phase
1	Agnique PG 8107-U	Edenor ME	Water
2	Agnique PG 8107-U	Xylene	Water
3	Agnique PG 8107-U	Agnique BL 7001	Water
4	Agnique PG 8107-U	Agnique BL 7002	Water
5	Agnique PG 9116	Edenor ME	Water
6	Agnique PG 9116	Xylene	Water
7	Agnique PG 9116	Agnique BL 7001	Water
8	Agnique PG 9116	Agnique BL 7002	Water
9	Tween 20	Edenor ME	Water
10	Tween 20	Xylene	Water
11	Tween 20	Agnique BL 7001	Water
12	Tween 20	Agnique BL 7002	Water

TABLE-3
PERCENTAGE OF ISOTROPIC AREA IN PHASE DIAGRAM SYSTEM ACCORDING TO THE DECREASING ORDER

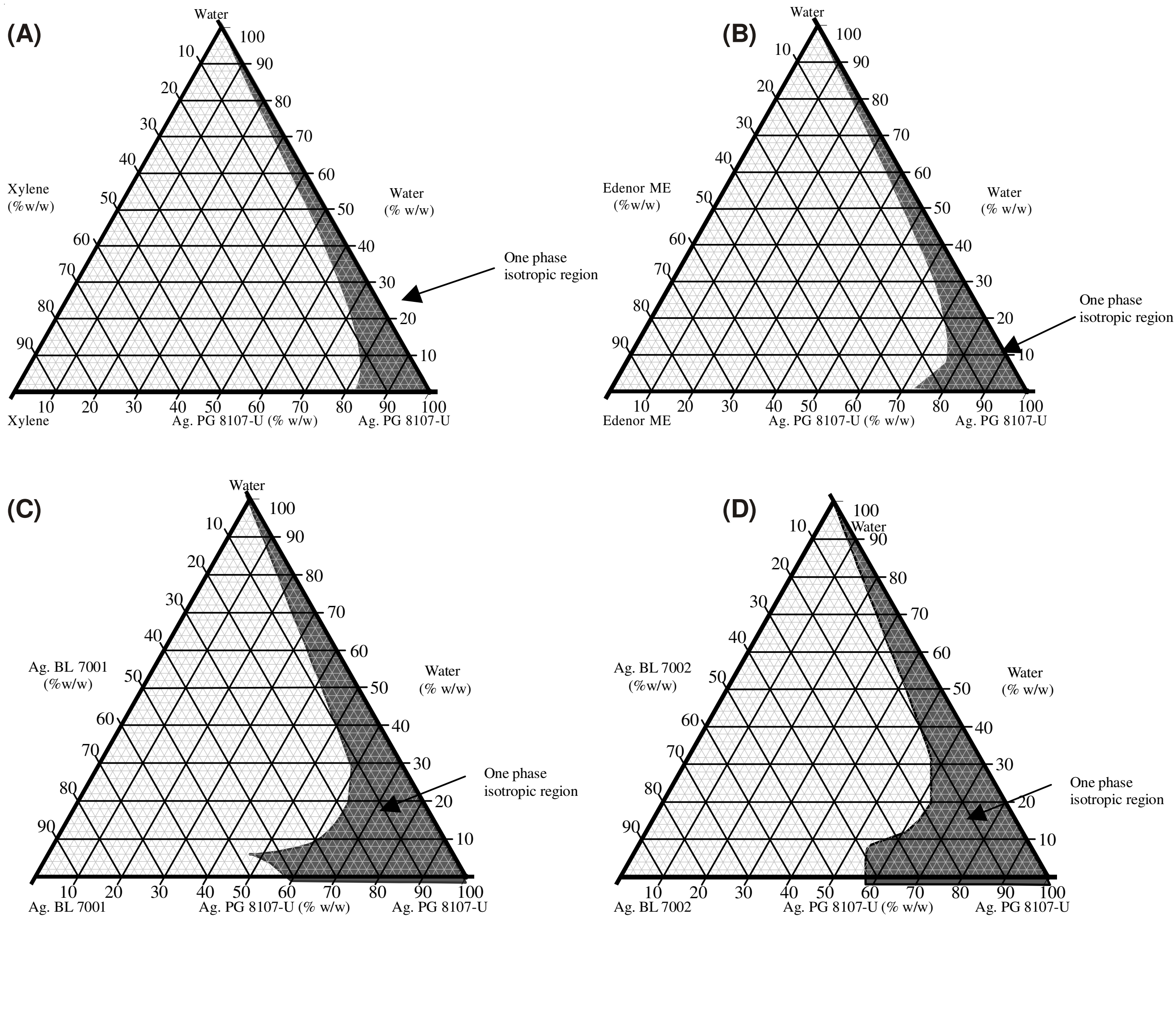
Phase diagram	Total one phase isotropic area (%)
Tween 20/Agnique BL 7002/water	48
Tween 20/Agnique BL 7001/water	45
Tween 20/Edenor ME/water	31
Agnique PG 9116/Agnique BL 7001/water	26
Agnique PG 8107-U/Agnique BL 7001/water	24
Agnique PG 8107-U/Agnique BL 7002/water	24
Tween 20/xylene/water	23
Agnique PG 9116/Agnique BL 7002/water	17
Agnique PG 9116/xylene/water	15
Agnique PG 8107-U/xylene/ water	14
Agnique PG 8107-U/Edenor ME/water	10
Agnique PG 9116/Edenor ME/water	6

RESULTS AND DISCUSSION

The phase diagram showed the occurrence of one phase isotropic area with Agnique PG 8107-U as surfactant (Fig. 1A). The narrow isotropic region obtained in this system revealed that Agnique PG 8107-U was not easily dissolved (Table-3). The microemulsions began to form when water was added to the system. Mixture of Edenor ME/Agnique PG 8107-U at ratio 5/95 was found to assist solubilization of Edenor ME in water. The continuous addition of water to the transparent solution gradually changes to two-phase solution at ratio 8/92 of Edenor ME/Agnique PG 8107-U. Narrow isotropic region was obtained in range 1-18 % w/w of xylene composition (Fig. 1B); and in Agnique PG 9116/Edenor ME/water system (Fig. 1E). At 50 % w/w water, it was observed that microemulsion was formed with 7 % w/w xylene and 44 % w/w Agnique PG 8107-U composition (Fig. 1B). The microemulsion region increased with increasing of Agnique PG 9116 (> 96 % w/w) content in the system. After titration of water at 95 % w/w and 5 % w/w of Agnique PG 9116 and Edenor ME, the transition from turbid to transparent solution were observed after the weight fraction of water was above 24 % w/w and the microemulsion region began to decrease (Fig. 1E). The existence of microemulsion regions in the systems prepared using Agnique BL 7001 and Agnique PG 8107-U in which the aqueous phases were 94 % w/w of water (Fig. 1C). A sharp end of isotropic region was produced near the Agnique BL 7001 corner at 57 % w/w of Agnique BL 7001 and 46 % w/w of Agnique PG 8107-U (Fig. 1D). The microemulsion region was produced at high concentration of Agnique PG 9116 (above 84 % w/w) (Fig. 1F). A minimum microemulsion region obtained at ratio 85/15 of Agnique PG 9116/xylene towards water corner.

A wider microemulsion region obtained in Agnique PG 9116/Agnique BL 7001/ water (Fig. 1G); Agnique PG 9116/ Agnique BL 7002/water (Fig. 1H); and Tween 20/Agnique BL 7002/water system (Fig. 1L). The transparent region stretched up to 65 % w/w of Agnique PG 9116 towards the water corner. The diagram of Tween 20/Edenor ME/water system showed that the system containing Tween 20 as surfactant has a wider microemulsions region compared with Agnique PG 8107-U and Agnique PG 9116 systems (Fig. 1I). The wider isotropic region was produce until it reached 60/40 of Tween 20/xylene ratio before water addition (Fig. 1J). After additional of water, the isotropic region spread on the Tween 20 corner and began to decrease until minimum of 8 % w/w xylene. The isotropic region has increased at 13/39 % w/w of xylene/Tween 20 before it began to decrease towards the water corner. A one-phase microemulsion system was not existed above 37% and 63% w/w Tween 20 and xylene ratio (Fig. 1J). An outline of the composition internal structures of a microemulsion system were illustrated (Fig. 1K). A small curve formed between these lines caused non isotropic area that gave a unique pattern of the isotropic region (Fig. 1K). On dilution of solutions having different oil/ surfactant ratios with the aqueous phase, one-phase transparent solutions were showed the special appearance of isotropic area observed in this diagram (Fig. 1K). Microemulsions could only be formed on dilution of an oil-surfactant mixture with water[12].

A small isotropic jelly-like area was observed in the middle of shaded area that might effect of unknown interaction caused by surfactant, oil and water (Fig. 1L). The maximum water can be diluted at ratio 20/80 of Agnique BL 7001/ Tween 20 was 23% w/w (Fig. 1L). This observation revealed that at this jelly-like area, microemulsion formulation cannot be formulated because of highly viscous properties that might not suitable for liquid spray application. The relationship between the water-poor and the water-rich regions in phase diagrams above may be predicted that the microemulsion structure was vary greatly, but progressively, as the composition varies over such a wide range as mentioned previously[13]. The widest o/w microemulsion region (48%) in phase diagram system was obtained in Tween 20/Agnique BL 7001/water system



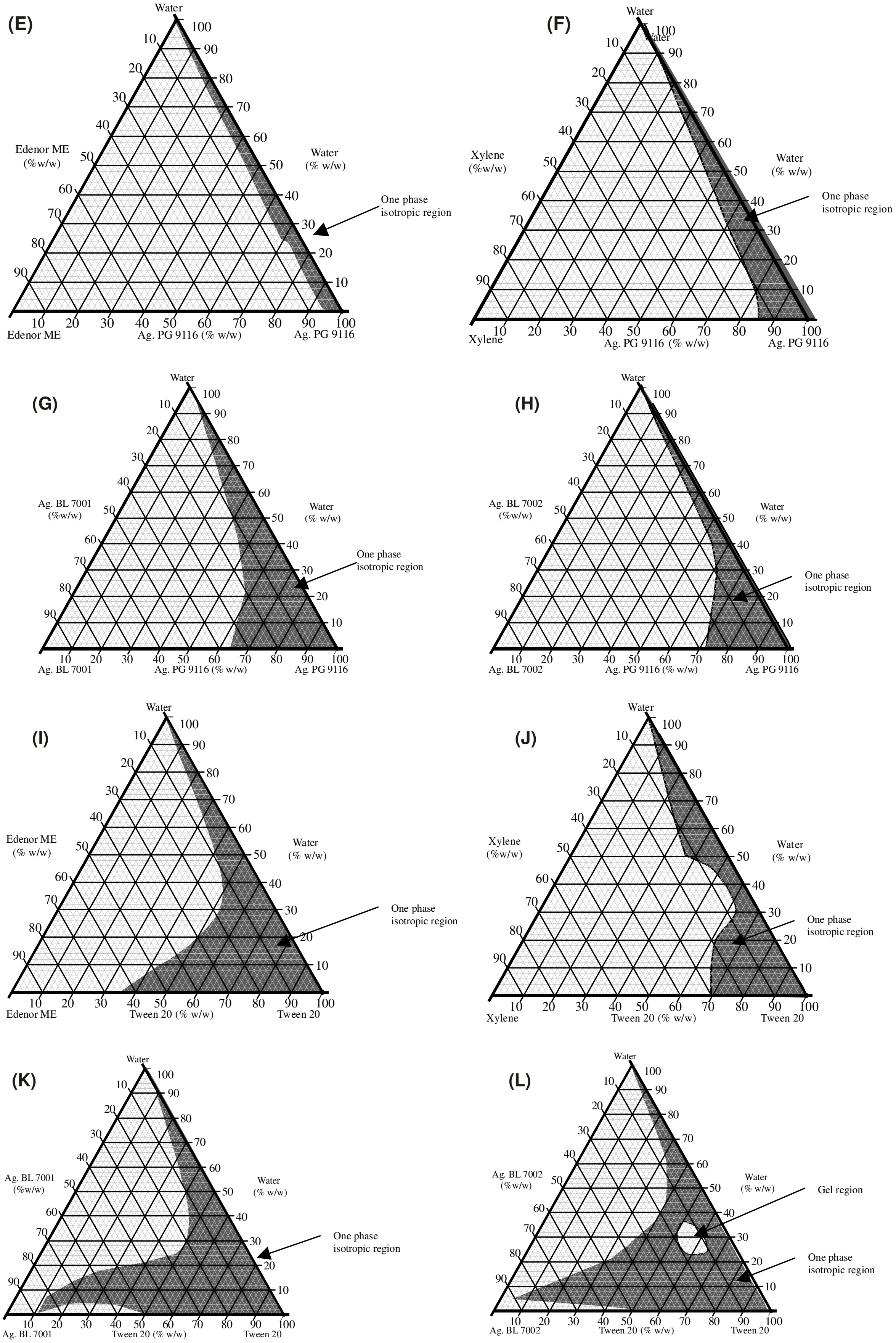


Fig. 1. Phase diagram system containing (A) Edenor ME/Agnique PG 8107-U/water, (B) Agnique PG 8107-U/xylene/water, (C) Agnique PG 8107-U/Agnique BL 7001/water, (D) Agnique PG 8107-U/Agnique BL 7002/water, (E) Agnique PG 9116/Edenor ME/water, (F) Agnique PG 9116/xylene/water, (G) Agnique PG 9116/Agnique BL 7001/water, (H) Agnique PG 9116/Agnique BL 7002/water, (I) Tween 20/Edenor ME/water, (J) Tween 20/xylene/water, (K) Tween 20/Agnique BL 7001/water and (L) Tween 20/Agnique BL 7002/water

compared with others, while the narrowest was Agnique PG 9116/Edenor ME/water (6% isotropic area) (Table-3). The widest isotropic area of system containing alkyl polyglycoside surfactant was Agnique PG 9116/Agnique BL 7001/water which produce 26 % isotropic area (Table-3). In this study, all alkyl polyglycosides used (Edenor ME, Agnique BL 7001 and Agnique BL 7002) gave the greater microemulsion region in all phase diagrams compared with xylene.

Conclusion

In order to formulate microemulsion of rotenone for insecticidal purpose, it is necessary to choose microemulsion area in phase diagram that form over a wide range of oil, surfactant and water composition. The solution in transparent region might be useful to formulate microemulsion. This novel approach for insecticide formulation of rotenone might be useful for the control of insect that will provide the maximum utilization of botanical insecticide concerning environmental friendly strategy.

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