A Study of Various Factors Determining the Stability of Molecules

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Abstract: An emulsion is a mixture of two or more that are normally immiscible. Emulsions find numerous applications in different fields. They play a major role in materials processing, from metal working to textile finishing, and have found an essential place in formulated cosmetic, pharmaceutical and food products. The droplet diameter of these emulsions is usually of the order of $0.1-10\mu$ m. The quality of an emulsion is related to its stability. In the present study, was undertaken to physiochemical and experimentally investigate the effects of different factors on emulsion stability. The factors are studied include effect of mixing time, the effect of processing conditions, oil polarity, emulsifier polarity and composition, emulsifier concentration, stirring intensity, emulsifying temperature on emulsion stability is covered.

Key words: Emulsion, Tween 80, Emulsifier, HLB, Emulsion Stability.

1. Introduction

An emulsion consists of two or more completely or partially immiscible liquids, such as oil and water, where one liquid (the dispersed phase) exists in the form of droplets suspended in the other (the continuous phase). Because the surface of each droplet is an interface between hydrophobic and hydrophilic molecules, it is inherently thermodynamically unstable. An emulsion is formed when two immiscible liquids are mechanically stirred (Rieger et al.1976). During the stirring process both liquid tend to form phases. If surfactant is added to system it tends to stabilized, forming a continuous and a dispersed phase, with the latter presenting a droplets shape. During above mentioned stirring process droplets are formed in both phase, the continuous phase being formed as a result of instability within their droplets. Emulsions are unstable with respect to the component bulk phases. So, for these purpose small surfactants molecules are also known as emulsifiers are added to the system to slow down the breaking of emulsion such as coalescences and creaming Becher (1983). Stability of emulsion is dependent upon the various type of factors including physical nature of the interfacial film, presence of steric barriers on the droplets, viscosity of the continuous phase, droplets size, oil/water ratio, Temperature, and mixing of stirring time. Emulsion stability is also related with the amounts of surfactant that get adsorb at the interface. When more surfactant get adsorb at the interface, the interfacial tension is decreased and the surfactant molecules act as a barrier delaying the coalescence of droplets.

Emulsions are thermodynamically unstable due to increased interfacial area and the fact that the separation of two liquids is expected to be spontaneous. Several breakdown processes of emulsion may be distinguished (Lewis 1995): (1) Creaming or sedimentation (caused by gravity) (2) Flocculation caused by Vander walls attraction when there is not sufficient repulsion between the droplets. (3) Ostwald ripening caused by the differences in solubility between the small and large droplets. (4) Coalescence induced by thinning and disruption of the liquid film between the droplets. (5) Phase inversion whereby the disperse phase and medium interchange. (6) Coalescence and Marangoni effect. For stabilization the emulsion, the mechanical energy is needed. . Mechanical emulsification is stable for a short period of time. Surfactants adsorb at the oil/water interface, lowering surface free energy, thus stabilizing the emulsions. Adsorption of surfactant at the oil water interface changes the characteristics of the electrical double layer. Due to the presence of electrical double layer reduces the coalescence of oil droplets by collision. Emulsions thus produced a long period of time and convenient for transport and utilization.

Emulsion stability or instability has features with the suspensions. Settling under gravity may occur when the density of 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 oil has densities lower than the continuous aqueous phase. Flocculation of emulsion may occur under condition when the Vander walls attractive energy exceeds the repulsion energy. Coalescence which results from 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 from the continuous phase. In present study we studied the effect of the processing condition, oil polarity, emulsifier polarity, phase volume ratio, mixing time and temperature on emulsion stability, the relative volume of the dispersed phase, average size of droplets, the nature and the concentration of the emulsifier.

2. Experiments

The emulsifiers used in the experiments are span 80 and Tween 80.Predetermined amounts of oil and emulsifier were introduced to a 100 ml.Colloid mill. All the measurements were made under the following conditions: ratio of oil to water was 1:1 by volume, the stirring intensity 2500 rpm, the mixing time 15 min and the emulsifying temperature 30° c. The stability of emulsion may be estimated by a turbidity method Pearce and Kinsella (1978) or by monitoring the droplets size distribution as a function of storage time using a laser light scattering instrument.

3. Result 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. A surfactant is a chemical compound or molecules which contains both a water-compatible group and an oilcompatible group. Surfactants are often characterized by their hydrophilic/lipophilic balance or HLB.Hydrophilic has a water-compatible group has polar constitutes, which are readily hydrated and confer to some degree the property of aqueous solubility on the molecules. Lipophilic is an oilcompatible group is composed hydrocarbon, miscible with the oil and insoluble in water. Hydrophilic/lipophilic balance or HLB scale was chosen as 1 to 20. The lower part of the scale 1-10 is lipophilic while the upper part of the scale is 10-20 is hydrophilic. The Hydrophile, Lipophile Balance, (HLB) system is a useful tool in finding a suitable emulsifying systems. In order to emulsify a mixture of water and oil one or more emulsifiers are required. Each surfactant system (pure or Mixture) can be characterized by a so-called "required HLB" value. This value depends on the nature of the oils 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 oil in water (O/W) system. In the other type is essentially water in oil (W/O). Thus an oil-compatible surfactant (HLB=1-10) promotes oil as the continuous phase (water in oil dispersion) and a water compatible surfactant (HLB = 10-20) promotes water as the continuous phase (oil in water emulsion) Sherman (1968).

4. Emulsifier Polarity and Oil Polarity

Emulsifier polarity and Oil polarity are important factors for emulsion stability. For paraffin oil emulsion (fig.1) surfactant 2 and for canola oil emulsions the surfactant 5 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. (1): Effect of oil polarity

5. Effect of Mixing Time and Stirring Intensity

According to Verbich et al. (1997) reported that the radii of the droplets in the emulsion decreased with increasing stirring speed and emulsifying time. The emulsifier becomes more effective with increased mixing time. If the mixing time is too long the effectiveness of emulsifier will be decreased because the intense stirring will cause the emulsifier to drop out from the oil-water interface. Fig. shows that the relative volume of emulsion increased as mixing time increased from 3 to 15 min. Further mixing time increased emulsion stability decreased. This experiment also shows that the mean size of the particles decreased in the first few seconds and then gradually attained the limiting after 15 min.



The purpose of stirring is to form a stable and homogenous emulsion by breaking large liquid drops into smaller drops. Fig. shows that the relative volume of emulsion as a function of stirring intensity after stirring the mixture for 15 min. The relative volume of emulsion prepared using 1000 rpm stirring speed decreased sharply with time indicating that a 1000 rpm was not sufficient for the emulsion system. A stirring speed higher than 2500 rpm was not required because higher stirring speed will lead the emulsifier to break away from the oil-water interface.

6. Effect of HLB Value

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

HLB	Span80 (%)	Tween80 (%)	Surfactant Sample
4	100		
6	83	17	1
7	74	26	2
8	65	35	3
9	56	44	4
10	46	54	5
12	28	72	6
13	19	81	7
14	9	91	8
15		100	

Table 1: HLB value of different emulsifier composition

7. Effect of Emulsifier Concentration

Figure (3) Shows that the relative volume of emulsion increased as surfactant concentration increased from 0.25% to 0.50%. Emulsion stability decreased if the concentration

is further increased. This is because at low surfactant concentration, the emulsion is not stable due to agglomeration of the oil droplets; at high surfactant concentration, the emulsion destabilization occurs as a result of rapid coalescence. The optimal Tween 80 concentration for the emulsion system was 0.50%.



Figure (3) Effect of emulsifier concentration

8. Effect of Temperature:

Temperatures often have indirect effects on emulsification as a result of altering the interfacial tension, adsorption of emulsifier and viscosity. The relative emulsion volume was determined at a temperature ranging from 30 to 70 $^{\circ}$ c. The mixture was stirred for 15 min at

different temperatures, with increments of 10 $^{\circ}$ c. The emulsion was more stable at lower temperature, and the most stable was generated at 30 $^{\circ}$ c. There is some evidence that a sharp increase or decrease of temperature tend to coagulate the particles, thereby causing the deterioration of emulsions. From the figure (4), we can see that emulsion stability decrease the stability decreases when temperature is increased.



Figure (4) Effect of temperature

9. 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. Difference between oil polarity and emulsifier polarity should be minimum. At lower emulsifier concentration the emulsion stability was unstable and instability at higher concentration was a result of rapid coalescence and concentration. The optimul emulsifier concentration was 0.5% by volume. The optimum stirring intensity was 2500 rpm for the emulsion system investigated. Higher temperature reduced emulsion stability, and the optimum emulsifying temperature was 30 $_{0}^{0}$ c.

References

[1] Binks B.P. (Ed.), (1998).Modern Aspects of Emulsions Sciences, Royal Society of Chemistry Publications, Cambridge.

[2] Deyaguin B.V., Landau L., (1941) Acta Physiochim. USSR14633.DickinsonE. McClements D.J., 1996 Advances in food Colloids, Blackie Academic and Professional, Glasgow, UK.

[3] D.J.McClements, Current Protocols in Food analytical Chemistry (vol.1), New York, NY:John willey & sons Inc. (2001).

[4] Fings M.F.,Fieldhouse B.,Bier L.,Conrod D.,Tennyson E., (1994) Author Affiliation: Environmental Technology Cent source: ASTM special Technical Publication, 1252, ASTM, Philadelphia, PA, USA, 41-54

[5] G.Li, R. Guo, China Petroleum Industry Press (1995) 54.

[6] H.Barnes, Colloids Surface A: Physicochem. Eng. Aspects, 91 (1994) 89-95.

[7] K.N. Pearce, J.E. Kinsella, J. Agriculture and food Chemistry, 26 (1978) 716-723.

[8] P. Becher, Emulsions Theory and Practice, Seconded.,Reinhold, New York,1993.

[9] P.Becher, Encyclopedia of Emulsion Technology, Dekker, New York, 1983

[10] P.Sherman, Emulsion Science(1968) 18-23.

[11] R.P.James, R.P.Charles Petroleum spills (1985) 3.

[12] T.F.Tadros, Colloids Surfaces A: Physicochem. Eng. Aspects, 91 (1994) 39-55

[13] T.F.Tadros, in: Holmberd (Ed.), novel Surfactants, Dekker, New York 2003

[14] T.F. Tadros, K.Booten, B.Levecke, Cosmet.Toiletries, 119 (2004) 51.