LINOLEIC ACID INFLUENCE ON RHEOLOGICAL BEHAVIOR OF CONCENTRATED OIL IN WATER EMULSION BASED MIXED NONIONIC SURFACTANT SYSTEMS

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ABSTRACT

Oil in water concentrated emulsion of mixed glucopon 215 and brij 30 surfactant systems was prepared via phase inversion concentration method. The ratios of glucopon 215 to brij 30 and mixed surfactant to water was fixed at 3:7, whilst the oil dispersion of isopropyl palmitate was varied between 70 to 90 wt%. Linoleic acid (LA) was incorporated at constant concentration (10 wt%) in oil phase to investigate the effect of LA on the viscosity and viscoelastic response of the emulsions. Droplets size of emulsion was measured by zeta nanosizer. The type of droplets was confirmed by the increasing of size as a function of oil content. The size was found to be ranging from 0.6 – 1 μm and has slightly increased after 7 month storage under room temperature. Incorporation of LA into emulsion droplets has reduced the droplets size. This is due to increased of interfacial tension at emulsion droplet core provided by polar domain of LA. Rheological properties studies showed that the concentrated emulsions are viscoelastic. The elastic storage, G' was significantly increased with increasing of oil content. However, the G' value was drastically decreased with the presence of LA. Oxidative stability of LA in oil in water concentrated emulsion through formation of conjugated diene and peroxide value as a function temperature were also carried out.

***Keyword**: mixed nonionic surfactant; concentrated emulsion; rheology; oxidative stability;*

INTRODUCTION

Concentrated emulsion or popularly known as high internal phase emulsions (HIPEs) are classed as emulsions with an internal phase volume above 74.05% (Lissant and Mayhan, 1973). Because the droplet sizes are of the order of 1 μm in diameter, their formation requires more surfactant than that for the preparation of typical emulsions, and the systems display gel-like properties. They have a number of actual and potential applications, some of which are mayonnaise in food, gels and creams in cosmetic products, and petroleum gels as safety fuels, (Cameron and Sherrington, 1996). Essential oils such as linoleic acid are commonly used in cosmetic product and dermatology due to their skin's barrier function and restorative properties. However, its sensitivity to oxidation and tendency to go rancid prevent its use in cosmetic preparations. Fundamental studies of its behavior in emulsion properties will opens up the possibility of using linoleic acid in various cosmetic formulations and personal care products.

Materials and Method

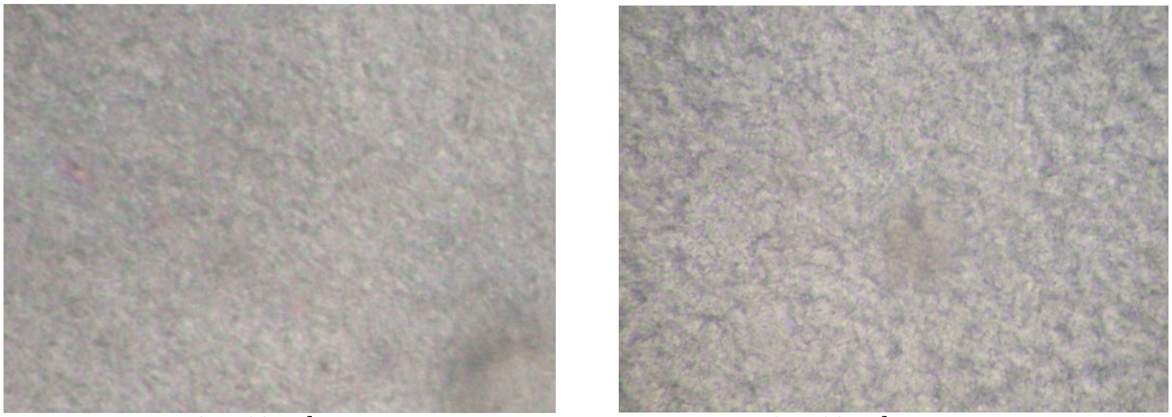
Glucopon 215 (G-215) represents a mixture of α- and β-glucosides (a) and is supplied as a 65 wt% solution in water. The surfactant was used without any further purification. Linoleic Acid, Isopropyl palmitate (IPP), and Brij 30 were purchased from Fluka. The water used in this study was double distilled. The G-215 was prepared by weighing the surfactant into a glass bottle and diluting it to the desire concentration with water by taking into account that the G-215 is a 65 wt% solution in water. Concentrated emulsion phases were prepared through phase inversion concentration method. An amount of oil solution (containing weight percent of Brij 30 in IPP) was continuously added into fixed amount of aqueous solution (containing weight percent of G-215 in water) in screw cap glass tubes to the desired final composition ratio under vigorous mixing using vortex mixture at room temperature (25^{o}C). The well-mixed samples were then centrifuged to remove the bubbles and to confirm the formation of highly viscous of concentrated emulsion. In order to study the effect of LA, 10 wt% of LA was firstly added into IPP before preparing the oil solution. The type and mean size of droplet was identified using optical microscopy and zetasizers nanoseries (Malvern, UK). Rheological measurements were performed with a PAR PHYSICA rheometer. Steady flow and dynamic scillation experiments were carried out at 25 ± 0.1^{o}C. Oxidative stability of LA in oil in water concentrated emulsion through formation of conjugated dienes and peroxide value as a function of temperature were also carried out.

RESULTS AND DISCUSSIONS

Figure 1 showed the optical microscopy of concentrated oil in water emulsion at 70 wt% and 90 wt% of oil. It was observed that the emulsion was very closely packed and concentrated. No oil droplets of sphere form were observed. The emulsion is categorized as concentrated oil in water emulsion due to the large amount of oil content (70 to 90 wt%) can be incorporated into the phase. This type was confirmed by diluting the emulsion with oil and water separately. The mean droplet size of emulsion at different oil content, without and with the presence of 10 wt% LA in oil phase are summarized in Table 1. Result shows a direct relationship between oil content and mean size of emulsion droplets. However, incorporation of LA which is slightly polar molecule into oil phase has interrupted the microstructure of emulsion. The emulsion phase at 70 wt% of oil was breakdown and becomes to two phase. Though emulsion phase at higher oil content is not changed upon incorporation of LA, but its droplets size is significantly decreased almost 2-fold especially for emulsion at 80 wt% of oil.

Flow curve studies, the steady-state shear viscosity was plotted against the shear rate, γ^* as shown in Figure 2. All emulsions studies show shear thinning responses, and the shear viscosity beyond the shear rate of 0.1 s^{-1} decreases with the slope of -0.59 and -0.93 for low (70%) and high (80% and 90%) oil content, respectively. This is due to colloidal structure breaks down while shear rate increases, displaying reduced viscosity (Barnes, 1999). Direct relationship of shear viscosity and oil concentration at low shear rate (below 18.18 s^{-1}) exhibits the role of droplet size. Viscosities of dispersion systems are well-known to strongly depend on the volume fraction of the dispersed phase in the continuous phase (Masami et. al., 2000). On the other hand, the shear viscosity of the emulsion prepared slightly decreases with incorporation of 10 wt% LA in oil phase indicating the alteration in microstructure of the emulsions. The addition of the LA modifies the viscosity values of the emulsions but their dependence on shear rate is similar.

The behavior of the concentrated emulsion in a small amplitude oscillatory shear flow offers an opportunity to study macroscopic properties, such as ability of such structures to store (*G'*) and dissipate (*G"*) energy, which is important to the emulsion for stability, processing, transportation, and storage. Representative data of the dynamic frequency sweep measurements performed in the



70 wt% Oil 90 wt% Oil

Figure 1: Optical microscopy image of o/w concentrated emulsion at different oil content at 25^{o}C.

Table 1: Mean Droplets Size.

Oil Content (wt%)	Without LA		10 wt% LA	
	Size	Polydispersity	Size	Polydispersity
70	624.03	0.57	-	-
80	817.00	0.50	464.07	0.53
90	991.95	0.75	637.07	0.59

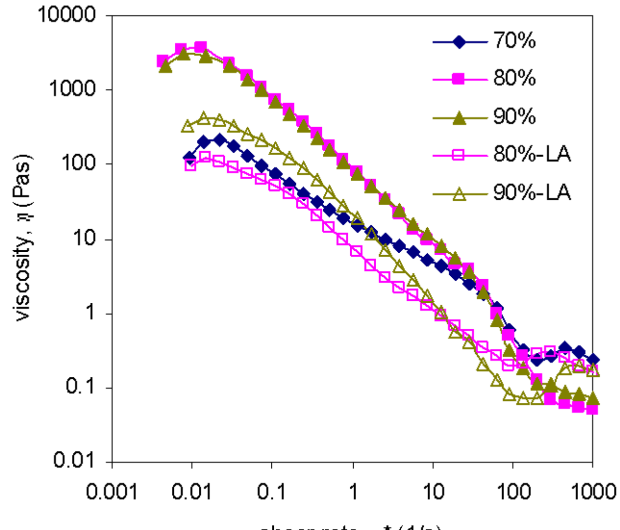
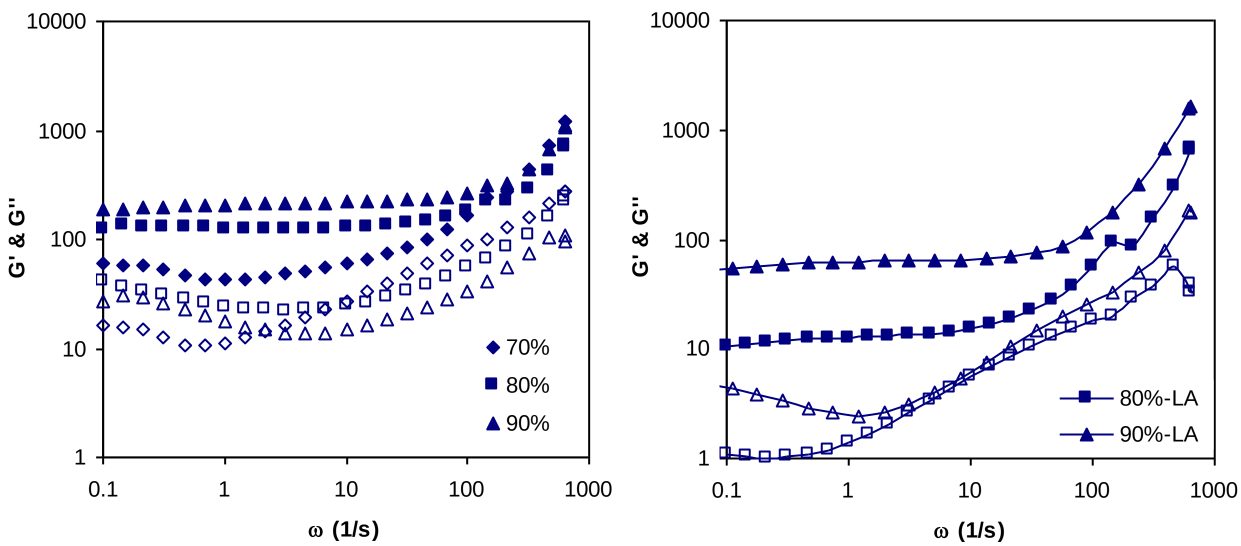


Figure 2 : Flow curve and of concentrated oil/water emulsion for different oil content at 25°C; with and without the presence of 10 wt% LA.



(a) (b)

Figure 3 : Frequency sweep of concentrated oil/water emulsion for different oil content at constant strain (5%); (a) without and (b) with the presence of 10 wt% LA at 25°C. (G', solid symbols and G", open symbols)

concentrated gel emulsion varying oil concentration at a fixed mixed surfactant/water (1/1) and G-215/Brij 30 (3/7) ratios, absent and present of LA (10wt%) are presented in Fig. 3(a) and (b), respectively. The *G'* is nearly constant in the whole frequency or slightly increases at higher frequency (especially at high oil content) but dominating over the *G" wi*thin measured frequency range indicates gel type structure (Ross-Murphy, 1995). Furthermore, the increase of oil content leads to the increase in G' value. At close range the adhesive nature of the interaction between the layers contributes to the microstructure and rheology of concentrated emulsions. The presence of LA into oil phase of emulsion droplet has disrupted the microstructure in which the system being less elastic by about a factor of 4.

Oxidative stability studies of linoleic acid in concentrated emulsion are performed through conjugated diene (CD) and peroxide value (PV) measurements as shown in Figure 4. The emulsion at two different oil content which are 80 and 90 wt% oil were namely as E-80 and E-90, respectively. Both emulsions were compared with their control emulsion counterpart (in the presence of 1 wt% BHT). At room temperature, the increment of CD formation relatively to its control emulsion of E-80 was higher compared to E-90. The CD formation of E-80 has reached the optimum value at 35^{o}Ct. Meanwhile, for E-90 it has reached a plateau after 35^{o}C. For control emulsion, the CD of E-80 was only drastically increased at 75^{o}C and it was seemed to be consistent for E-90. No significant changes of PV as a function of temperature for E-90 compared to gradually increase for E-80 reflects the greater oxidative stability of E-90. The results showed that the oxidation in emulsion is influenced by the size of the oil droplets. Small droplet size signifies a large surface area, implying a high potential of contact between diffusing oxygen, water soluble free radicals and antioxidants, and the interface (Laurent, et. al. 2002).

CONCLUSIONS

The increase of emulsion droplets of higher oil content resulting in lower surface area pervolume of droplets, thus prevent the radical from attacking the active site of lipid molecule. Thus, the results should provide useful information on the role of participants of LA in concentrated emulsion properties that can be applied in industrials emulsion generally and cosmetic or food industry particularly.

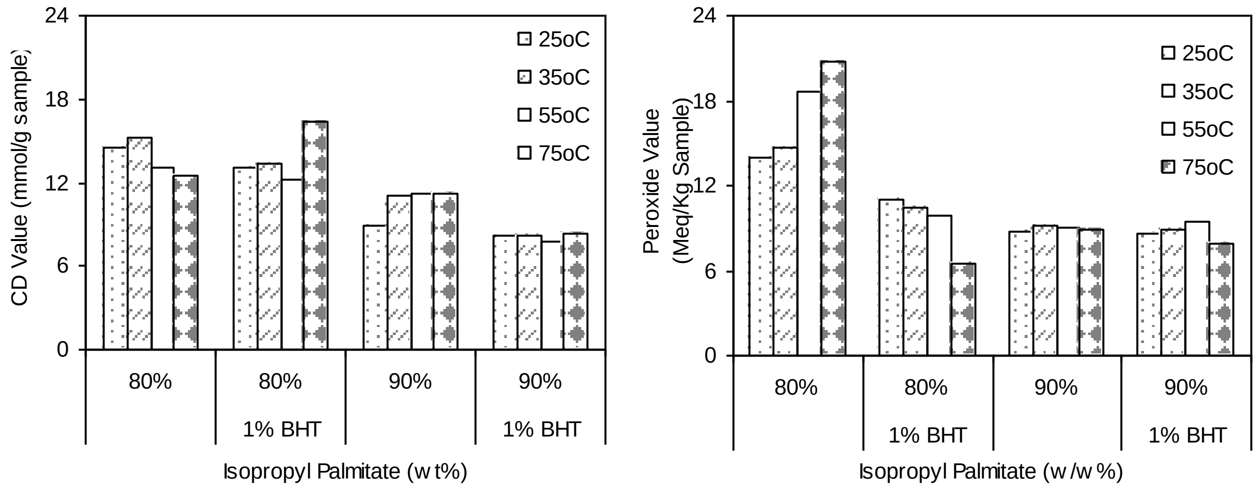


Fig. 4 : CD and PV of concentrated o/w emulsion as a function of temperature (incubation for 1 hour at each temperature point).

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