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# Phase Behaviour of Nonionic Surfactants in New Palm Oil Esters-Based Emulsion for Glyphosate Isopropylamine Formulation

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Phase behaviour of emulsion system palm oil esters/nonionic surfactant (s)/water with 41 % (w/w) pesticide active, glyphosate isopropylamine was studied *via* construction of pseudoternary phase diagrams. The nonionic surfactants were long-chain alkylpolyglucosides (LAPG), medium-chain alkylpolyglucosides (MAPG) and polyoxyethylene (4) lauryl ether (Brij 30). Phase behaviour study showed that no monophase region was found with LAPG, MAPG and Brij 30 alone. Isotropic region, a transparent monophase was successfully obtained with mixed surfactants LAPG:Brij 30 and MAPG:Brij 30 at ratios 9:1, 8:2, 7:3 and 9:1, 8:2, 7:3, 6:4, respectively. Hydrophilic-lipophilic balance (HLB) values of the mixed surfactants calculated for the largest isotropic regions were 11.62 and 11.87, respectively. This preliminary study of phase behaviour determination is important for the selection of composition in the stable pesticide formulations.

**Key Words: Phase behaviour, Alkylpolyglucosides, Palm oil esters, Glyphosate isopropylamine, Pesticide formulation.**

## INTRODUCTION

In the global agrochemical market, pesticides are formulated with adjuvants which serve as the predominant formulation constituents to augment biological activity. Adjuvants have been implemented in pesticide formulations to enhance physical characteristic of spray deposits such as atomization and retention effects, thus the ameliorated penetration and translocation of pesticide[1]. For instance, the adjuvants are stickers, defoamers, humectants, spreaders, drift control agents, surfactants and penetrants[2]. The use of adjuvant types are strongly dependant on the physicochemical characteristics of the pesticide. Glyphosate isopropylamine (IPA), a non-selective zwitterionic herbicide active is suitable for controlling monocotyledonous and dicotyledonous weeds. This herbicide is absorbed through leaves and translocated into plant *via* phloem[3]. Concomitantly, the off-target deposition of glyphosate runs into soil and binds strongly with the soil particles to form ligand complexes thus unavailable for uptake. To reduce the pesticide dissipation, design on adjuvant system for the pesticide formulation is necessary.

Recently, due to the rising of environmental awareness, the use of sustainable resources and renewable-based adjuvants are becoming increasingly important criterion. Emulsion is proposed to be the formulation adjuvant due to its green characteristics. Emulsion contains oil phase and water phase which could be stabilized by surfactants. Oil phase could increase glyphosate's bioavailability when this water-soluble herbicide does not penetrate well into the waxy layers and cuticles[4]. Water phase provides a hydration and solubilization medium to suppress glyphosate crystallization in the foliar uptake[5]. Surfactant is capable of bridging oil and water, imparts herbicide a uniform spreading, increases it retention, penetration and improves rainfastness of spray droplets[6]. Palm oil esters (POEs), the long chain wax esters are non-irritant with high moisturizing property[7]. Renewable surfactant alkylpolyglucosides (APG) could replace largely dominated petrochemical-based adjuvants such as alkylbenzene sulphonates and alkylaryl ethoxylates for fostering sustainable agriculture. Ultimately, the combination of oil, water and surfactant could form nano-emulsion to aid glyphosate with enhanced absorption and penetration.

Market pesticide formulations are usually sold in concentrated form. Commercial glyphosate isopropylamine (IPA) is formulated in soluble liquid concentrate before its dilution and application to weeds. For emulsion-based formulation, optimization of the adjuvants composition in the emulsion is vital to decide the stability of formulation. The solubility/types of surfactant in the oil/water should be compatible with the herbicide[6]. The amount of oil and water in the formulation is equally important factor in affecting the glyphosate's bioactivity. Therefore, phase behaviour study of adjuvant mixtures for the pesticide formulation is the preliminary step and is crucial to determine physical characteristics of the mixtures which could contribute to the pesticide bioefficacy. In this study, phase behaviour of different formulation composition was conducted *via* construction of pseudoternary phase diagrams using single surfactants and surfactant mixtures.

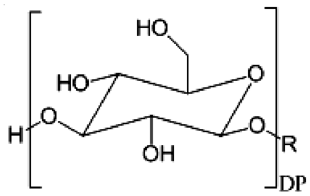
## EXPERIMENTAL

Surfactants alkylpolyglucosides (APG), dodecyl/tetradecyl/hexadecyl (68/26/6 (w/w)) polyglucosides (long-chain APG; LAPG) with a degree of polymerization (DP) = 1.6 and octyl/decyl/dodecyl/tetradecyl/hexadecyl (30/27/22/19/2 (w/w)) polyglucosides (middle-chain APG; MAPG) with a DP = 1.6 were gifts from Cognis (Malaysia). Surfactant polyoxyethylene (4) lauryl ether (Brij 30) with 98 wt % purity was purchased from Sigma-Aldrich (Germany). Palm oil esters (POEs) was synthesized in our laboratory using enzymatic transesterification of palm oil and oleyl alcohol[7]. Deionized water was prepared using Milli-Q water system from Millipore (USA). Pesticide active, aqueous glyphosate IPA with 62 wt % was provided by Crop Protection (Malaysia).

**Construction of pseudoternary phase diagrams:** Different nonionic surfactants were used in the emulsion-based formulation by constructing various pseudoternary phase diagrams using water titration method. A total of 0.5 g mixtures of POEs and surfactant were prepared at 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9 and 0:10 (w/w) in different ampoules. An amount of 5 % (w/w) water was added into the initial mixtures to form emulsion. Pesticide active, glyphosate IPA was added at 41 % (w/w) into the emulsion. The samples were vigorously shaken with vortex mixer Model VTX-3000L (Japan) and then centrifuged using Hermle Model Ettek (Germany) at 4000 rpm and room temperature (25 ºC) for 15 min. The centrifuged samples were visualized through two crossed polarized light for identification of physical phase characteristics. The above steps were repeated with increment of 5 % (w/w) water and then with increment of glyphosate IPA to 41 % (w/w) until the amount of POEs and surfactant was 0 % (w/w). Pseudoternary phase diagrams were constructed using mixed surfactants APG:Brij 30, with mixed surfactant ratios (MSRs) at 9:1, 8:2, 7:3, 6:4 and 5:5. The pseudoternary phase diagrams were constructed using software, Chemix version 3.5 phase diagram plotter (UK). The chemical structures of nonionic surfactants LAPG, MAPG and Brij 30 are shown in Fig. 1.

## RESULTS AND DISCUSSION

The phase behaviour of mixtures for formulation at different composition can be accurately predicted quantitatively by the construction of phase diagrams. For emulsions, the phase appearances are monophase; optically isotropic, homogenous, liquid crystals, gel network and multiphase[8]. Primarily, surfactant plays a crucial role for stabilizing oil and water




(a) Alkylpolyglucosides (APG), R = dodecyl/tetradecyl/hexadecyl (LAPG), R = octyl/decyl/dodecyl/tetradecyl/hexadecyl (MAPG)

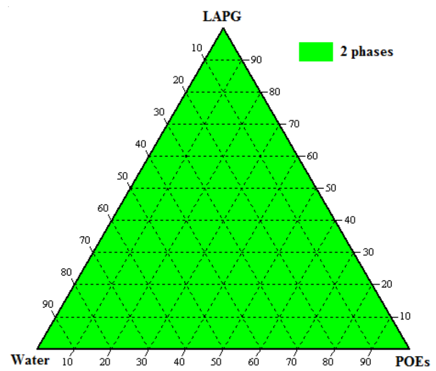
$C_{12}H_{25}(OCH_2CH_2)_4OH$

(b) Polyoxyethylene (4) lauryl ether (Brij 30)

Fig. 1. Molecular structures of (a) alkylpolyglucosides (APG): LAPG (R = dodecyl/tetradecyl/hexadecyl) (MW = 466.02), MAPG (R = octyl/decyl/dodecyl/tetradecyl/hexadecyl) (MW = 437.40) with DP = 1.6 and (b) polyethylene glycol dodecyl ether (Brij 30) (MW = 362.55)

to form emulsions either oil-in-water (o/w), water-in-oil (w/o) or bicontinuous structures[9]. These emulsions are used as carrier for optimizing the bioavailability of active ingredient in pharmaceutical, cosmetics, neutraceutical and agrochemical formulations. Therefore, the selection of surfactant is important to determine the phase characteristics of emulsion for formulation preparation.

Fig. 2 shows the pseudoternary phase diagrams constructed in the 59 % (w/w) emulsion system of POEs/single surfactant/water (manipulated variable) and 41 % (w/w) glyphosate IPA, as pesticide active (constant variable). Two-phase region was observed in the phase diagrams using homologue surfactants, LAPG (Fig. 2(a)) and MAPG (Fig. 2(b)) while three-phase region was obtained using Brij 30 (Fig. 2(c)). This indicated that the single surfactants were not suitable to stabilize the formulations to a monophase region. A hydrophilic-lipophilic balance (HLB) concept was adopted to assess the relative hydrophilicity of the surfactant head group to the hydrophobicity of the surfactant tail group. This concept influences the incorporation of oil and water in emulsion system and the stability of emulsion with glyphosate IPA. The HLB values of nonionic surfactants LAPG, MAPG and Brij 30 were 12.1, 12.8 and 9.7, respectively. Higher HLB value indicates higher hydrophilicity of the surfactant system. Glyphosate IPA behaved as zwitterionic compound thus high water content was used for the pesticide active solubilization. Consequently, O/W emulsion was used for incorporating 41 % (w/w) glyphosate IPA, in conjunction with the selection of hydrophilic surfactant's HLB values which was ranged from 9.6-17.6[10].




(a)

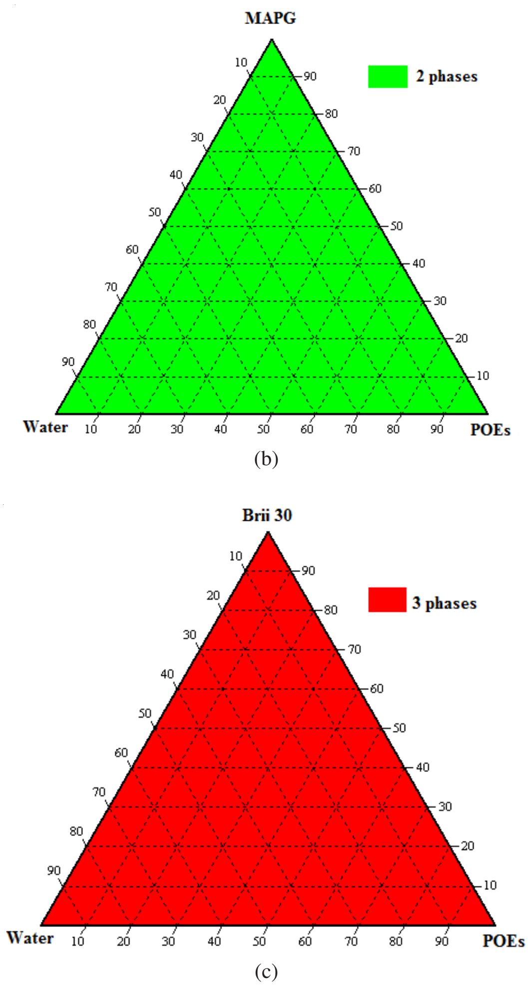
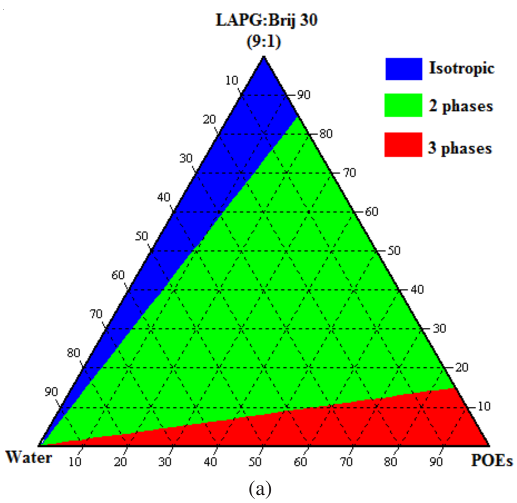
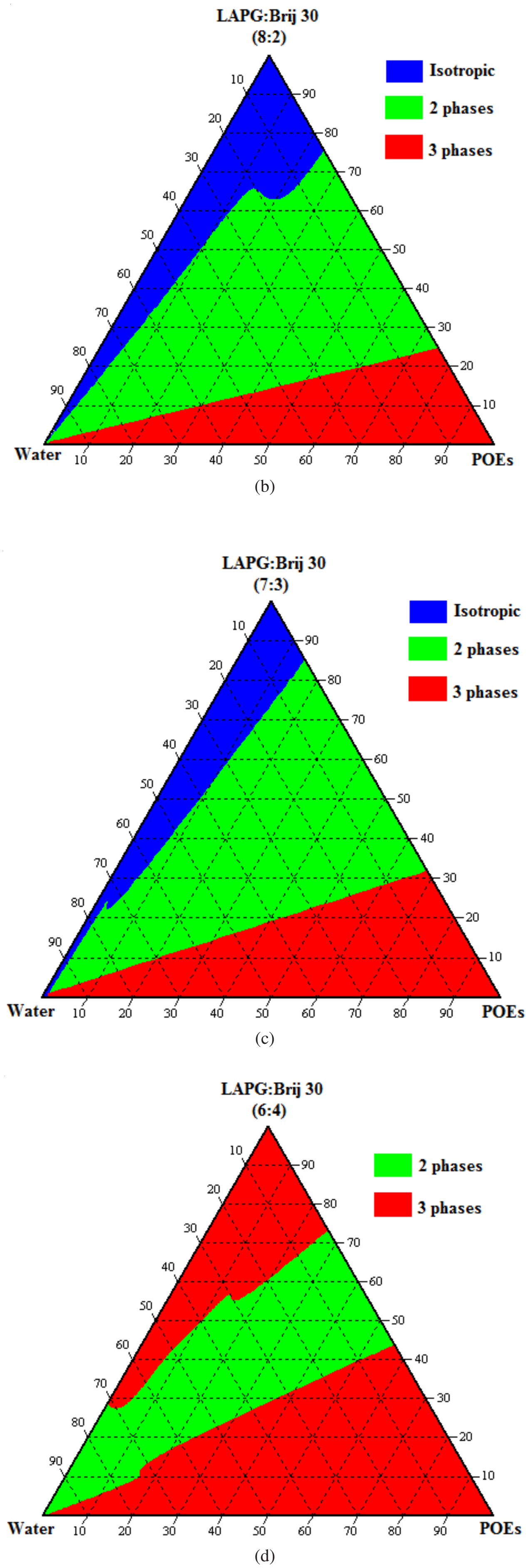
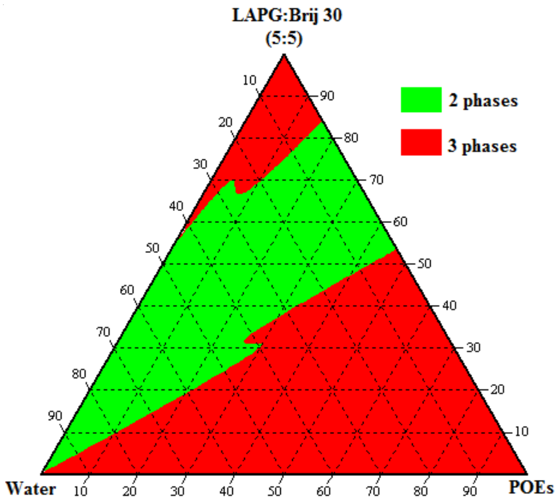



Fig. 2. Pseudoternary phase diagrams of system POEs/surfactant/water with 41 % (w/w) glyphosate IPA using: (a) LAPG, (b) MAPG and (c) Brij 30

Pseudoternary phase diagrams were developed with mixed surfactants LAPG:Brij 30 and MAPG:Brij 30. Fig. 3(a-e) shows the phase diagrams of emulsion system POEs/LAPG:Brij 30/ water with glyphosate IPA at mixed surfactant ratios (MSRs) 9:1, 8:2, 7:3, 6:4 and 5:5, respectively with corresponding HLB values at 11.86, 11.62, 11.38, 11.14 and 10.90. The HLB values of the mixed surfactant was calculated using Griffin's equation (eqn. 1)[11].





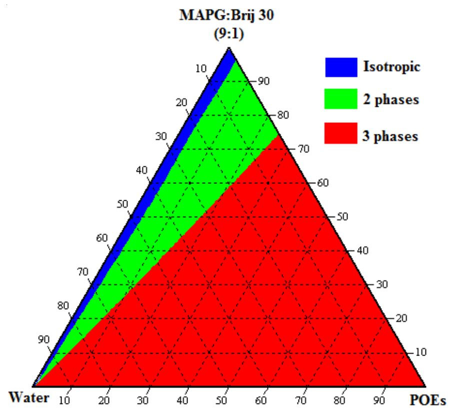

(e)

Fig. 3. Pseudoternary phase diagrams of system POEs/mixed surfactant/water with fixed 41 % (w/w) glyphosate IPA using LAPG:Brij 30 at MSR: (a) 9:1, (b) 8:2, (c) 7:3, (d) 6:4 and (e) 5:5

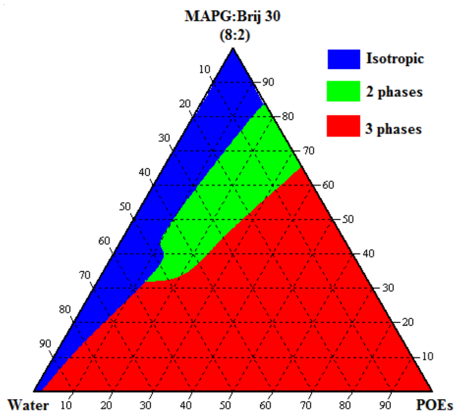
$$\text{HLB}_{\text{mix}} = \frac{(\text{wt \% of surfactant A})}{100} \times (\text{HLB}_A - \text{HLB}_B) + \text{HLB}_B \quad (1)$$

Isotropic region, a monophase liquid state was successfully obtained in the phase diagrams at MSRs 9:1, 8:2 and 7:3. Mixed surfactants exhibited synergism due to the nonideal mixing effects which substantially reduced the interfacial tensions in emulsions and imparted the stable formulations[12]. Mixture of nonionic surfactants APG with organosilicone was reported to exhibit distinctive micelle structures of multilamellar vesicle and wormlike network than APG alone with rodlike micelles[13] thus the disparity of micelles contributing to the formation of isotropic region. The largest isotropic region was at MSR 8:2 (HLB = 11.62) which indicated that the highest amount of POEs incorporated in the emulsions was at mixed surfactant:POEs ratio 8:2. Palm oil extracts provides wetting behaviour which could suppress the formation of glyphosate crystals thus the increase of herbicide uptake. Palm oil extracts as the oil phase in the emulsions could improve the hydrophilic herbicide adsorption and penetration *via* hydrophobic cuticle and waxy layer of leaves.

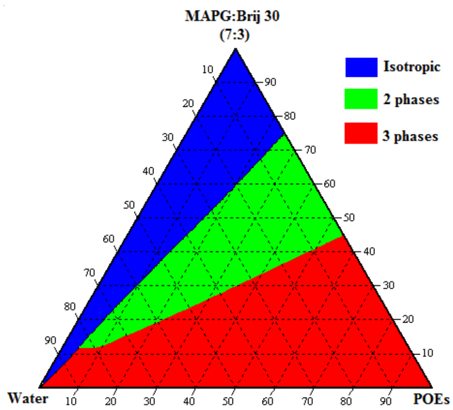
Fig. 4(a-e) shows the pseudoternary phase diagrams using mixed surfactant MAPG:Brij 30 at MSRs 9:1, 8:2, 7:3, 6:4 and 5:5, respectively, with the corresponding HLB values 12.49, 12.18, 11.87, 11.56 and 11.25. The isotropic region was obtained at MSR 9:1, increased at MSR 8:2, achieved the largest region at MSR 7:3 (HLB = 11.87) and greatly reduced at MSR 6:4. The MAPG:Brij 30 produced largest isotropic region at MSR 7:3 using higher Brij 30 concentration than the homologue mixed surfactant, LAPG:Brij 30 at MSR 8:2. The decrease in alkyl chain length thus the hydrophobicity of the MAPG in mixed surfactant system was replaced by the increase of lipophilic Brij 30 concentration. The appearance of isotropic region was at the mixed surfactant-water axis which indicated that the formulations were stable at high mixed surfactant content with less amount POEs. Increase of POEs content towards the triangular corner of POEs, changed formulations into two phases and then further to three phases.



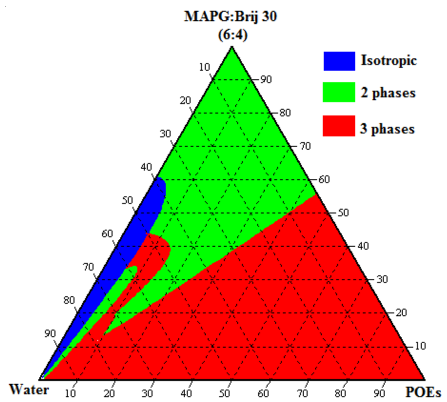

(a)



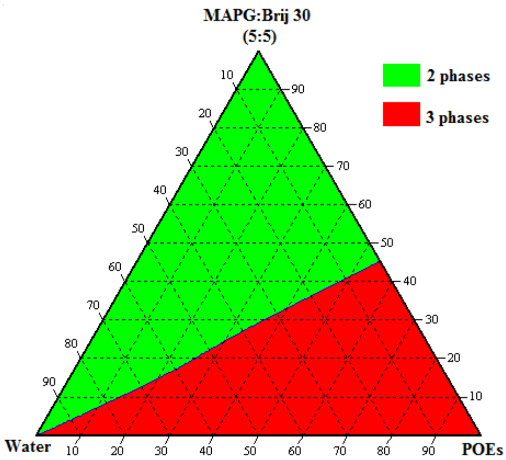

(b)




(c)




(d)




(e)

Fig. 4. Pseudoternary phase diagrams of system POEs/mixed surfactant/water with fixed 41 % (w/w) glyphosate IPA using MAPG:Brij 30 at MSR: (a) 9:1, (b) 8:2, (c) 7:3, (d) 6:4 and (e) 5:5

## Conclusion

The pseudoternary phase diagrams showed that monophasic isotropic regions were obtained using mixed surfactant systems of LAPG:Brij 30 and MAPG:Brij 30. The HLB value range of the mixed surfactants LAPG:Brij 30 and MAPG:Brij 30 for obtaining stable isotropic regions was 11.38-12.49. This monophase could be used in the optimum selection of stable pesticide formulations.

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