Evaluation of Emulsion Phase Separation Prepared With Different Oil and Emulsifiers Ratios

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Abstract:

The objective of this study was to investigate the Phase separation and inversion of emulsions prepared with different water: oil ratios. The combinations of emulsifiers PGPR/ sucrose ester and PGPR/span40 showed an ability of forming W/O emulsions up to ratio of 55/40 water/oil respectively. This is because of the PGPR emulsifier is the oil soluble emulsifier with law HLB. Combination of PGPR/Tween80 formed W/O emulsions up to ratio of 45/50 water/ oil respectively. Moreover, combination of polyglycerol/ sucrose ester was not able to form W/O emulsions it formed O/W emulsions in all water: oil ratios. Furthermore, Combination of polyglycerol/sucrose ester which formed O/W system showed higher physical stability followed by combination of PGPR/span40, PGPR/Tween80 and then PGPR/ sucrose ester was the lowest physical stability.

Keywords: W/O emulsions; O/W emulsions; emulsion stability; phase inversion.

Introduction:

An emulsion is traditionally defined as a dispersion of droplets of one liquid in another, when the two liquids are immiscible. Many products can exist as emulsions, including mayonnaise, milk, cosmetics, insecticides, crude oil and some pharmaceuticals.[1] In order to attain a state of minimum energy the surface of any liquid will always orientate itself to the smallest possible area. In order to increase this surface area work documented as free surface or free interfacial surface energy must be expended, this energy, numerically is equal to the surface or interfacial tension. Surface tension refers to liquids in contact with air or their saturated vapour, whereas interfacial tension refers to two immiscible liquids in contact with each other. Interfacial tensions are less than surface tensions, because the adhesive forces between the molecules of the two phases forming the interface are greater than the adhesive forces between molecules in a liquid phase interacting with molecules in a gaseous phase. Increasing the adhesive force will give rise to a decrease in the surface tension. As emulsions are thermodynamically unstable systems [2], they tend to phase separate quickly. Stabilisation is usually achieved by the addition of a protein or an emulsifier or surfactant (surface active agent)[3], however the coexistence of both proteins and emulsifiers could lead to destabilisation and partial coalescence as the proteins and emulsifiers will compete for space at the interface, which can be beneficial in the production complex food colloids like ice cream.[4] Small molecular surfactants/ emulsifiers are preferentially adsorbed at the interface displacing proteins and in the process weakening the membrane causing destabilisation and partial coalescence. This partial coalescence is essential to enable the fat globules to produce a structured network in the frozen product to entrap the air bubbles.[5] A surfactant lowers the interfacial tension between the two immiscible phases via adsorption at the interface[6] thus forming a mechanically cohesive interfacial film around the droplets after emulsification, preventing coalescence.[7] It is important to stress that cohesive forces are the forces that exist between molecules of one phase, whilst adhesive forces are the forces that exist between molecules of two different phases. As the interfacial tension can be defined as the work required in producing or creating a unit area of surface; by reducing the interfacial tension, stable droplets of higher overall surface area can be produced. The nature of the interface established through the adsorption of emulsifiers, influences the two immiscible liquids to such an extent that one breaks up during the emulsification process to form droplets (disperse phase) while the other retains its continuity (continuous phase). How and why this occurs is due to the fact that the emulsifiers at the interface are wetted by both liquids which individually have different surface tensions on either side.

As a result of this the interface will always bend so that the side with the higher surface tension becomes concave, thus producing droplets giving rise to either water-in-oil (W/O) or oil-in-water (O/W) emulsion.[8] In order to maintain stability, the interfacial film should be firm and permanent. Likewise, the electric charge produced on the surface of the droplets is important, as its presence will produce repulsion between any approaching droplets thus increasing stability. These two factors are predominantly important during emulsification in order to reduce droplet flocculation, film drainage and subsequent rupture of the interface as droplets formed during the emulsification process will inevitably collide with one another giving rise to incessant coalescence. With regards to solid water-in-oil (W/O) emulsions they carry less significance after the crystallisation/ solidification of the continuous phase as the solid matrix will inevitably help to stabilise the lipstick emulsion. In oil-in-water (O/W) emulsions where the interfacial film is electrically charged this produces an overall charge on the oil droplets balanced by the total charge in the double layer within which there is an excess of oppositely charged ions (counter-ions). This is known as the electric diffuse double layer or ionising atmosphere, produced by the ionised water continuous phase. If however the oil were the continuous phase the dispersed water droplets would be susceptible to flocculation and coalescence due to the oil being a non-ionising medium absent of any electric diffuse double layer or ionising atmosphere[9] The most common emulsions are oil-in-water (O/W), where the water constitutes the continuous phase and the oil the dispersed phase; and the reverse, water-in-oil (W/O), where the oil constitutes the continuous phase and the water the dispersed phase. It is also possible to stabilize multiple (double) water-in-oil-in-water (W/O/W) emulsions using a 2-step method and a combination of hydrophilic and hydrophobic surfactants[10] and similarly oil-in-water-in-oil (O/W/O) emulsions.[11]

Emulsifiers and surfactants vary widely and can be classified as anionic (negatively charged), cationic (positively charged), amphoteric or zwitterionic (both positively and negatively charged) or non-ionic (no charge). Additionally, they are all amphiphilic molecules, meaning they have a distinct hydrophobic (oil-soluble water- hating) part and a distinct hydrophilic (water-soluble water-loving) part. The charged substances usually contain a polar group attached to a hydrocarbon chain, thus exhibiting both hydrophobic (hydrocarbon chain portion) and hydrophilic (polar group) characteristics[12] An additional important point to mention with regards to anionic and cationic surfactants is their ability to form these specific charges in aqueous solution. Amphoteric surfactants behave like cationic surfactants at low pH, and like anionic surfactants at high pH. At medium pH, they carry both positive and negative charges and they have the structure of a bipolar ion. Non-ionic emulsifiers tend to be condensation products of long chain alcohols with ethylene oxide for example, where the ethylene oxide is hydrophilic and the hydrocarbon chain hydrophobic. With regards to formulation the choice is heavily dependent on the type of emulsion required, the ingredients in the product and its intended use.[13]

Emulsions are dispersions of one liquid phase in the form of fine droplets in another immiscible liquid phase. The immiscible phases are usually oil and water, so emulsions can be broadly classified as oil-in-water or water-in-oil emulsions, depending on the dispersed phase. There is a considerable interest within the food industry in the use and development of water-in-oil (W/O) emulsions because they have a number of potential benefits over conventional oil. For example, Water-in-oil emulsions have been used widely to grease moulds of bakery products. Backwaren W, has prepared water-in-oil system as mould release oil from vegetable oil, waxes, emulsifiers and antioxidant.[1] The idea of using water-in-oil emulsions to grease the moulds of bakery products has been invented by William, H However, researches have been done to evaluate the quality parameters of water-in-oil emulsions, but still it needs researches to be done to evaluate the viscosity, stability and smoke point of water-in-oil emulsion.

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. It is well-known that certain mixtures of surfactants can provide better performance than pure surfactants for a wide variety of applications It is of importance to be able to disperse the largest quantity of water possible with the smallest quantity of surfactant and still generate emulsions with long-term stability.

The synergism can be defined like a situation where surfactant mixtures provide better states of minimum energy than a simple alone surfactant. Viscosity of water-in-oil (W/O) emulsions is strongly augmented by increasing its water volume ratio and by decreasing the temperature. There are several correlations between the relative viscosity (μr) of the water-in-oil (W/O) emulsions and their water volume content and oil phase density. The reduction in droplet size gives a large increase in the viscosity of concentrated water-in-oil (W/O) and oil-in-water emulsions (O/W). The rheological properties of food emulsions are of great interest to many industrial applications influenced by the flow behavior such as mixing units, pipelines and pumps.

HLB System

Whilst there are hundreds of emulsifiers to choose from the HLB (Hydrophile- Lipophile Balance) system enables one to assign a number to the emulsifier or emulsifier blend. This number indicates or expresses the relative simultaneous attraction of the emulsifier or emulsifier blend for water (hydrophilic), oil (lipophilic) or the two phases to be emulsified. While the theory of the system sounds simple, in practice the task unfortunately is not so clear-cut, as emulsifier classification via HLB only permits some prediction of behaviour.[8b]

Prior to making use of the HLB system for selecting a satisfactory emulsifier or blend of emulsifiers, it is imperative to evaluate exactly what is required. Issues such as; is the required emulsion water-in-oil or oil-in-water? How stable does one require the emulsion to be during storage and in use? Must it be non-toxic or non-irritant to the skin? These are some of the factors that will help to eliminate certain types and groups of emulsifiers and aid one in selecting others.

By applying the HLB system, one will be able to obtain an indication of what the emulsifier will do. That is, produce a water-in-oil (W/O) or oil-in-water (O/W) emulsion or behave as a detergent or solubilizing agent. It is important to note that the correct chemical type is just as important when selecting emulsifiers. As detailed in Table 1.1 an emulsifier that is hydrophilic in character and water soluble is assigned a high HLB number (above 11.0) and will produce an O/W emulsion. One that is lipophilic and oil soluble is assigned a low HLB number (below 9.0) and will produce a W/O emulsion. Two or more emulsifiers can also be blended to achieve an ideal HLB; these blends usually work best in achieving stable emulsions. For the purpose of this research and the production of mould release oil, emulsifiers with HLB values below 9.0 and with HLB values above 11.0 will be utilised in mixtures to produce W/O emulsion.

Material and methods:

Materials:

PGPR (Polyglycerol polyricinoleate) was obtained from Danisco (Shanghai, China). Sucrose fatty acid ester HLB-15 was provided by Hangzhou jinhelai food additive Co., LTD. Polyglycerol, span40 (sorbitan monopalmitate), Tween80 (sorbitan monooleate ethoxylate), sorbitan laurate (span20), sorbitan oleate (span80), sodium stearate, and alcohol were obtained from Sinopharm chemical Reagent Co., LTD. tert-butylhydroquinone (TBHQ) added to the soybean oil by the manufacturers as antioxidant. Flour, sugar, egg, baking powder, salt, milk and soybean oil were purchased from the local market. Double distilled water was used for the preparation of all emulsions. Local market release agent (B) and local market release agent (C) were kindly provided by Shanghai Run Wei Trading Company Limited.

Methods:

Preparation of Emulsions:

Emulsions were prepared with different ratios of water: oil and emulsifier's ratios were kept constant, as follows 3.5% (w/w) glycerol, 0.05 % (w/w) Sodium Stearate and combination of emulsifiers PGPR 1% (w/w)/ sucrose ester 0.5% (w/w) were added to the 15:80, 25:70, 35:60, 45:50, 55:40, 65:30 and 75:20 % (w/w) W: O ratio respectively. The mixtures were heated to 75°C for 15 min (to help the emulsifiers to dissolve completely), then were blended with a Model T18 Ultra-Turrax high-performance disperser (Ika-Werke Gmbh & Co., Staufen, Germany) at 17,500 rpm for 10 min, followed by passing through a high-pressure homogenizer (2MPa for the first stage and 20MPa for the second stage) valve homogeniser twice. At least, two separate emulsions were prepared for each treatment. The change was made for the combination of emulsifiers, which was as follows PGPR 1% (w/w)/ span20 0.5% (w/w), PGPR 1% (w/w)/ Tween80 0.5% (w/w) and Polyglycerol 1% (w/w)/ sucrose ester 0.5% (w/w) respectively.

Emulsion Stability by Centrifugation Methods

Emulsion stability was determined according to [14] the freshly prepared emulsions were accurately weighted into a 10 mL centrifuge tube and centrifuged at 3500 rpm for 30 min at room temperature. The total height of each emulsion in the centrifuge tube was then measured. Centrifugation produced layers of an oil phase on top, an emulsion phase in the middle and an aqueous phase in the bottom. The height of the separated layers oil phase, emulsion phase and aqueous phase was measured and converted to a relative percentage as follows for the same lubricant, % layer = (the height of the separated layer / the total height of the emulsion) ×100%.

Results:

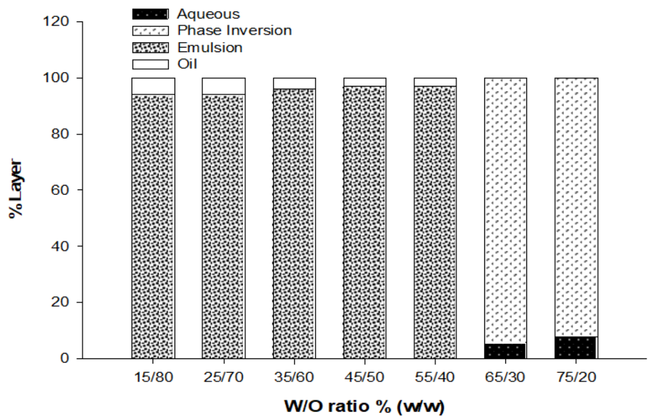

Figure 1 Phase separation of emulsions prepared with different water: oil ratios (15/80, 25/70, 35/60, 45/50, 55/40, 65/30 and 75/20 % (W/O) w/w) and different combinations of emulsifiers (PGPR and sucrose ester)

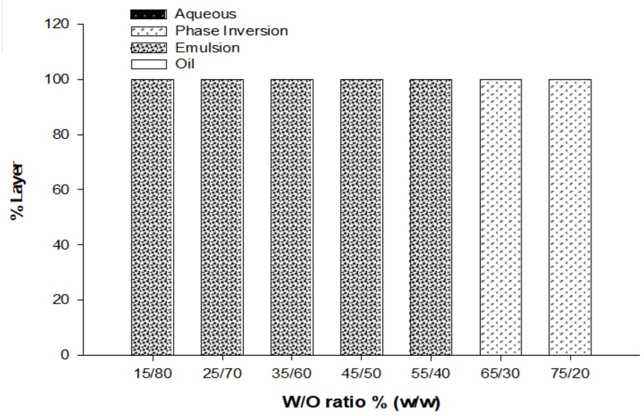

Figure 2 Phase separation of emulsions prepared with different water: oil ratios (15/80, 25/70, 35/60, 45/50, 55/40, 65/30 and 75/20 % (W/O) w/w) and different combinations of emulsifiers PGPR and span40.

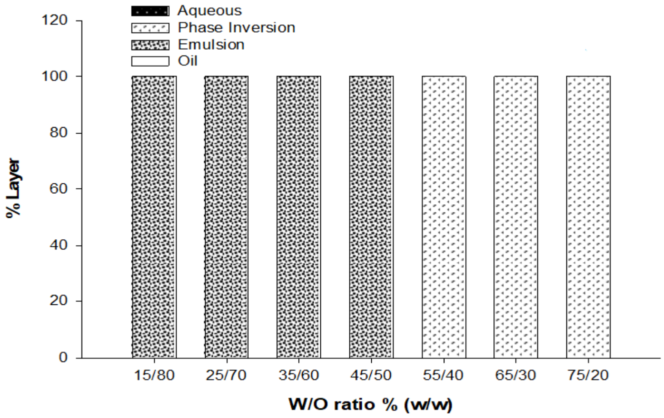

Figure 3 Phase separation of emulsions prepared with different water: oil ratios (15/80, 25/70, 35/60, 45/50, 55/40, 65/30 and 75/20 % (W/O) w/w) and different combinations of emulsifiers PGPR and Tween80.

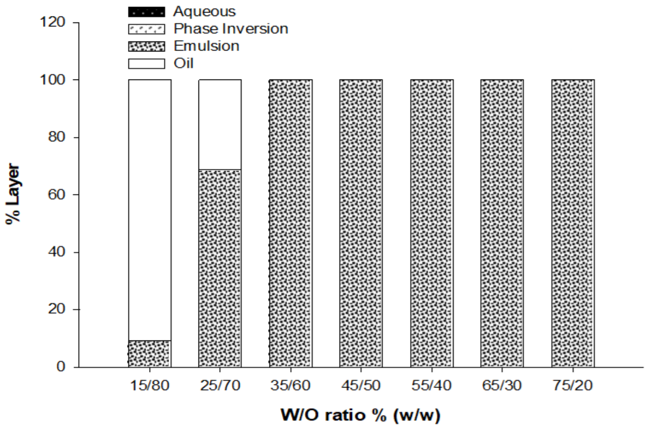

Figure 4 Phase separation of emulsions prepared with different water: oil ratios (15/80, 25/70, 35/60, 45/50, 55/40, 65/30 and 75/20 % (W/O) w/w) and different combinations of emulsifiers Polyglycerol and sucrose ester.

Discussion:

Phase separation by centrifugation force

Figure 1 shows extend of phase separation by centrifugation force. It is a combination of PGPR/ sucrose ester, although ratios from 15/80 % (w/w) to 55/40 % (w/w) were formed with an increase in water ratio and decrease in oil ratio, but it showed W/O emulsions with an oiling off on the top. Meanwhile, further increase in water ratio and decrease in an oil ratio resulted in phase inversion was taken place as in ratios of 65/30 % (w/w) and 75/20 % (w/w), and this phase inversion was not forming stable structure that is indicated by formation of an aqueous phase in the bottom.

Figure 2 shows a combination of PGPR/ span40, although ratios from 15/80 %(w/w) to 55/40 %(w/w) were formed with an increase in water ratio and decrease in oil ratio, but showed stable W/O emulsions. Moreover, phase inversion was taken place by a further increase in water ratio and decrease in the oil ratio as in ratios of 65/30 %(w/w) and 75/20 %(w/w), that is due to high-water ratio and low oil ratio in the system. This phase inversion formed stable structure that is indicated by no aqueous phase or oiling off in the system.

Figure 3 is a combination of PGPR/ Tween80, although ratios from 15/80 %(w/w) to 45/50 %(w/w) were formed with an increase in water ratio and decrease in oil ratio, but showed stable W/O emulsions. However, phase inversion was taken place by a further increase in water ratio and decrease in an oil ratio as in ratios from 55/40 %(w/w) to 75/20 %(w/w) that is due to high-water ratio and low oil ratio in the system. This phase inversion formed stable structure that is indicated by no aqueous phase or oiling off in the system. Comparing data of figure1 and figure 2 with figure 3, the phase inversion structure in figure3 and figure 2 was more stable than the phase inversion structure in the figure1

Figure 4 is a combination of Polyglycerol/ sucrose ester, ratios of 15/80% (w/w) and 25/70 % (w/w) showed severe separation, and that is probably because of this series of emulsions formed O/W emulsions, high oil ratio and low water ratio in the system do not allow the water to cover oil drops. However, ratios from 35/60 % (w/w) to 75/20 % (w/w) showed stable emulsions.

Conclusion:

Phase separation and inversion of emulsions prepared with different water: oil ratios and different emulsifiers was taken place in high water phase ratios. Properties of W/O emulsion affected by surfactant ratios, water fraction, concentration were evaluated. Different ratios of surfactant mixture (PGPR/ span40) were systematically screened to find the most stable emulsions.

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