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Emulsion Properties of Mixed Tween20-Span20 in Non-Aqueous System

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ABSTRAK

Emulsi minyak-dalam-gliserol (O/G) telah disediakan dari campuran surfaktan Tween20-Span20 dengan nisbah berat yang berbeza. Emulsi O/G didapati terbentuk bila kandungan minyak kurang dari 50 wt% dengan kepekatan campuran Tween20-Span20 3 wt%. Sifat-sifat fizikal emulsi ditentukan dengan mengguna mikroskop, penganalisis partikal dan pengukuran reologi. Kajian perkaitan antara nilai HLB campuran Tween20-Span20 dengan kestabilan emulsi juga dilakukan.

ABSTRACT

Oil-in-glycerol (O/G) emulsion was prepared in the presence of different weight ratios of mixed Tween20-Span20 surfactants. O/G emulsion was observed to form below 50 wt% of oil content at 3 wt% of mixed Tween20-Span20 surfactants. Physical properties of the emulsion were determined by using a microscope, particle counting and rheological measurement. An attempt to correlate HLB values of mixed Tween20-Span20 with emulsion stability was also carried out.

Keywords: Tween20, Span20, nonaqueous emulsion, droplets size, stability, rheology

INTRODUCTION

Emulsions have been defined as heterogeneous systems of one liquid dispersed in another in the form of droplets usually exceeding 0.1 μm in diameter. The two liquids are immiscible, chemically unreactive, and form systems characterized by a minimal thermodynamic stability. One of the important components for making an emulsion is the emulsifier, and a systematic selection of emulsifier type for a particular emulsion is frequently based on the hydrophilic-lipophilic balance (HLB) concept (1). It is known that mixtures of emulsifiers can have

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*To whom correspondence should be addressed synergistic effects in enhancing stability of emulsions. A suitable combination of emulsifiers leads to a greatly enhanced stability as compared to individual emulsifiers (2). Various reasons have been given for this, such as formation of intermolecular complexes at the oil/water (O/W) interface (3) and development of strong interfacial films that prevent coalescence by virtue of their high dilational elasticity (4).

Water-in-oil (O/W) and oil-in-water (O/W) emulsions have been widely studied since emulsion was recognized. In contrast, oil-in-glycerol (O/W) emulsion has not been fully explored and therefore remains rather limited. Thus, this paper presents some of the physical properties (emulsion stability, droplet size and flow behaviour) of a non-aqueous emulsion formed by mixing Tween20 and Span20.

MATERIALS AND METHODS

Materials

Polyoxyethylene (20) sorbitan monolaurate (Tween20) and sorbitan monolaurate (Span20) from Sigma were used as received. Glycerol (G) of 99.5% purity purchased from Sigma was also used throughout the experiment. Medium chain triglyceride (MCT) oil, obtained from a local manufacturer, was used as an oil phase.

Methods

Preparation of Emulsion

O/G emulsion was prepared by first dispersing a required amount of mixed emulsifier (Tween20-Span20) in glycerol (9.0 ml). The MCT oil (1.0 ml) was then added and the mixture was homogenised (using an IKA-T25 disperser) for 3 min at 8000 rpm to produce an emulsion. The emulsions were kept at 30.0±5°C for 24 hours to equilibrate before being analysed. The emulsifiers were blended together, to obtain HLB values within the range 8.7-16.7. HLB of mixed emulsifiers can be calculated as follows:

$$HLB_{mixture} = f\,HLB_A + (1-f)HLB_B \quad (1)$$

Where f is weight fraction of emulsifier A and (1-f) is weight fraction of emulsifier B.

Particle Size

The O/G emulsions samples were viewed directly under a microscope (Olympus AX70) with a camera attached, and the stage of the microscope was thermostatically controlled. The undiluted samples were placed on a slide and were illuminated from below, i.e. transmitted light was used. The droplet sizes of emulsions were subjected to a laser light scattering instrument (Malvern Zetasizer 5000) for particle size determination.

Viscosity Measurement

The steady flow behaviour was studied using a Brookfield Rheometer (Model DV-III), which was attached to a cone and plate sensor system. The samples were allowed to reach the required test temperature in a suitable sensor system. Subsequently, the rheometer was operated at a steady rate and the shear rate was increased gradually from 1 and 250 $^{s-1}$ and then decreased back to 1 $^{s-1}$ over a period of scanning time. The flow behaviour of O/G emulsions systems containing different MCT:G ratio at 3% wt/wt of mixed emulsifiers was studied.

RESULTS AND DISCUSSION

The results of emulsion stability through visual observation in Table 1 showed that the emulsion was stable in the range of 10:90 to 30:70 of MCT:G ratios. The emulsions were unstable at higher content of MCT (i.e. 40:60 and 50:50 of MCT:G ratios). This might be due to the collapse of oil droplets in the emulsion system. Comparison among different weight ratios of mixed surfactants, 20:80 weight ratio of Tween20-Span20 system has the smallest stable emulsion region (between 10:90 and 20:80 of MCT:G ratios) as observed under a microscope. The decrease in emulsion region might be due to the strong repulsion between Tween20 and Span20 at the oil-glycerol interface, which was not able to retain the increase of oil droplets in the system.

Fig. 1 shows the variation of the emulsion droplets size of different HLB numbers for 10:90 of MCT:G weight ratio. On the first day, the droplet size increased with the increase of the HLB number. This means the increase of the HLB number - increase of Tween20 - played an important role in the increment of oil droplet in the continuous phase. On the seventh day, it was observed that the oil droplet at lower HLB numbers (8 to 13) increased to about the size of higher HLB numbers (13 to 16.7). This was due to the coalescence of the oil droplet cluster to form a more stable droplet. In contrast, there was no change in the droplet size of higher HLB number. The particle size was rather constant as compared to the first day. This suggests that the oil droplet in the emulsion

TABLE 1

Emulsion stability of mixed surfactants (3 wt%) in MCT/G emulsion systems

Tween20-Span20 (HLB)	MCT-in-G (%) 0:100	10:90	20:80	30:70	40:60	50:50
100:0 (16.70)	clr	S	S	S	B	B
80:20 (15.11)	clr	S	S	S	B	B
60:40 (13.82)	clr	S	S	S	B	B
40:60 (12.26)	clr	S	S	S	B	B
20:80 (10.41)	clr	S	S	B	B	B
0:100 (8.60)	clr	S	S	S	B	B

* clr -clear solution; S - stable emulsion; B - emulsion break

system was more stable even after seven days. This implied that the emulsion was more stable with the increase of Tween20 as it did not affect the oil droplet size.

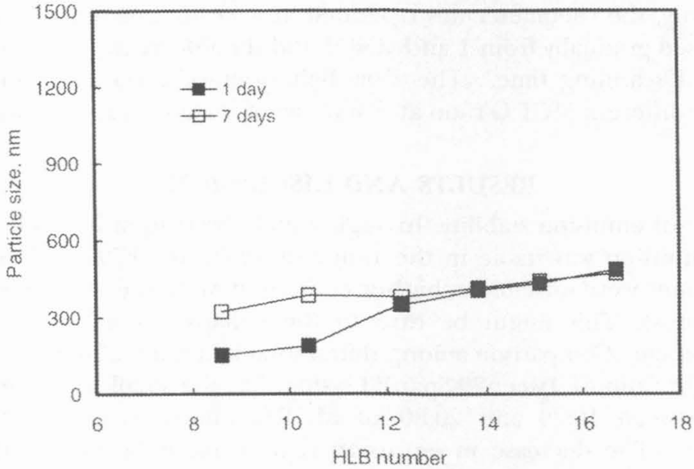

Fig. 1: O/G emulsion in mixed surfactants system of various HLB values (MCT:G, 10:90 weight ratio)

A similar phenomenon occurred in MCT:G of 20:80 weight ratio in mixed surfactants system as shown in *Fig. 2.* On the first day, the oil droplets increased steeply from 244 to 527 nm as the HLB number increased from 8 to 13. Further increase in HLB numbers from 13 to 16.7 did not show any significant increase in droplet size. After seven days, the oil droplet sizes of lower HLB (8 to 13) increased, whereas at higher HLB number, (13 to 16.7) the emulsion exhibited a rather constant droplet size. However, the droplet size of 20:80 weight ratio of MCT:G system was larger than the 10:90 system. The weak oil-glycerol interface of the 20:80 weight ratio contributed to the instability of the oil droplet as more oil droplet coalescence produced large oil droplets.

The oil droplet was further increased from 924 to 1061 nm (1st day) with the increase of oil (MCT) content as shown in *Fig. 3.* However, at lower HLB numbers, a rather consistent particle size was obtained after seven days. In contrast, at higher HLB numbers, the droplet size increased. This increase of size was due to the contribution of oil (MCT) content in the O/G emulsion system. The results showed that the increment of oil was still able to maintain the stability of emulsion except 20:80 weight ratio of Tween20-Span20 system.

Fig. 4 shows the plotted shear stress versus shear rate of O/G emulsion of different Tween20-Span20 weight ratios in MCT:G (10:90) in the mixed surfactants system. It was observed that the shear stress increased with the increase of shear rate. All mixed Tween20-Span20 studies showed a similar flow behaviour. The tangents of the curve indicate no changes in viscosity. The

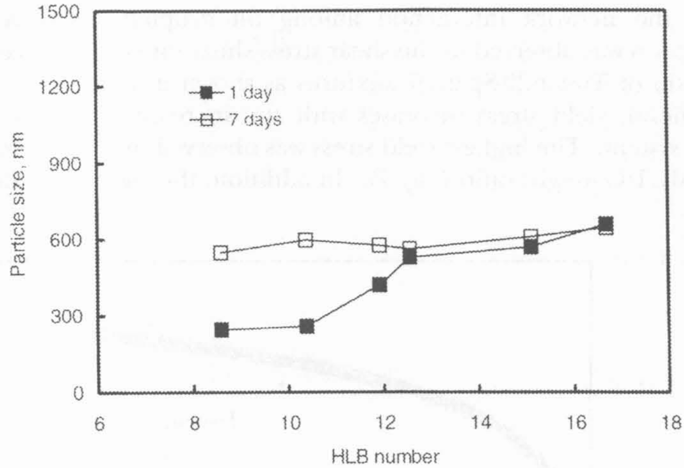

Fig. 2: O/G emulsion in mixed surfactants system of various HLB values (MCT:G, 20:80 weight ratio)

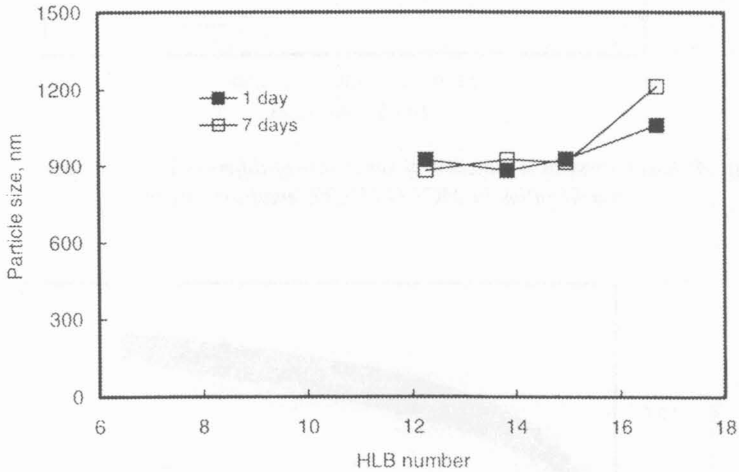

Fig. 3: O/G emulsion in mixed surfactants system of various HLB values (MCT:G, 30:70 weight ratio)

viscosity is constant regardless of the shear rate that shows Newtonian characteristics. As oil content increased to 20:80 of MCT:G in the mixed surfactant system, hysterisis loop was observed for all weight ratios of Tween20-Span20 mixtures except 0:100 and 20:80 of Tween20-Span20 (see *Fig. 5*). This indicates that the emulsion system was disturbed and unable to return to its original form. The network among oil droplets in the emulsion system was broken due to shear action. The increase of oil content in the emulsion system increases the network interaction among oil droplets. As a result, larger hysterisis loop was observed in the shear stress-shear rate curves except for 0:100 weight ratio of Tween20-Span20 mixtures as shown in *Fig. 6.*

In general, yield stress increases with the increase of oil content in the emulsion system. The highest yield stress was observed in the system containing 30:70 of MCT:G weight ratio (*Fig. 7*). In addition, the yield stress does not vary

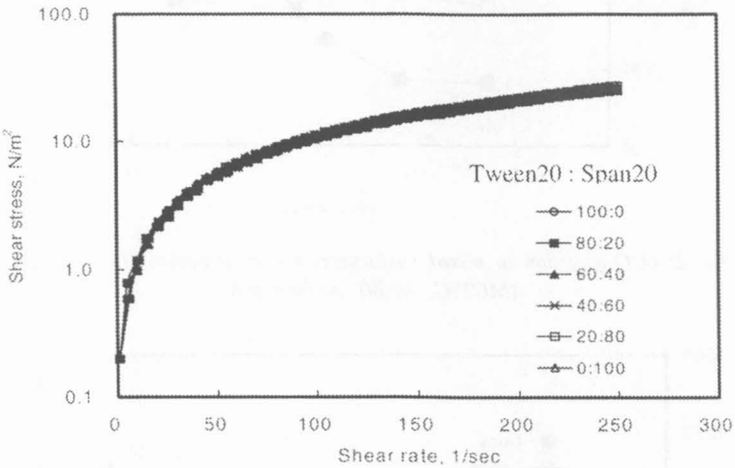

Fig. 4: Shear stress as a function of shear rate of different Tween20-Span20 weight ratios in MCT:G (10:90) emulsion system

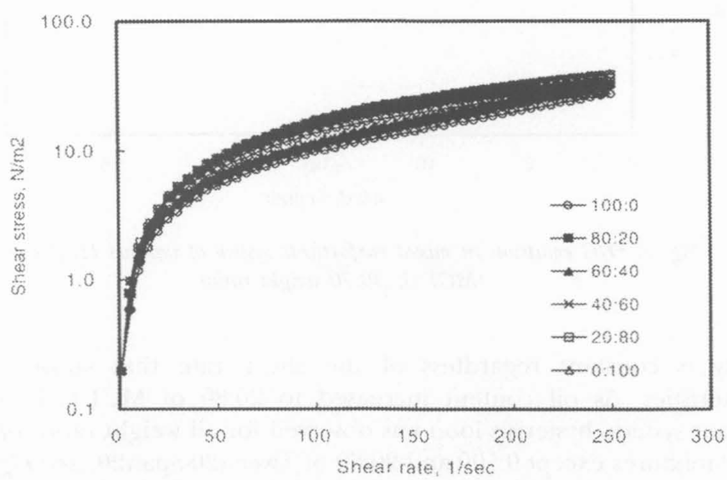

Fig. 5: Shear stress as a function of shear rate of different Tween20-Span20 weight ratio in MCT:G (20:80) emulsion system

significantly after storage for one week. *Fig. 8* shows the variation of viscosity with HLB of the mixed Tween20-Span20 (3 wt%) emulsion systems after applying shear at 10 rpm. The viscosity of the emulsion decreases with the HLB number and increases with oil content in the mixture.

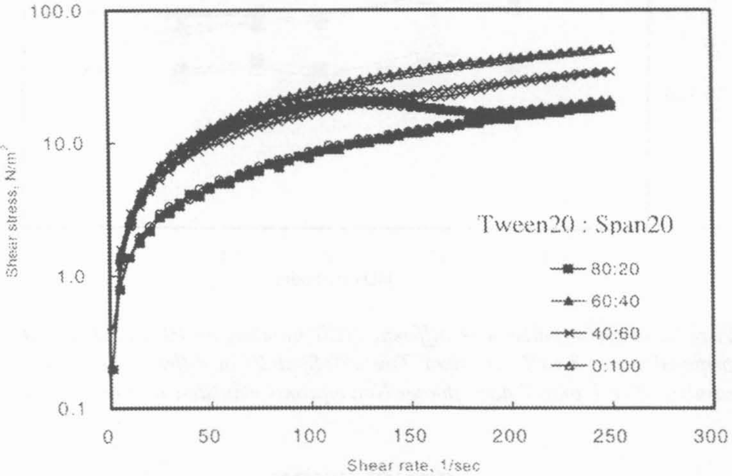

Fig. 6: Shear stress as a function of shear rate of different Tween20-Span20 weight ratio in MCT:G (30:70) emulsion system

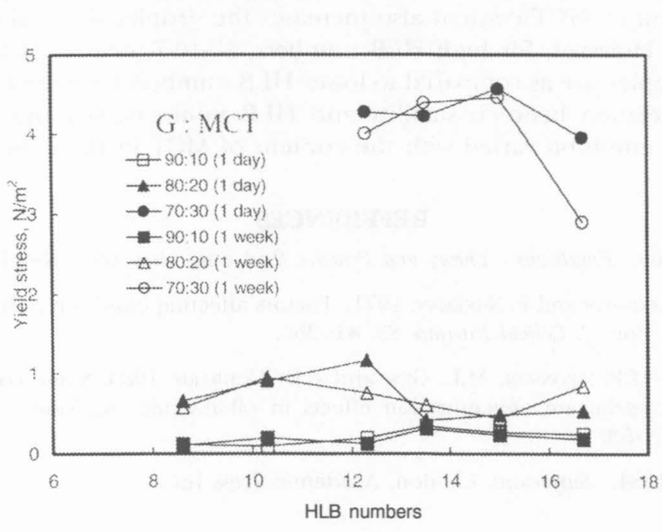

Fig. 7: Yield stress of O/G emulsions at different HLB numbers in 1 and 7 days. The emulsions were prepared using 3 wt% of mixed Tween20-Span20 in different MCT:G ratios

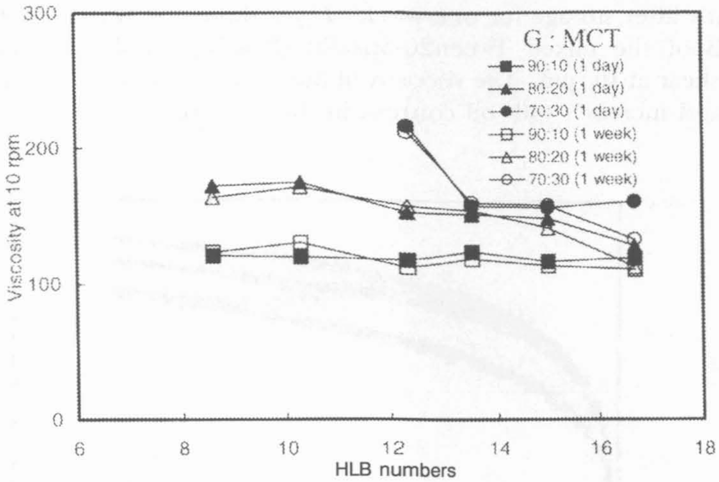

Fig. 8: Viscosity of O/G emulsion of different HLB numbers at 10 rpm shear rate. Emulsions were prepared using 3 wt% of mixed Tween20-Span20 in different MCT:G ratios and measured after 1 and 7 days storage.Non-aqueous emulsion of mixed surfactants

CONCLUSION

Stable O/G emulsion was obtained between 10:90 and 30:70 of MCT:G weight ratios. Further increase of oil content breaks the emulsion system. The increase of oil or MCT content also increases the droplet size and viscosity of the system. However, for high HLB numbers, 13-16.7, emulsions exhibited a stable oil droplet size as compared to lower HLB numbers between 8-13. There was no correlation between stability and HLB numbers, but the stability of nonaqueous emulsion varied with the content of MCT in the emulsion.

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