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Research report

# Influence of an optimized non-ionic emulsifier blend on properties of oil-in-water emulsions

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**Abstract**

Properties of oil-in-water emulsions containing non-ionic emulsifiers were evaluated in relation to nature of the dispersed phase, emulsifier composition and processing parameters. Particle size of mineral oil (hydrocarbons)-in-water emulsions was independent of the HLB of an optimized emulsifier blend, whereas, the particle size of olive oil (triglycerides)-in-water emulsions was the smallest at the optimum HLB of the emulsifier blend. The non-ionic emulsifiers reduced the particle size of mineral oil emulsions more efficiently than that of olive oil emulsions. Contrary to previously published reports, the nature of the dispersed phase, HLB of the emulsifier blend or the initial particle size of emulsions showed no influence on the final particle stability of the emulsions. This difference was attributed to the optimization of the emulsifier blend and processing parameters in the preparation of emulsions. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Emulsions, Stability, Particle size, Polarity, Hydrocarbons, Triglycerides

## 1. Introduction

Emulsifiers are essential for the initial formation and the long-term stability of emulsions [1]. Emulsifiers are thought to form a film around the suspending dispersed phase droplets and strengthening of this film could attain a much greater degree of the droplet stability [2,3]. This could be accomplished by using a combination of hydrophilic and lipophilic emulsifiers [4]. In such a system the hydrophilic and lipophilic emulsifiers are thought to align alongside each other imparting more rigidity and strength to the emulsifier film through hydrogen bonding [5].

The effects of blending a ethoxylated sorbitan monoester type (Tween®) hydrophilic emulsifier and a sorbitan monoester type (Span®) lipophilic emulsifier on the stability and properties of mineral oil-in-water emulsions were investigated previously [3,6]. It was shown that the particle size of these emulsions reduced and the stability of the emulsions improved when the difference in the HLB of the two emulsifiers in the blend was kept to a minimum. The authors proposed that blending emulsifiers with two extreme HLB values would result in the strongly hydrophilic emulsifier mostly dissolving in the water phase, whereas, the strongly lipophilic emulsifier mostly dissolving in the oil phase. This could lead to weakening of the O/W interfacial film due to insufficient interaction between the two emulsifiers. Selection of emulsifiers based on their structural features over the HLB was also a subject of discussion [2,7]. Boyd et al. [2], disregarding the resultant HLB value of the emulsifier blend and the required HLB of the oil, considered the improved stability of emulsions containing sorbitan monooleate (Span 80) and ethoxylated sorbitan monopalmitate (Tween 40) to be a result of a convenient meshing of the molecules at the oil droplet-water interface due to steric considerations.

Many reports have been published on the influence of various formulation and process parameters on the stability and properties of pure hydrocarbon-in-water emulsions containing non-ionic emulsifiers [3,6,8,9]. The dispersed phase in pharmaceutical and food emulsions is often composed of a vegetable oil or more precisely a mixture of triglycerides [10,11] with an O/W interfacial tension value different from that of a mixture of hydrocarbons [12]. Therefore, it is interesting to investigate the comparative effect of the HLB and the structure of the non-ionic emulsifiers at a hydrocarbon/water interface versus a triglyceride/water interface.

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## 2. Materials and methods

### 2.1. Materials

Light mineral oil NF (Mallinckrodt, Inc.) and olive oil (Super Refined™, Croda) were used as the dispersed phases. Polyoxyethylene sorbitan fatty acid esters (Tween) and sorbitan fatty acid esters (Span) from Emulsion Engineering, Inc were used as emulsifiers. Methylparaben USP from Sigma and propylparaben from Eastman Kodak were used as preservatives. All the materials were used as received.

### 2.2. Selection and preparation of emulsions

An emulsifier blend for a stable oil-in-water emulsion was determined using the Atlas HLB method [13]. A series of Tween and Span type non-ionic emulsifiers was screened to determine the required HLB, chemical type and concentration of the emulsifier blend for the preparation of a stable oil-in-water emulsion. During the initial screening process, emulsions were prepared by adding the oil phase containing the emulsifier blend at 70°C to the aqueous phase, also at 70°C with propeller mixing at 2000 rev./min. The aqueous phase contained 0.18% (w/w) methylparaben and 0.02% (w/w) propylparaben as preservatives. A larger cream volume at a given time and a smaller initial particle size of the dispersed phase droplets were used as indictors of the stability of emulsions.

Studies were carried out to evaluate the effect of the type and degree of mixing and the order of addition of emulsifiers on the properties of the selected emulsions. The effect of the type and degree of mixing was investigated using a propeller mixer (IKA WERK, Inc.) and a homogenizer (OMNI™ 2000, OMNI International, Inc). The effect of the order of addition of emulsifiers was investigated by adding either both emulsifiers to the oil phase, both emulsifiers to the aqueous phase or the hydrophilic emulsifier (Tween) to the aqueous phase and the lipophilic emulsifier (Span) to the oil phase before preparation of emulsions.

The criterion for selecting a preparation technique was the reproducible preparation of emulsions that showed maximum stability, as determined in terms of a higher cream volume and a smaller particle size. Based on the process optimization studies, emulsions were prepared as follows: The aqueous phase containing the preservatives and the oil phase containing the emulsifier(s) were heated separately to 70°C. The oil phase at 70°C was added to the aqueous phase of the same temperature, while stirring with a propeller mixer at 2000 rev./min. Stirring was continued for 5 min to obtain a coarse emulsion. The emulsion container was placed in a water bath (13 ± 1°C) and the coarse emulsion was homogenized for 5 min at 25 000 rev./min. Additional water was added to the emulsion as necessary to make up for water lost due to evaporation. The emulsion was further homogenized for 1 min after adjusting the water content. Five hundred gram quantity emulsions were prepared in duplicate using the optimized emulsification procedure.

### 2.3. Measurement of emulsion properties

Particle size distributions of emulsions were determined by the centrifugal sedimentation method using a HORIBA™ CAPA-700 particle size analyzer (HORIBA Instruments, Inc). The instrument is based on the principle of liquid-phase sedimentation with measurements being done using an optical transmission method. In this method, the Stokes' sedimentation equation is combined with the proportional relationship between the absorbency and particle concentration. The instrument was calibrated using standard polystyrene divinylbenzene beads and optical microscopy. The emulsion sample was mixed gently in order to obtain a homogeneous sample for particle size measurement. Approximately five drops of emulsion were diluted with approximately 30 ml of distilled water. Particle size was measured immediately after dilution. Triplicate measurements were made and an average median $D_{\mathrm{vol}}$ was determined. The particle size was measured initially and after 2, 4 and 6 months to evaluate stability.

In addition, the particle size distributions were also evaluated using an optical microscope (WILD™ M21, Heerbrugg, Inc.) equipped with a calibrated eyepiece micrometer and a photomicrographic attachment. Particle size distributions determined from the instrumental and microscopic methods were found to be in agreement.

Creaming profiles of emulsions were evaluated visually at ambient temperature (~25°C). To measure the creaming profiles, 100 ml of each emulsion sample were poured into a 100 ml graduated cylinder immediately after preparation. Emulsions were observed for creaming at 24-h intervals during the first week and at 2-week intervals for the following 6 months. The percent volume of the dispersed phase creamed at the upper portion of the graduated cylinder was measured.

## 3. Results and discussion

### 3.1. Selection of an emulsifier blend

The HLB method has been proven to be a useful tool in choosing the optimal type of emulsifier(s) for a given oil phase. The HLB system predicts that an emulsifier system having the same HLB number as that of the oil to be emulsified is the best emulsifier [14]. Emulsions were prepared initially with 67% (w/w) aqueous phase, 30% (w/w) oil phase and 3% (w/w) emulsifier blend of Tween 80 and Span 80 at HLB values ranging from 5 to 15 to determine the 'required HLB' of the oil phase. An HLB of 10 was found to be the required value for the preparation of a stable olive oil emulsion (Fig. 1A) and a stable mineral oil emulsion (not shown). Emulsions prepared at this HLB value

A. Effect of HLB on on emulsion stability → B. Effect of emulsifier type on emulsion stability

Tween 80 & Span 80

| HLB | Cream volume 24 hrs, % |
|---|---|
| 5 | 37 |
| 6 | 37 |
| 7 | 37 |
| 8 | 40 |
| 8.5 | 40 |
| 9.0 | 43 (16.8 μ) |
| 9.5 | 45 (17.3 μ) |
| **10** | **61 (14.3 μ)** |
| 10.5 | 55 (17.0 μ) |
| 11 | 53 (17.3 μ) |
| 12 | 42 |
| 13 | 40 |
| 14 | 38 |
| 15 | 37 |

| Emulsifier blend type at HLB 10 | Creaming in 96 hrs |
|---|---|
| Tween 80 & Span 80 | Creaming |
| **Tween 80 & Span 40** | **No creaming** |
| Tween 80 & Span 20 | Creaming |
| Tween 40 & Span 80 | Creaming |
| Tween 40 & Span 40 | Creaming |
| Tween 40 & Span 20 | Creaming |
| Tween 20 & Span 80 | Creaming |
| Tween 20 & Span 40 | Creaming |
| Tween 20 & Span 20 | Creaming |

Fig. 1. Selection of an emulsifier blend for the preparation of a stable olive oil-in-water emulsion.

yielded a larger percent cream volume (61% v/v) and a smaller particle size (14.3 μm).

A series of emulsifier blends at the required HLB value of 10 was screened to select an appropriate 'emulsifier type' (Fig. 1B). Then, emulsions were prepared containing the appropriate emulsifier type at HLB 10 in the concentration range of 0.5–3.0% to determine the required 'emulsifier concentration'. It was found that a 2% emulsifier blend of Span 40 (sorbitan monopalmitate) and Tween 80 (polyoxyethylene sorbitan monooleate) at HLB 10 produced olive oil (glyceryl trioleate) emulsions with a larger percent cream volume and a smaller particle size. Whereas, a 2% emulsifier blend of Span 20 (sorbitan monolaurate) and Tween 40 (polyoxyethylene sorbitan monopalmitate) at HLB 10 was found to be optimum for mineral oil (refined saturated hydrocarbons) emulsions. Thus, it appears that an emulsifier blend containing at least one emulsifier with an unsaturated $C_{18}$ fatty acid of a similar chain length as of olive oil could produce emulsions with a maximum stability. These results are in agreement with the notions that: (a) the use of mixtures of emulsifiers all with the same HLB would result in emulsions of varying degrees of stability (Fig. 1B) [3] and (b) the degree of structural similarity between the hydrocarbon moieties of an oil phase and the surfactant is essential to affect the efficiency of emulsion stabilization [15,16].

### 3.2. Selection of an emulsification procedure

During the process optimization phase, the emulsion formulation with the selected optimized emulsifier blend was initially prepared by mixing with a propeller mixer at 2000 rev./min for 5 min. The coarse emulsion so formed from this mixing procedure creamed rapidly (Fig. 2A). Mixing was continued on this coarse emulsion for 15 more min to study the effect of 'mixing time' on the stability of the emulsion. Although the emulsion showed improved creaming stability with longer mixing times, the particle size remained essentially unchanged from the initial coarse emulsion. To study the effect of 'type of mixing', the initial coarse emulsion was mixed with a homogenizer at 25 000 rev./min for 5 and 10 min. A homogenization time of 5 min was selected for the preparation of a fine emulsion, as there was no further reduction in particle size after 5 min.

The 'method of emulsifier addition' was reported to influence the emulsion type, viscosity and the particle size in an emulsion [8,9]. This behavior was thought to be due to the difference in the solubility of the emulsifier in the continuous and dispersed phase. In the present study, emulsions prepared with the three methods of emulsifier addition showed essentially similar particle size (Fig. 2B). It appears that optimization of the formulation and high mixing speed used for emulsification process caused the method of emulsifier addition to be of no significance on the particle size. However, the creaming stability of emulsions was better when both emulsifiers were added to the oil. Therefore, measurement of the two parameters, initial particle size and percent cream volume is a better indicator than the use of a single measurement parameter in the selection of a suitable method of emulsifier(s) addition to prepare a stable emulsion.

### 3.3. Influence of optimized emulsifier blend on emulsion properties

The influence of the nature of the dispersed phase and the HLB and concentration of the optimized emulsifier blend on the properties of emulsions prepared using optimized process is summarized in Table 1. There was a substantial reduction and narrowing of the particle size distributions of olive oil emulsions as the HLB value of the emulsifier blend increased from 7 to 9 or 10 and thereafter, the particle size increased above the HLB value of 10. There was essentially no change in particle size of emulsions at HLB values 9 and 10. However, only the emulsion formulation at HLB 10 (optimum) showed no creaming beyond the first 2-week period.

The particle size distributions of mineral oil emulsions remained essentially unchanged between HLB values 9 and 14 and so did the percent cream volume during the first 2

A. Effect of type of mixing on emulsion stability → B. Effect of order of emulsifier addition on emulsion stability

Propeller mixing at 2000 rpm for 5 min.
*Coarse emulsion; rapid creaming*

| Propeller mixing at 2000 rpm for 15 min. | **Homogenization at 25 000 rpm for 5 min.** |
|---|---|
| 9.3 ± 3.9 μ | 5.1 ± 2.8 μ |
| Creaming within 7 days | No creaming in more than 7 days |

| Order of emulsifier addition | Particle size, μ<br>Cream volume in 7 days, % |
|---|---|
| **Tween 80, Span 40 in oil phase** | **4.95 ± 2.5**<br>**No creaming** |
| Tween 80, Span 40 in water phase | 5.07 ± 2.5<br>46 |
| Tween 80 in water, Span 40 in oil | 5.01 ± 2.5<br>45 |

Fig. 2. Selection of an emulsification procedure for the preparation of a stable olive oil-in-water emulsion.

Table 1
Influence of HLB of optimized emulsifier blend on emulsion properties

| Emulsifier | | Olive oil emulsion Tween 80 and Span 40 blend | | Mineral oil emulsion Tween 40 and Span 20 blend | |
|---|---|---|---|---|---|
| HLB | Conc. % | Initial particle size (SD), μm | Cream volume 2 week, % | Initial particle size (SD), μm | Cream volume 2 week, % |
| 7 | 2.0 | 9.67 (5.4) | N/A | N/A | N/A |
| 8 | 2.0 | 8.97 (4.4) | 46 | 5.15 (2.3)[a] | 100[a] |
| 9 | 2.0 | 5.40 (2.8) | 46 | 2.50 (1.7) | 100 |
| 10[b] | 2.0 | 5.26 (2.8) | 100 | 1.97 (1.6) | 100 |
| 10 | 1.0 | 8.21 (4.2) | N/A | 3.69 (2.0) | N/A |
| 10 | 0.5 | 10.47 (4.4) | 41 | 4.18 (1.9) | 48 |
| 11 | 2.0 | 6.36 (3.4) | 42 | 1.68 (1.2) | 100 |
| 12 | 2.0 | 6.44 (3.5) | 42 | 1.79 (1.4) | 100 |
| 13 | 2.0 | 8.45 (4.1) | 40 | 1.90 (1.5) | 100 |
| 14 | 2.0 | N/A | N/A | 2.42 (1.7) | 100 |

[a] HLB 8.6 (HLB of pure Span 20).
[b] Optimum emulsifier system.

weeks. However, only the emulsion formulation at HLB 10 (optimum) showed no creaming for more than 3 months. These observations are in contrast to those of Takamura et al.'s [3] study, which indicated that the particle size distributions of mineral oil-in-water emulsions were strongly dependent on the HLB value of Tween 40 + Span 20 blend.

The particle size distributions of both olive oil and mineral oil emulsions increased rapidly as the concentration of the optimized emulsifier blend (HLB 10) was reduced from the optimum value of 2%–0.5% (Table 1). The particle sizes were substantially higher for all olive oil emulsions than those of mineral oil emulsions at any given HLB and concentration values, even after thorough optimization of the emulsifier blend and emulsification procedure for both dispersed phases. Thus, the non-ionic emulsifiers reduced the particle size of mineral oil (hydrocarbons)-in-water emulsions more effectively than that of olive oil (triglycerides)-in-water emulsions. It is interesting to note that the emulsifiers aided the emulsification of mineral oil in water more efficiently than olive oil in water, though, the interfacial tension between mineral oil and water ($\gamma \approx 50$ mNm$^{-1}$) [17] is much larger than that between olive oil and water ($\gamma \approx 23$ mNm$^{-1}$) [12]. However, neither the nature of the dispersed phase, the initial particle size of the dispersed phase nor HLB of the optimized emulsifier blend affected the final stability of emulsions as indicated by the absence of any change in particle size for 6 months (Fig. 3). The observed effect of (or more precisely 'lack thereof') HLB value on the emulsion particle size stability is directly in contrast to that of a previous study [2], which indicated that the stability of O/W emulsions as measured by changes in particle size distributions was strongly dependent on the HLB of the emulsifier blend.

Stability of an oil-in-water emulsion, as measured by changes in particle size with time, was reported to decrease with an increase in polarity of the dispersed phase [18,19]. The interactions between polyoxyethylene type emulsifiers and a polar oil or a vegetable oil (triglycerides) were proposed to result in a portion of the polyoxyethylene chain of the emulsifier dissolved in the polar oil phase [20,21]. This type of behavior was thought to be not possible with a nonpolar oil (hydrocarbons). These authors concluded that a polyoxyethylene type non-ionic emulsifier might not be a good emulsifier for polar oils. However, the results of the present study indicated that the nature of the dispersed phase had no effect on the particle size stability of emulsions formulated with an optimized emulsifier blend at the HLB values under investigation (Fig. 3A,E). Apparently, optimization of the emulsion formulation and processing parameters caused the effect of oil polarity to be of no significance on the particle size stability of emulsions. However, the adverse influence of the polarity of the dispersed phase on the stability of emulsions was apparent only when the concentration of the emulsifier blend was reduced substantially from the optimal value (Fig. 3B,F). Therefore, it is essential to select an optimized emulsifier blend for each dispersed phase to relate the influence of nature of the dispersed phase to the emulsion stability.

An emulsifier blend consisting of Span 20 and Tween 40 was found to be optimum for the preparation of stable mineral oil-in-water emulsions. Span 20 (sorbitan monolaurate) molecules would presumably orient at the mineral oil/water interface in such a way that the lipophilic laurate chain of the emulsifier lies on the mineral oil side of the interface and the hydrophilic sorbitan ring lies on the aqueous side. It appears that this simple arrangement of Span 20 molecules alone (HLB 8.6) at the mineral oil/water interface is strong enough to prevent any coalescence of mineral oil droplets as indicated by no significant changes in the particle size for more than 6 months (initial: 5.15 ± 2.3 μm; 6 months: 5.62 ± 2.4 μm). Incorporation of increasing amounts of Tween 40 (polyoxyethylene sorbitan monopalmitate) into this system would probably result in the Tween 40 molecules aligning at the oil/water interface in such a way that a part of each palmitate chain lies within the mineral oil phase and the other part along with the polyox-

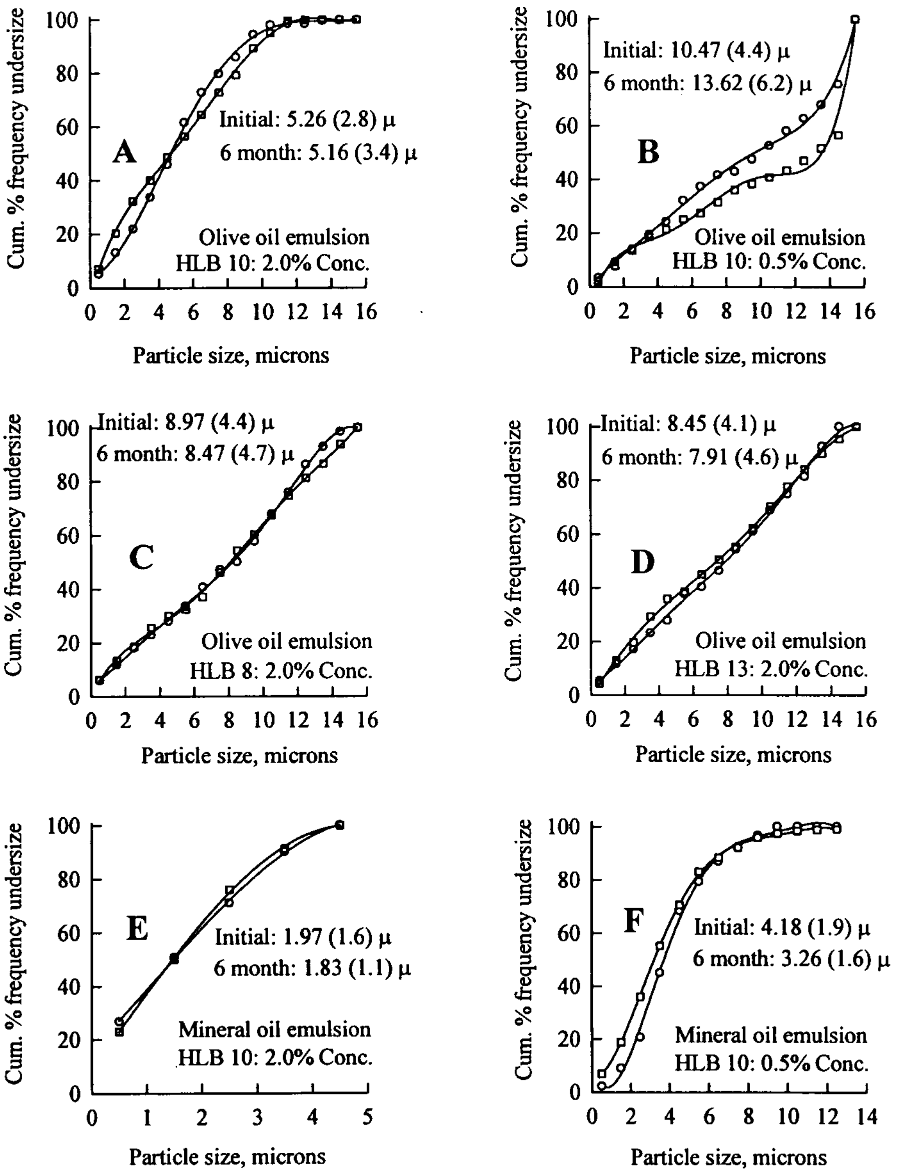

Fig. 3. Influence of dispersed phase and emulsifier blend on particle size stability of emulsions. Particle size measured initially (□) and after 6 months (○).

yethylene chains lies within the water phase. When Span 20 and Tween 40 are used together, those parts of the Tween 40 hydrocarbon chains that are located in the oil phase penetrate between the adsorbed Span 20 molecule, whereas the hydrated polyoxyethylene chains interweave to provide a gel-like structure in the aqueous phase at the oil/water interface [2]. This structure at the mineral oil/water interface provides a good stability against droplet coalescence.

The refined olive oil used in the present study is a mixture of high purity natural triglycerides, which are made essentially of 75% oleic acid ($C_{18:1}$), 9.5% linoleic acid ($C_{18:2}$), 2% stearic acid ($C_{18:0}$), 11.5% palmitic acid ($C_{16:0}$) and a small portion of other shorter chain fatty acids [22]. Tween 80 (polyoxyethylene sorbitan monooleate) molecules would likely orient at the olive oil/water interface in such a way that the lipophilic oleate chain of the emulsifier penetrates and embeds itself within the oleate chains of a triglyceride molecule. Whereas, Span 40 (sorbitan monopalmitate) molecules would probably align at the olive oil/water interface in such a way that the lipophilic palmitate chain of the emulsifier penetrates and inserts itself in between two triglycerides molecules. This structure at the olive oil/water interface provides a good stability against droplet coalescence.

## 4. Conclusions

The non-ionic emulsifiers reduced the particle size (i.e. aided emulsification) of mineral oil (hydrocarbons)-in-water emulsions more effectively than that of olive oil (triglycerides)-in-water emulsions. The nature of the dispersed phase had no effect on the particle size stability of emulsions formulated with an optimized emulsifier blend. As stable oil-in-water emulsions of two chemically different dispersed phases could be prepared with different emulsifier blends at the same HLB value, the structural similarity of the emulsifier blend to the dispersed phase appears to be more critical than the resultant HLB of the blend in obtaining stable emulsions.

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