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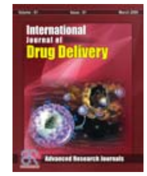

Research Article

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Study of Pseudoternary Phase Diagram Behaviour and the Effect of Several Tweens and Spans on Palm Oil Esters Characteristics

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Abstract

Palm oil esters are high molecular weight esters oil that has been newly synthesized by University Putra Malaysia researchers. It has received a lot of attention for its pharmaceutical and chemical application. The aim of this study is to study the effects of the palm oil esters with different HLB surfactant mixture on the ternary diagrams behaviour and to confine the various systems resulted from these combinations. These systems include traditional emulsion, gel area, transpernat micro-emulsion area, O/W and W/O emulsions. In this study, pseudoternary phase diagrams of water, POEs and non-ionic surfactant mixture of several HLB values were constructed using water titration method. The resultant mixtures collected after each addition and mixing of water were analysed visually, along with conductivity, dilution in water and dye test (methylene blue) to classify them as O/W emulsion (transparent and opaque) or W/O (opaque) and liquid or gel. As a conclusion, palm oil esters were found to be suitable for the formulation of different types of emulsion. Additionally, different HLB value of non-ionic surfactant(s) exhibited different pseudoternary phase diagram characteristics.

Keywords: palm oil esters, Tween, Span, Pseudoternary phase diagram, O/W emulsion

Introduction

Palm oil esters (POEs) are constituent of a modified form of Palm olein oil known simply as palm oil. It is a main and important agriculture commodity of which received great attention from researchers especially Malaysian researchers. Palm oil is a derivative of the fruit of the palm tree Elaesis guineenis that is constituted from even carbon numbers fatty acids [1,2]. Structurally, palm oil is a mixture of triglyceride compounds. Palm oil is edible oil and is used through out the world as main ingredient in many food products. Palm oil, as a raw material, had also attracted many researchers to study its use in topical delivery products and in the effort to synthesize new derivatives with beneficial properties for chemical and pharmaceutical applications. Universiti Putra Malaysia (UPM) had led the way in the production of new

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derivatives of palm oil [3]. Palm oil had been discovered to react with oleyl alcohol and the reaction was catalysed by the use of lipase enzyme to produce POEs contained high molecular weight esters of alcohol with an even number of carbon ranging from 12-32 [4].

It was found that POEs has skin hydration activity of 40.7% after 90 minutes of its application [2]. The emollient effect of POEs had been proven thereby making this oil highly recommendable for its incorporation into the topical preparation as oil phase.

Generally, emulsion, micro or nano-emulsion are dispersed systems of different ratios of oil, surfactant(s) and aqueous phase. Pseudoternary phase diagrams can be used to show the influence of changes in the volume fractions of the different phases on the phase behavior of the system. Micro or nano-emulsions are clear, stable, isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant. The region or composition of micro-emulsion is usually defined or identified by constructing ternary-phase diagrams. In this study, we undertook the project in collaboration with Basri M et al of Universiti Putra Malaysia to study the effect of different non-ionic surfactants with different HLB values on pseudoternary diagrams of palm oil esters and water as external phase.

Materials and Methods

Materials

Palm oil ester was a gift from UPM. Tween 80, Tween 85, Span 20, Span 85 and sodium benzoate were purchased from Sigma-Aldrich (USA).

Method

The study achieved with the assessment of POEs for use as the emulsion´s oil phase by constructing various pseudoternary phase diagrams of oil phase, water and surfactant of different HLB values by using water titration method. Mixtures of oil and surfactant(s) were prepared at ratios of 9.5:0.5 to 0.5:9.5 and 0:10 in separate containers. Distilled water (DW) was added in amounts equal to 5% w/w of the initial of the mixture into each container, followed by mixing for 5 min. After each addition and mixing of water, 0.5 gm of the resultant mixture was removed for analysis purpose and 0.5gm of (DW) was added to the remaining mixture in the container and mixed untill reaching the maximum water content (the amount of oil phase in the mixture is almost 0%).

The types of emulsions formed were confirmed by electrical conductivity and microscopic examination of emulsion stained with methylene blue which is known as the water soluble dye method. The visual qualities of the mixtures were noted as opaque or transparent fluid or as viscous cream. Gel was physically identified as the formulae that do not flow if the container is tilted at 90°. To facilitate the accurate evaluation of the mixtures physical state, air bubbles were cleared by sonication method. All the mixtures forming O/W transparent systems were marketed and plotted onto the triangle graph as the O/W micro-emulsion area. Similarly, all other mixtures of W/O (opaque), O/W (opaque) and gel were marketed and plotted to represent the three respective areas in the ternary phase diagram.

Six pseudo-ternary phase diagrams were constructed each representing the phase diagram of water, oil and surfactant or it´s mixture having specified HLB value. HLB 15 pseudo-ternary phase diagram was constructed by using Tween 80 as the emulsifier. HLB 11 pseudo-ternary diagram was constructed using Tween 85 as single emulsifier. Mixtures of Tween 80 and Span 20 in ratios of (80:20), (53:47) and (6.25:93.5) were used to construct ternary phase diagrams of mixtures containing the emulsifier having HLB values of 13.72, 12 and 9 respectively. Additionally, a mixture of Tween 80 and Span 85 in a ratio of 77:23 was used to construct the phase diagram of mixture containing HLB 12 emulsifier.

Results and Discussion

The mixing of oil, water and surfactant in different ratio, can produce different types and structures of emulsion and micro-emulsion systems. They depend on the chemical nature, molecular structure and concentration of surfactant and other ingredients. Surfactant type plays a major role in determining the rheological properties and droplets size of the systems [5]. Similarly, oil type whether it is triglyceride form or long chain hydrocarbon can change the physical properties of the systems. Oil can affect the interfacial tension and surface pressure as well as the stability of the system [6, 7].

This study is concerned with the evaluation of palm oil ester as the internal phase of O/W cream for topical application. The rheological properties and types of emulsion, micro-emulsion and gel produced by mixture of POEs, water and surfactant at various HLB values were assessed to select the promising O/W cream formulae. Those exist as gel formulae were the preferable ones as they are semisolid preparations and are suitable for topical applications. Surfactants present at certain percentage have the ability to build the gel structure within the emulsion system without addition of any polymer or thickening agent [8].

POEs is a modified long chains esters of palm oil triglyceride which is safe for normal consumption. Non-ionic surfactants in general and Tween and Span in particular are safe agents for all biological tissue in general and for skin in specific [9, 10]. These non-ionic emulsifiers are compatible with various ingredients used in the preparation of emulsions and are not affected by pH. They supposed to have an enhancement effect on the skin barrier [11]. Combination of lipophilic and hydrophilic non ionic surfactants is able to build highly structured emulsion [12, 13].

Different combinations of oil, surfactants and water when mixed together produce either traditional emulsion or micro-emulsion in the form of O/W or W/O. Bicontinuous system can also be formed in case of micro-emulsion system where each phase of water and oil is found as a continuous phase [14].

Construction of pseudoternary phase diagrams is the best way to study all types of formulations that can originate from mixing of surfactants, water and oil and these diagrams can cover the whole probabilities of mixing ratios. Fig.s 1.1 to 1.6 are phase diagrams of mixtures of POEs, water and surfactant or its mixture of HLB 15, 13.72, 12, 12, 11 and 9 respectively. All figures showed the presence of a transparent micro-emulsion area with the exception of Fig. 1.6 representing the diagram for mixture of oil, water and surfactant mixture of HLB 9. The transparent micro-emulsion areas were found to be attached to the margins of diagrams where water or oil ratios are low and the surfactant ratio is high. From conductivity measurements, it can be found that each point in the transparent micro-emulsion areas was able to conduct electricity and when tested with agent methylene blue solution, it was found to have a blue background of methylene blue with oil droplets dispersed in it, indicating that the system is O/W micro-emulsion. Formation of micro-emulsion system by using nonionic surfactant or mixture of nonionic surfactants, were reported by many researchers [15, 16].

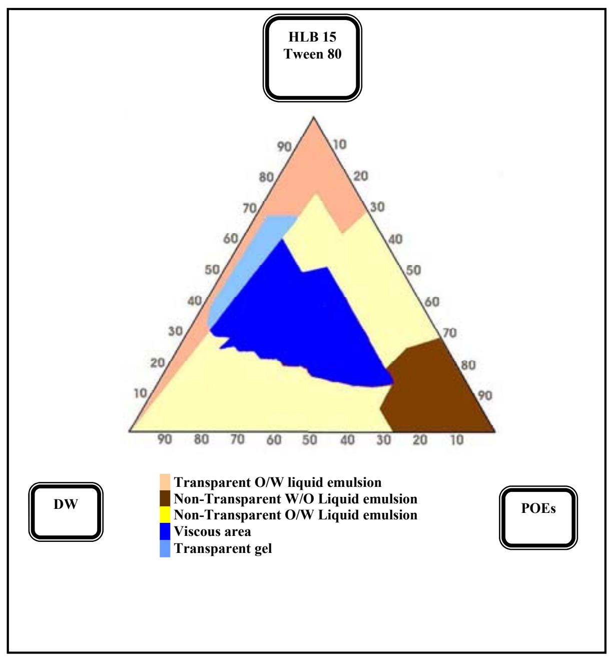

Fig 1.1

Pseudoternary phase diagram produced from mixtures containing surfactant of HLB 9 showed no transparent O/W micro-emulsion area and no gel area. On the other hand, it exhibited the biggest W/O area. The absence of transparent

O/W micro-emulsion might reflect the insufficient association of the mixed surfactants at the interface [17]. In this case, the amount of Tween 80 might not be enough to form a mixed surfactants layer at the interface that is responsible for producing the micro-emulsion system. The phase diagrams obtained also showed that areas of W/O dispersions decreased as the HLB value of the surfactant system increased, reaching the smallest area at HLB 15. This is in accordance with the theory of HLB of surfactant which stated that surfactant used has more tendency to produce the emulsion type in which it is more soluble in the external phase [18].

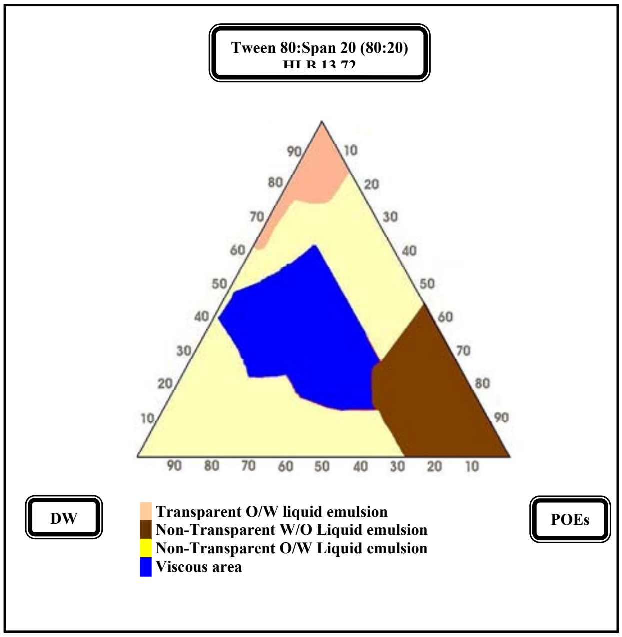

Fig 1.2

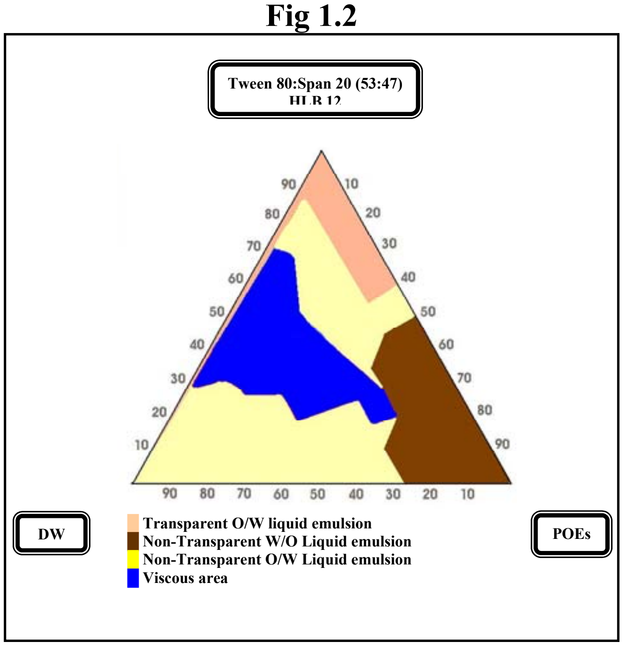

Fig 1.3

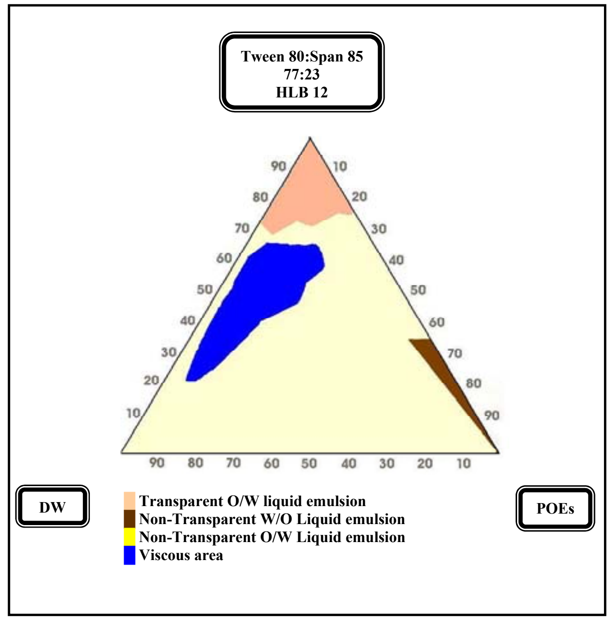

Fig 1.4

From Fig.s 1.1, 1.2, 1.3, 1.4 and 1.5, it is evident that gel area is formed when the water content in the system was in the range of 25 to 60%. It was found that water content below 25% is insufficient to hydrate the polyoxyethylene groups which are critical for the swelling of surfactant chains to demonstrate the gel structure. Accordingly, water content of more than 60% will increase the distance between the polyoyethylene groups an destabilize the gel structure leading to breaking of the swelled gel [19]. The phase diagrams for mixture containing surfactant HLB12, 13.72 and 15 as represented by Fig.s 1.1, 1.2 and 1.3, illustrate that increasing the concentration of surfactant results in stronger and more rigid gel-emulsion structure.

Pseudoternary diagrams containing Tween 80 alone and those containing mixtures of Tween 80 (HLB 15) and Span 20 (HLB 8.6) exhibited higher gelly area compared to mixtures of Tween 80 and Span 85 (HLB 3). The results showed that

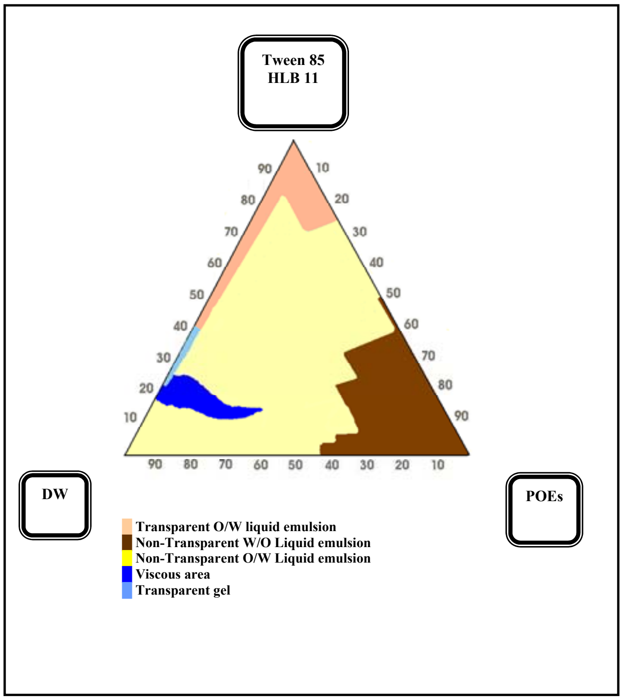

Fig 1.5

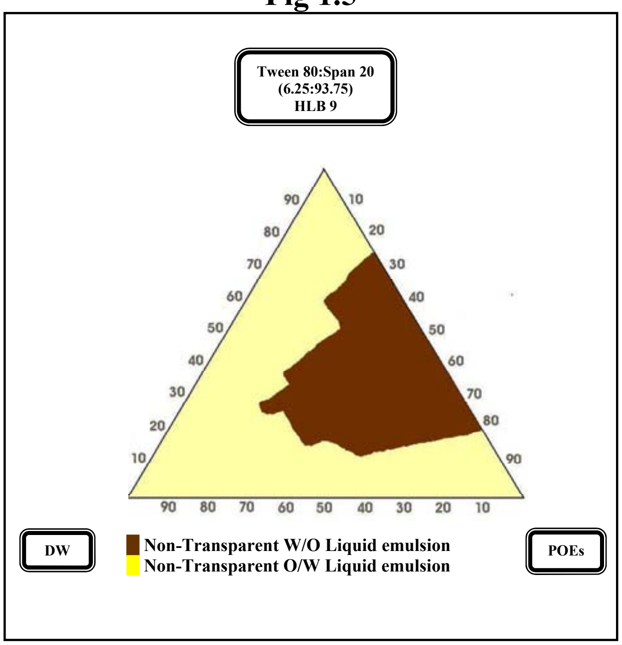

Fig. 1.6

at very low concentration of oil and high concentration of water and surfactants mixture, mixture of Tween 80 and Span 85 having HLB value of 12 formed smaller gel area than that of the mixture of Tween 80 and Span 20 having HLB value of 12. Since the mixture of Tween 80 and Span 85 formed a small viscous gel area, this surfactants combination was excluded from further study. The results obtained indicated that a mixture of two non-ionic surfactants with big difference in HLB values between them might not be able to produce stable preparations. This may be due to the fact that the majority of surfactant molecules with very low HLB value dissolved in the oil phase and the surfactant with high HLB value dissolved more in the water [20] that enables them to function together well enough, thus exerting less synergistic effects than mixture of surfactants having closer HLB values.

Fig. 1.5 (HLB 11) containing Tween 85 alone as surfactant was constructed for comparison with Fig. 1.1 of HLB 15 containing Tween 80 alone. When Tween 85 was used, the gel area formed was smaller than when the surfactant was Tween 80. Tween 85 with tri-oleate ester chains is expected to be more soluble in the internal oil phase. This would lead to insufficient numbers of polyoxyethylene chains available to form H-bonds at the interface and the external phase [21]. These results indicated that Tween 80 would be a better surfactant than Tween 85 for formulating emulsions especially those with gel properties.

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