

EFFECTS OF FUNCTIONAL GROUP OF NON-IONIC SURFACTANTS ON THE STABILITY OF EMULSION

(Kesan Perbezaan Kumpulan Berfungsi Surfaktan Bukan Ionik Terhadap Kestabilan Emulsi)

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Abstract

Three mixed blend non-ionic surfactants: fatty acid polyethoxylates (POE) (20), POE (20) sorbitan monooleate (or Tween 80) and fatty alcohol POE (25) bounded by 20 -25 moles of ethylene oxides (EO) mixed with Laureth-1 were chosen to analyse their different functional group and its properties to the emulsion. The oil phase used is palm methyl ester C₁₂₋₁₈. The emulsification process was carried out at 52 ± 2°C by using high speed homogeniser. Emulsifying properties were investigated through a hydrophil-lipophil balance (HLB) value range from HLB 10, 11, 12, 13 and 14. The formation and stability of the emulsions were characterized through mean droplet size, zeta potential and surface tension. This study shows blend fatty alcohol POE (25EO) with HLB 11±1 shows optimum mean droplet size 1.970 µm to 2.099 µm, stable zeta potential at -37.91 mV to -40.8 mV and low surface tension value at 31.186 mN/m to 32.865 mN/m.

Keyword: surfactant, Hydrophil-lipophil balance (HLB), polyoxyethylene (POE)

Abstrak

Tiga campuran surfaktan bukan ionik: asid lemak polietoksilat (POE) (20), POE (20) sorbitan monooleat (Tween 80) dan alkohol lemak POE (25) yang mempunyai 20 - 25 molekul etilena oksida (EO), dicampur dengan Laureth-1 telah dipilih untuk dianalisis sifat perbezaan kumpulan berfungsi dan sifat terhadap emulsi. Fasa minyak yang digunakan adalah metil ester sawit C₁₂₋₁₈. Nilai keseimbangan hidrofilik-lipofilik (KHL) oleh ketiga-tiga campuran surfaktan dihasilkan pada KHL 10, 11, 12, 13 dan 14. Pembentukan dan kestabilan emulsi dicirikan melalui saiz titisan, keupayaan zeta dan tegangan permukaan. Hasil kajian menunjukkan campuran alkohol lemak POE (25EO) dengan KHL 11±1 mempunyai optimum saiz titisan 1.970 µm hingga 2.099 µm, keupayaan zeta yang stabil pada -37.91 mV hingga -40.8 mV dan tegangan permukaan rendah pada 31.186 mN/m hingga 32.865 mN/m.

Kata kunci: surfaktan, Nilai keseimbangan hidrofilik lipofilik (KHL), polietoksilat (POE)

Introduction

An emulsion is defined as a system consisting of two or more liquid immiscible phases which the droplets of one of the liquid phase are dispersed in another immiscible liquid phase. There are two types of simple emulsion which are oil in water (o/w) emulsion and water-in-oil (w/o) emulsion. The oil in water emulsion consists of oil droplets dispersed in the aqueous phase, whereas the water in oil emulsion have a reverse arrangement which water droplets were dispersed in the oil phase. From a physicochemical point of view, emulsions are thermodynamically unstable and tend to separate oil and phase state due to destabilization. Destabilization of emulsion can occur due to coalescence, flocculation, phase inversion, creaming and sedimentation, and Ostwald ripening [1].

Many reports have been published on the influence of various formulation and process parameters on the stability and properties of oil-in-water emulsions containing non-ionic emulsifiers. The factors including the amphiphile

chain length, the structure of the head group, the structure of the alkyl chain and polar additive [2]. The main problem regarding the stability is the presence of two thermodynamically unstable interfaces. Two different emulsifiers are therefore necessary for improving the stabilization of emulsion; one with low HLB for w/o interface and second with high HLB for o/w interface [2].

Hydrophilic-lipophilic balance (HLB) method established by Griffin (1954) was used to optimize compatible non-ionic surfactants for preparing stable emulsion [3]. Optimizing surfactant by using HLB number has been applied to almost all industries wherever surfactants are needed in product development, including food, pharmaceutical, cosmetic, pesticide and herbicide formulation [4-7]. In addition, other data such as droplet size [8], zeta potential [9] and surface tension [10] can be helpful in characterizing the emulsion.

The aim of this study was to investigate the effect of different mixed blend non-ionic emulsifier in the preparation of the o/w emulsion at different HLB values. This study also concerns the interaction or association between polyoxyethylene fatty ester, fatty alcohol or fatty acid to the emulsion. The emulsion was characterized in term of droplet size, zeta potential and surface tension.

Materials and Methods

Palm methyl ester C_{12-18} was supplied by Emery Oleochemical Sdn. Bhd. used as the dispersed phase. Fatty acid polyethoxylates (POE) (20), POE (20) sorbitan monooleate (or Tween 80), fatty alcohol POE (25) and Laureth-1 were used as emulsifiers. The detail of the surfactants is shown in Table 1 and Table 2. Distilled water was used for emulsion preparation. All materials were used as received without further purification. Samples of o/w emulsion consisted of 3%-5% (w/w) mixed non-ionic emulsifier (with different ratios of HLB value), 20% (w/w) palm methyl ester C_{12-18} , thickener and 80% (w/w) of water were prepared.

The mean droplet size of oil-in water emulsion was determined by laser diffractometer, Mastersizer E (Malvern Instrument). Droplet size measurement was reported as the mean diameter. Zeta potential was measured by using zeta sizer (Malvern Nano ZS90). Surface tension analysis was studied using Tensiometer (Sigma model with Sg server).

Table 1. Details of surfactant fatty acid POE (20) and POE (20) sorbitan monooleate (or Tween 80)

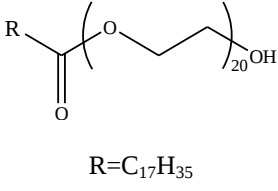
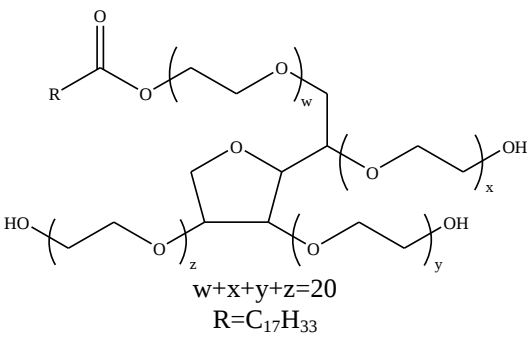
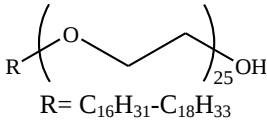
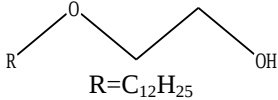
Surfactant	Fatty acid POE (20)	POE (20) sorbitan monooleate (Tween 80)
Molecular formula	$C_{58}H_{116}O_{21}$	$C_{64}H_{124}O_{26}$
Structural formula	 $R=C_{17}H_{35}$	 $w+x+y+z=20$ $R=C_{17}H_{33}$
Molecular weight (MW)	1149.53 g/mol	1310 g/mol
HLB value	13.6	15

Table 2. Details of surfactant fatty alcohol POE (25) and Laureth-1 (DLS1)

Surfactant	Fatty alcohol POE (25)	Laureth-1 (DLS1)
Molecular formula	$C_{30}H_{62}O_{10}$	$C_{14}H_{30}O_2$
Structural formula	 $R = C_{16}H_{31}-C_{18}H_{33}$	 $R = C_{12}H_{25}$
Molecular weight (MW)	1345.77 g/mol	230.39 g/mol
HLB value	16.5	3.6

Results and Discussion

The most important task in preparation of emulsion is the selection of suitable surfactant(s), which will satisfactorily emulsify the chosen ingredients and maintain its stability. All the surfactants chosen are the non-ionic surfactants. Non-ionic surfactants consist of molecules that have both hydrophilic and lipophilic groups and they will balance the size and strength of these opposing groups that is called as a hydrophilic-lipophilic balance (HLB) number [3]. Two surfactants may have a same HLB number, but exhibit different wetting characteristics because of the differences existing in chemical groups [11]. The range in the polarity of the molecule, which the polar hydrophilic head and nonpolar lipophilic tail with same homologous series of surfactants can give different properties to the surfactant(s) system [12].

Fatty acid POE (20), Tween 80 and fatty alcohol POE have many / large molecules of POE attached to the surfactants. These polymers are amphiphilic and soluble in water and helping in binding the molecules of water in the emulsion. Besides, ethoxylate-based ($O-CH_2-CH_2-$) surfactants have distinct properties such as temperature dependence [12]. Meanwhile, fatty alcohol DLS 1 has long chain alkyl group, and its hydrophobicity properties is high as compared to other primary surfactants above. It is also binding sites for the hydrophobic part of o/w emulsion. The long hydrocarbon (hydrophobic) tail of emulsion molecule penetrates more into non-polar (oil) region of o/w interface and gets attached electro-statistically to a larger number of oil droplets. The combination of non-ionic emulsifier will increase the accessibility of emulsifier in non-polar (oil) and polar region (water).

Stable emulsion can be formulated with emulsifier or combination of emulsifiers, which compatible with required hydrophy-lipophyl balance (HLB) of oil phase used [3]. HLB number system was used to optimize compatible non-ionic surfactants. Required HLB of the oil is different depends on types of oil used in emulsion. In order to determine the required HLB, the emulsions were prepared with different ratios of emulsifier blends and were evaluated. The selection of HLB 10, 11, 12, 13 and 14 was based on ranges of o/w formation [13]. Once a potential surfactant or mixed surfactants has been chosen using HLB guidelines, its performance can be tested and optimized by assessing some physical properties including droplet size, zeta potential and surface tension.

Several researchers found that surfactant mixtures could provide more stable emulsion with minimum size compared to one surfactant [14-17]. To attain high stability, a combination of hydrophilic and lipophilic emulsifier is often used, which align alongside each other results more strength and rigidity emulsifier [18]. In this study, mixed blend non-ionic surfactants was applied in the preparation of the emulsion according to the HLB method. The average HLB number can be calculated by using the following formula (1):

$$\text{Hydrophilic-lipophilic balance (HLB)} = x_1 HLB_1 + x_2 HLB_2 \quad (1)$$

where x_1 and x_2 are the weight fraction of the two surfactants with HLB_1 and HLB_2 respectively.

Droplet size analysis

Droplet size measurement is one of the most commonly used for determination of the stability of the emulsion. The degree of dispersion or size distribution of an emulsion can give an indication in the selection of the surfactant [18]. The HLB of an emulsifier blend that providing a minimum dispersion ratio can be accepted as stable formulation [18]. Plots of the mean droplet size of different non-ionic emulsifier against HLB values were shown in Figure 1. There was a significant difference in the mean droplet size between different blend non-ionic emulsifier. Blend of fatty acid POE shows the lowest average mean droplet size compared to other blend emulsifier ranged from 0.482 μm to 1.301 μm . Meanwhile, blend POE (20) sorbitan monooleate shows moderate average mean droplet size ranged from 1.233 μm to 1.577 μm . The highest mean droplet size of blend emulsifier was obtained at fatty alcohol POE (25) ranged from 1.970 μm to 2.099 μm . The figures also illustrated the increase in HLB values results in increasing of droplet size. However, the patterns of the increasing were not same. Blend fatty acid POE (20) showed a rapid increase in droplet size with increasing HLB values. However, blended POE (20) sorbitan monooleate and blended fatty alcohol POE showed moderately increase and gradually increase of droplet throughout all HLB. The difference between the droplet size of mixed blend emulsifier can be explained through the nature and strength of the structure as well as the composition of the adsorbed layer at the o/w interfaces [8]. Blended fatty alcohol POE (25) showed a stable mean of droplet size due to surfactant fatty alcohol POE (25) that have high HLB and hydrophilicity that can give immediate formation of o/w droplets and rapid spreading of the formulation in the aqueous media [19, 20]. In addition, the increase of the droplet size always refers to the aggregation of the droplets into larger unit [2, 11]. Besides, coalescence of droplet size can occur where the process of thinning and disruption of the liquid film between droplets which involve the fusion of two or more droplets to form larger droplets [2, 11].

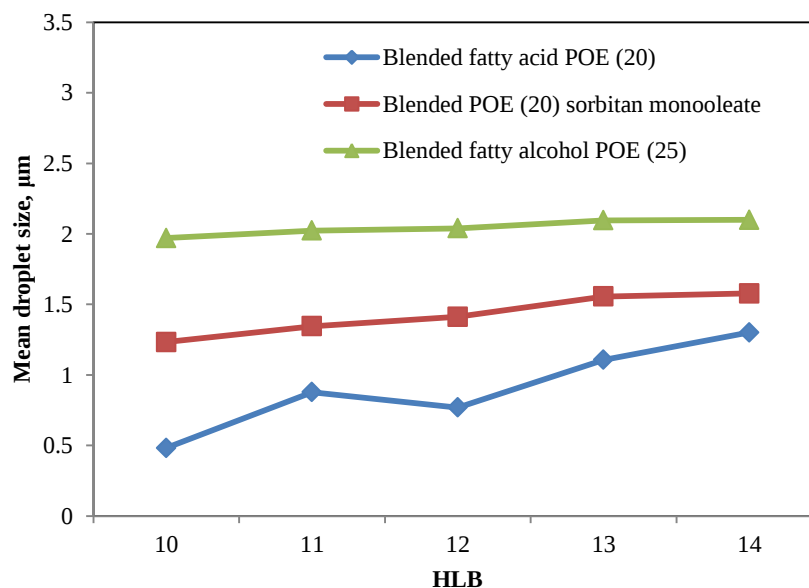


Figure 1. Mean droplet size of emulsion at different blended non-ionic emulsifiers. Vertical bar shows standard deviation.

Zeta potential

Zeta potential of o/w emulsion using different emulsifier is shown in Figure 2. Zeta potential of o/w is negatively charged. An increase in the negative value of zeta potential indicates the stability of o/w emulsion [11, 20, 21]. This means the stabilization arises from the mutual repulsion between the electrical double layer of particle and from the adsorption of molecules at the oil droplet. The negative surface charge of emulsion droplet resulted from the POE

ion, forming hydrogen bonds between the POE and water molecules in the boundary layer of o/w emulsion [22]. The obtained data showed all HLB ranges were satisfactory for non-ionic surfactants at various chemical group. It is observed that the zeta potential of o/w decreased with an increase in HLB value. This was because the compression of the electrical double layer around the emulsion droplets, which enhances with increasing ionic strength and the counter ion binding between the ions and the negatively charged emulsion droplets [22]. The results also showed that blended fatty alcohol POE (25) showed the lowest zeta potential value. This was due to POE of fatty alcohol POE (25) formed hydrogen bonds with water molecules and giving the lowest zeta potential value. Blended fatty acid POE also showed lower zeta potential value. In addition, the hydroxyl ions may interact with surfactant molecules and also influence the caboxyl $-\text{COOH}$ dissociation [10].

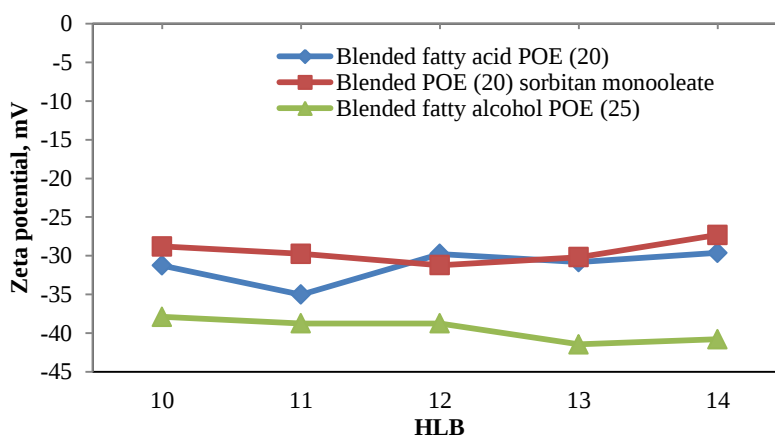


Figure 2. Zeta potential of emulsion at different blended non-ionic emulsifiers. Vertical bar shows standard deviation.

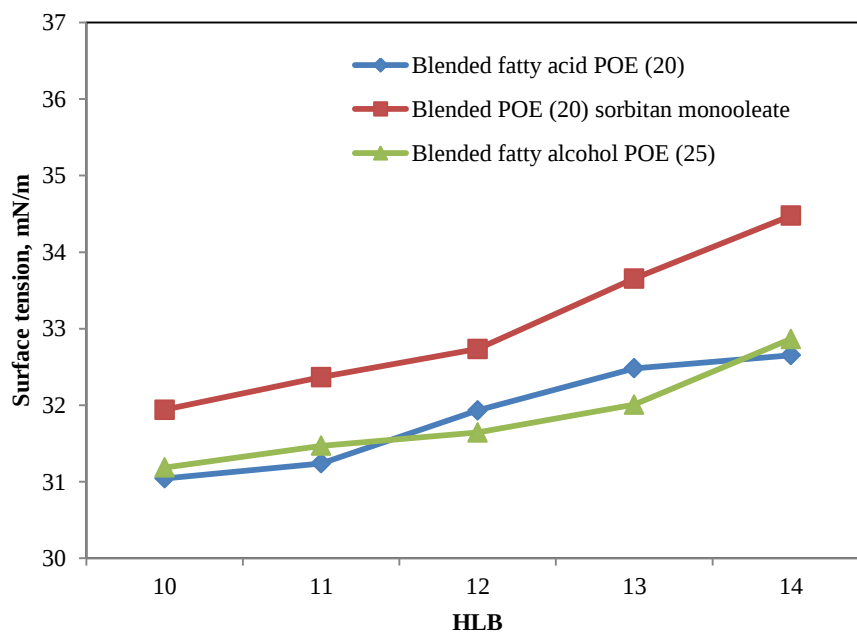


Figure 3. Surface tension of emulsion at different blended non-ionic emulsifiers. Vertical bar shows standard deviation.

Surface tension

Figure 3 shows surface tension curves, which were found to follow increasing pattern of HLB values of mixed emulsifiers. Blended POE (20) sorbitan monooleate showed high surface tension values ranged from 31.940 mN/m to 34.476 mN/m as compared to other mixed surfactants. Blended fatty alcohol POE (25) and blended fatty acid POE (20) showed surface tension values ranged from 31.186 mN/m to 32.865 mN/m and 31.043 mN/m to 32.654 mN/m respectively. Generally, the lower HLB values represent the surfactant induced more hydrophobic. This will increase the interaction between the hydrocarbon chain and the hydration of the hydrophilic head groups, thus the surfactant molecules started to associate at the surface of the solution as well as in bulk solution and result in lower surface tension value [20]. High HLB values represent the affinity of non-ionic surfactant for water. The additional POE of blend fatty alcohol POE (25) will bond with water and prevent water molecules from binding tightly to another, thus lowering the tension or strength of the surface [23].

Conclusion

Oil-in-water emulsion was successfully formed by mixing palm methyl ester with water in the presence of blended-non-ionic surfactants. The study of formation and stability of o/w emulsion indicated that the structure of the hydrophilic head group of the non-ionic surfactants is important for improving the stability of the emulsion stability, especially in determining how the blended surfactant molecules interact in emulsion. The different mixed non-ionic surfactants have significant effects on droplet sizes, zeta potential and surface tension values. This study found that fatty alcohol POE (25) mixed with DLS1 with HLB±1 was the optimum combination of mixed non-ionic surfactants to form the most stable o/w emulsion. This finding could be useful for further study in incorporating the active ingredient(s) to produce desired products for agrochemical-based applications.

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