Study of some physiochemical factors determining emulsion stability with mixed Emulsifiers

Navneet Rai¹ and I.P. Pandey²

¹Department of Chemistry, Dehradun Institute of Technology, Dehradun
²Oil Extraction, Environmental & Disaster Management Lab., D.A.V. (P.G.) College, Dehradun, Uttarakhand, India

*Corresponding author, E-mail: nraiin@gmail.com

ARTICLE INFORMATION

ABSTRACT

Emulsions are widely used in various fields such as pharmaceutical, agricultural, cosmetic, paint and food industries. The stability against coalescence of oil-in-water emulsions in the presence of mixed surfactants has been studied and effect of processing conditions, oil polarity, emulsifier polarity and composition, phase volume ratio, mixing time and temperature on emulsion stability is covered. No attempt was made to stop the emulsions from creaming and the stability of emulsions was characterized by the total liquid separated relative to the entire sample volume. These mixed emulsifier systems were found to induce long-term emulsion stability against coalescence via a synergistic mechanism in which both the surfactant have specific functions and induced stability was found to depend on the concentrations of both emulsifiers. It was found that for optimum stability, difference between oil polarity and emulsifier polarity should be minimum. Emulsion stability increases with processing time almost linearly and the emulsion stability increases with increasing oil to water ratio.

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1. Introduction

An emulsion is a dispersion of one liquid in another where each liquid is immiscible, or poorly miscible in the other (Tadros et.al., 1983). An emulsion is formed when two immiscible liquids (normally, one being of a lipophilic nature, oil, and the other one of a hydrophilic nature, water) are mechanically stirred (Rieger, 1976 & Tamilvanan et.al., 2010). During the stirring process, both liquids tend to form phases. If an emulsifier is added to the system, it tends to stabilize, forming a continuous and a dispersed phase, with the latter presenting a droplet shape. During the above-mentioned stirring process, droplets are formed in both phases, the continuous phase being formed as a result of the great instability within their droplets. For example, if water and oil are mixed to generate oil-in-water (O/W) system, as many drops will be formed within the water as those formed within the oil. However, due to the quick coalescence possessed by the water drops, they will yield the continuous phase. This continuous phase is known as the external phase and surrounds the dispersed (internal) phase in the system (Liberman, et.al., 1988 & Macedo et.al., 2006). When emulsions are applied to various commercial products, their physical properties such
as the particle size distribution and viscoelasticity are required to keep their original states regardless of time. The change of dispersion state of droplets, for example, flocculation and creaming, is also undesirable. However, in some applications it is necessary to break the emulsion in order to release the active material as the active ingredient is contained in the emulsion droplets. Thus, it becomes necessary to study the physicochemical factors determining emulsion stability.

Emulsifiers are usually added to oil/water mixture to enhance the formation of monomer emulsions and their stability (Celiset al., 2009). The molecules of emulsifier adsorb to the surface of oil droplets during homogenization and provide a protective membrane that prevents the droplets from flocculating or coalescing. Under certain circumstances, emulsifiers may have a negative impact on emulsion stability, because of their ability to form micelles that enhance mass transport processes, such as solubilization and oil diffusion through the aqueous phase (Pertzov et al., 1988 & Dickinson et al., 1996). These mass transport processes can cause significant changes in droplet concentration, composition and size distribution and may therefore adversely influence the bulk physiochemical properties of an emulsion, such as appearance, rheology and stability (Capek, 2004).

Emulsions are kinetically stable systems that is to say their free energy of formation is greater than zero and as such will show a tendency to break. The interfacial tension in emulsions is generally of the order of 1-10 mN m⁻¹, this in connection with the large interfacial area results in a large positive interfacial energy term. Emulsions are, however, kinetically stable due to the presence of an adsorbed layer at the o/w interface, this barrier may be electrostatic in nature, or steric (Grigoriev and Miller, 2009). These barriers not only prevent emulsion droplets from coming into the direct contact, but also serve to stabilize the thin film of liquid between two adjacent droplets. Several breakdown processes of emulsions may be distinguished: (i) Creaming or sedimentation (caused by gravity). (ii) Flocculation caused by vander walls attraction when there is not sufficient repulsion between the droplets. (iii) Ostwald ripening caused by the differences in solubility between the small and large droplets. (iv) Coalescence induced by thinning and disruption of the liquid film between the droplets. (v) Phase inversion whereby the disperse phase and medium interchange (Tadros, 2010).

Emulsion stability and instability have many common features with suspensions. Settling under gravity may occur when the density of the oil is higher than that of the medium. This may also occur with water-in-oil emulsions when the density of the aqueous droplets is higher than that of the oil phase. In most cases, creaming rather than sedimentation occurs, since most oils have densities lower than the continuous aqueous phase (Tadros, 2004). Flocculation of emulsions may occur under conditions when the vander walls attractive energy exceeds the repulsive energy (Deyaguin et al., 1941 &Verwey et al., 1948). One can also distinguish between weak and strong flocculation. Ostwald ripening may occur when the oil solubility is significant (the small droplets which have higher solubility than the larger ones, tend to dissolve on storage and become deposited on the larger ones). However, two distinct instability processes may be distinguished for emulsion systems: Coalescence which results from the thinning and disruption of the liquid film between the droplets, with the ultimate joining of these droplets and finally some oil separation can be observed (Binks, 1998). Phase inversion, whereby the disperse phase and medium exchange, i.e. the disperse medium forms the droplets and the dispersed droplets form the continuous phase (e.g. an O/W emulsion reverting to a W/O emulsion and vice versa) (Kruglyakov, and Nushtayeva, 2004).

Emulsions have found several applications in foods (McClements, 2009 &Friberg, 2003), cosmetics (Boonme, 2007 & Sakai, 2005), medicine (Nielloudet al., 2000), paints (Osemeahon, 2011), hydraulic fluids (Greaves and Knoell, 2009), polymerization (Anderson and Daniels, 2003), printing (Kutanane and Aghaei, 2011), fiber production (Litzinger, 1977), metal processing (Ohtake et al., 1988), wood processing (Liu et al., 2006), etc. When emulsions are applied to various commercial products, their physical properties such as the particle size distribution and viscoelasticity are required to keep their original states regardless of time. The change of dispersion state of droplets, for example, flocculation and creaming, is also undesirable. Accordingly, it is necessary to study the physiochemical factors determining emulsion stability. An effective testing procedure of water-in-oil emulsion stability was investigated by Fingas et al., (1994). Their work shows that viscosity provides a more reliable measure of emulsion stability but water content measurement is more convenient. They also researched the effect of stirring time and water to oil ratio on emulsification and concluded that stirring times longer than two hour adversely affect the emulsion stability. Emulsifier loses effectiveness with the increased dilution of higher water to oil ratio values. Surfactant concentration and the ratio of oil to water are important factors influencing the stability of emulsions. In the present work, we have studied the effect of processing conditions, oil polarity, emulsifier polarity and composition, phase volume ratio, mixing time and temperature on emulsion stability.

2. Experimental
2.1 Materials
Span 80 and Tween 80 from Sigma were used as received. Canola oil (Specific gravity: 0.914) and
paraffin oil (specific gravity: 0.860), obtained from a local manufacturer were used as oil phase.

2.2 Procedure
Predetermined amounts of oil (canola oil and paraffin oil) and emulsifier were introduced to a 100 ml. colloid mill (Charlotte G-10). All the measurements were made under the following conditions unless otherwise specified: the ratio of oil to water was 1:1 by volume; the stirring intensity, 3000 rpm; the mixing time, 40 minute and the emulsifying temperature, 30°C. The stability of emulsions was characterized by the total liquid separated relative to the entire sample volume.

3. Results and Discussion
The most important task in preparation of emulsions is the selection of suitable surfactant which will satisfactorily emulsify the chosen ingredients at a given temperature. Surfactants are often characterized by their hydrophilic/lipophilic balance or HLB. High HLB values indicate good water, or polar solvent solubility, of the surfactant while low HLB values are indicative of good solubility in non polar systems, such as oil.

The water loving, or hydrophilic character, of a surfactant is determined by the polarity of the head group. Typical head groups include, amine, quaternary ammonium, ethoxylate, sulfate, phosphate and carboxylate. The polarity of the head group may be altered in some cases by altering the pH or by increasing the degree of ethoxylation, e.g. increasing the ethoxylation levels increases the water loving character of the surfactant, and thus the HLB increases. Conversely, increasing the size of the fatty tail, or propoxylation of the head group will decrease the HLB.

The Hydrophile, Lipophile Balance, (HLB) system is a useful tool in finding a suitable emulsifying system. A vast number of emulsifiers are available to the formulator and the HLB system can be used as a guide to narrow the selection to those best suited to their specific system.

In order to emulsify a mixture of water and oil one or more emulsifiers is required. Each surfactant system (pure or mixture) can be characterized by an HLB value. Each oil/water system can be characterized by a so-called “required HLB” value (Robbers and Bhatia, 1961). This value depends on the nature of the oil and the product application. Basically, there are two types of product application. In one type water dominates; the oil forms droplets. This is designated as a oil in water (O/W) system. In the other type it is reversed. The system is essentially water in oil (W/O).

The HLB system predicts the optimum emulsion stability when the HLB value of the surfactant systems matches the required HLB of the oil/water system. The required HLB is the value at which enhanced emulsion stability will be attained.

Optimization of the performance can be achieved by only including surfactant systems with similar HLB values.

3.1 Effect of mixing time:
The radii of the droplets in the emulsion generally decreases with increasing emulsifying time (Verbich et.al., 1997). The emulsifier becomes more effective with increased mixing time. From the figure 1 we can see that in most cases stability increases with processing time almost linearly. In some cases, however, stability remains constant after about 10 minutes (figure-2). The optimum mixing time observed was 20 minutes. As the mixing time increased further, emulsion stability decreased.

Figure 1: Effect of Mixing Time on Emulsion Stability

3.2 Effect of Emulsifier polarity and oil polarity:
Oil polarity and emulsifier polarity are important factors responsible for emulsion stability. For canola oil emulsions (figure-1) the surfactant 5 (refer table 1) and for paraffin oil emulsions (figure-2) surfactant 2 proved to be most effective. Decreasing the polarity of the oil (canola oil → paraffin oil) the polarity of the emulsifier has to be reduced for optimum stability. Blending is often used to adjust the polarity of the emulsifier to the actual need. As obvious not only the average polarity is a key in determining emulsion stability, but even more the emulsified composition.

Figure 2: Effect of Polarity on Emulsion Stability
3.3 Effect of Phase Volume Ratio:

It has been reported that emulsion type is dependent on the relative phase volume. Ostwald, (1910) concluded that at a phase volume (oil to water) ø>0.74, the emulsion would be packed more densely than was possible. This means that any attempt to exceed a phase volume of 0.74 for the internal phase must result in either inversion or breaking.

For paraffin oil emulsions stabilized with the surfactant 6, at low phase ratio oil/water only low stability was obtained with the polar emulsifier due to low surfactant concentration at the interface. Increasing the phase ratio, surfactant availability increases accordingly leading to highly stable emulsions. Emulsions with phase volume ratio (oil/water) 8:2 were found to be highly stable. After stirring at 3000 rpm for 24 hours (continuously) for this emulsion of water in oil type an oil layer separated (0.02 v/v) and for emulsion with phase ratio 6:4 released a oil film (0.21 v/v) at the top. The water in oil emulsion with a phase volume ratio 9:1 is very unstable.

Figure 3: Effect of Phase Ratio on Emulsion Stability

3.4 Effect of HLB Value and Temperature:

Oil in water emulsions were prepared with paraffin oil/water at a ratio of 1:1 by volume using a mixture of an oil and a water soluble emulsifier. The HLB value of the emulsifier was varied by changing the emulsifier composition (refer table 1).

The temperature dependence of emulsion stability can easily be assessed by centrifugation at different temperatures. Temperature often has indirect effects on emulsification as a result of altering the interfacial tension, adsorption of emulsifier and viscosity. There is some evidence that a sharp increase or decrease of temperature tends to coagulate the particles, thereby causing the deterioration of emulsions. From the figure-4, we can see that emulsion stability decreases when temperature is increased. Near the optimum HLB value stability is less dependent on temperature. At higher temperatures the optimum HLB is shifted to higher values.

Table 1: HLB values of Surfactant Samples and emulsifier composition

<table>
<thead>
<tr>
<th>HLB</th>
<th>Span 80</th>
<th>Tween 80</th>
<th>Surfactant Sample</th>
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<tr>
<td>4</td>
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<td>8</td>
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<tr>
<td>15</td>
<td>100%</td>
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</table>

Figure 4: Effect of HLB Value on Emulsion Stability

4. Conclusion

Oil in water and water in oil emulsions were prepared using canola oil and paraffin oil and a blend of span 80 and tween 80 as emulsifiers. For canola oil emulsions surfactant sample 5 with HLB 10 and for paraffin oil emulsions surfactant sample 2 with HLB 7 proved to be most effective. The results of experiments can be summarized as follows:

a) For optimum stability, difference between oil polarity and emulsifier polarity should be minimum.

b) Emulsion stability increases with processing time almost linearly. The optimum mixing time observed in the experiments is 20 min.

c) The emulsion stability for water in oil emulsions increases with increasing oil to water ratio. The optimum ratio found to be 8:2.

d) High temperature reduced emulsion stability and the optimum emulsifying temperature was 35°C. Near the optimum HLB value stability was less dependent on temperature.
References


