Formulation practical – Emulsions

Introduction

An emulsion consists of two immiscible liquids, one liquid dispersed in another, the dispersed droplets being termed the *disperse phase*, which is a finely subdivided liquid that is uniformly distributed throughout the surrounding liquid, the *continuous phase*. Emulsions can be *water-in-oil (w/o)* or *oil-in-water (o/w)* systems. Multiple emulsions can also be formed, for example, an initial water-in-oil emulsion can be prepared, and then emulsified with an external water phase. This would produce a *water-in-oil-in-water (w/o/w)* emulsion. *An oil-in-water-in-oil (o/w/o)* emulsion would be produced in a similar way. An emulsion is stabilised by an emulsifier, which produces an interfacial film between the oil/water interphase, which is mechanically strong enough to prevent the emulsion from breaking. Emulsifiers have both hydrophilic and hydrophobic properties, but neither is completely dominant, however it should be more soluble in the continuous phase, so that it can adsorb quickly around the dispersed drop as a film, which should not thin out when two droplets collide, and thus will not permit coalescence (the fusion of droplets to separate the two liquid phases).

Surfactants are the most commonly used emulsifying agents. They adsorb at the water-oil interface to form dense monomolecular film and decrease the interfacial tension. Combination of surfactants forms a more rigid, stabilizing film at the interface. For example, a mixture of two non-ionic surfactants, Span 80 (lipophilic) and Tween80 (hydrophilic), Tween 80 penetrates between the Span 80 molecules, so that the interfacial film is more close-packed and is strengthened. This increases the stability of the o/w emulsion and decreases particle coalescence. The Hydrophile - Lipophile Balance (HLB) has been devised to measure the relative contributions of the hydrophilic and lipophilic regions of the molecule.

$$\text{HLB} = \Sigma \text{ (hydrophilic group numbers)} - \Sigma \text{ (lipophilic group numbers)} + 7$$

The values for HLB range from 0 to 20, where the low numbers, <10, represent the lipophilic (poorly water-soluble) surfactants and the high numbers, >10, represent the hydrophilic (water-soluble) surfactants. The HLB of a mix of two surfactants can be calculated as follows:

$$\text{HLB}_{mixture} = f \cdot \text{HLB}_A + (1-f) \cdot \text{HLB}_B \qquad \text{Equation (1)}$$

Where $\text{HLB}_{mixture}$ = HLB of a mix of two surfactants
HLB_A and HLB_B = HBL of surfactant A (Span 80; HLB 4.3) and surfactant B (Tween 80; HLB 15.0) respectively
f = fraction of Span 80
$1-f$ = fraction of Tween 80

Emulsions are thermodynamically unstable. The stability of the final product must be considered. Three major phenomena associated with physical stability are creaming/caking (particles float/sink in the emulsion depending on their density) flocculation (coagulation; coacervation; particles cluster together and float/sink) and coalescence (cracking; fusion of particles).

As the disperse phase droplets are brought closer together, creaming/caking can occur, which may facilitate the more serious problem of coalescence. Creaming is governed by Stoke's Law:

$$v = \frac{2gr^2 (\rho_d - \rho_c)}{9\eta} \qquad \text{Equation (2)}$$

where v = velocity of creaming
g = gravity
r = radius of particle
η = viscosity of continuous phase
ρ_d = density of disperse phase
ρ_c = density of continuous phase

Aim of experiment

- Determine whether a given emulsion is an oil-in-water (o/w) or water-in-oil (w/o) system
- Determine the optimum HLB value for an emulsion
- Measure the viscosity of the continuous medium and investigate the effect of increasing the viscosity of the continuous phase on emulsion stability
- Investigate the effect of reducing the size of the disperse phase droplets on emulsion stability

Methodology

Experiment A – Determination of emulsion system

The three most common tests carried out to determine the system of an emulsion are:

1. *Dilution test* – a small volume of the unknown emulsion was taken and dissolved with some water. The emulsion will only dissolve in the same liquid as the continuous phase.

2. *Conductivity test* – electrodes were connected to an electrical circuit and immersed into the unknown emulsion. Systems with aqueous continuous phases will readily conduct electricity, whereas systems with oily continuous phases will not.

3. *Dye-solubility test* – a water-soluble dye, Methlyene Blue, was added to a small volume of the unknown emulsion. A dye will only be soluble in and colour an emulsion that is the same phase as that of the continuous phase.

Experiment B – Determination of the optimum HLB value for an emulsion

Five emulsions were prepared with the formula:

Oil (projosine)	10ml
Surfactant	5g
Water	to 50ml

where the surfactants are Tween 80 (HLB 4.3) and Span 80 (HLB 15.0). The total amount of surfactant is 5g. The following table indicates the weights of the surfactants needed to achieve $HLB_{mixture}$ 9, 10, 11, 12 and 13:

$HLB_{mixture}$	Mass Span 80 (g)	Mass Tween 80 (g)
9	2.80	2.20
10	2.34	2.66
11	1.87	3.13
12	1.40	3.60
13	0.93	4.07

Two emulsions were made for each of the HLB values.

To prepare the emulsions, all the surfactant and oil were added into a clean, dry mortar, and mixed thoroughly with a pestle. Water was added gradually while mixing, to form the primary emulsion. This was then diluted with the rest of the water and made up to 50ml in a measuring cylinder.

The emulsions were labelled and left to stand. The creaming ratios of all the emulsions were measured 4 days later. The emulsion that creamed the least was the most stable has the optimal $HLB_{mixture}$.

Experiment C – The effect of increasing the viscosity of the continuous phase on emulsion stability

Emulsion stability can be characterised by creaming. To determine the effect of increasing the viscosity of the continuous phase on the rate of creaming, three emulsions were prepared and the extent of creaming was related to the viscosity of the continuous phase. The continuous phase was an aqueous phase containing methylcellulose (an emulsifier, is also a viscosity enhancer).

Viscosity measurements:
The viscosity of the 3% w/v, 4% w/v and 6% w/v methylcellulose (Methocel) solutions were measured using the falling sphere viscometer. The viscometer consisted of a cylinder into which the solution was poured. A ball, of nylon, Teflon, steel, was dropped through the liquid, and time taken for the ball to drop between two levels was measured. The more viscous the liquid, the slower the ball fell, i.e. the longer the time period. Three balls were dropped for each different viscosity and a mean was taken. The viscosity was calculated by rearranging Equation (2).

Emulsion preparation:
The oil phase (liquid paraffin; 15ml) was placed in a mortar. The aqueous phase (containing the methylcellulose) was gradually added while mixing, and then made up to 100ml in a measuring cylinder. A total of six emulsions were prepared, two of each continuous phase provided (3% w/v, 4% w/v and 6% w/v methylcellulose). 50ml of each prepared emulsion was used in Experiment D (see ahead). The remainder of the emulsions were left to stand and the extent of creaming was measured four days later.

Experiment D – The effect of homogenisation on emulsion stability

Homogenisation reduces the globule size of the disperse phase, hence increases the stability of an emulsion. 50ml of each emulsion, prepared in Experiment C, was homogenised. Using a light microscope, the change in the size of the globules was determined using a light microscope. The emulsions were left to stand and the extent of homogenisation was observed four days later.

The homogenised emulsions would be expected to have the least amount of creaming due to the increased amount of smaller dispersed droplets in the continuous phase. As a result, there would be an increased surface area for the emulsifier to work on, hence increasing the stability of the emulsion by reducing the amount of creaming. Increasing the number of globules, would increase the viscosity, thus increasing the stabilisation of the emulsion, from Stoke's Law.

Results and Discussion

Experiment A – Determination of emulsion system

1. *Dilution test* – the unknown emulsion diluted in water.

2. *Conductivity test* – the unknown emulsion conducted electricity.

3. *Dye-solubility test* – the water-soluble dye was able to dissolve in the unknown emulsion and successfully colour the unknown emulsion.

These observations suggest that the continuous phase was water, and so the disperse phase must have been oil. Therefore, the emulsion was an oil-in-water system.

Experiment B – Determination of the optimum HLB value for an emulsion

After four days, the extent of creaming was determined by the ratio of volume that creamed against the total volume of the emulsion. This is illustrated in the table below:

HLB	Creaming volume (ml)	Total volume (ml)	Creaming ratio
9	19	50	0.38
10	11	50	0.22
11	7	50	0.14
12	1	50	0.02
13	2	50	0.04

The results show us that the emulsion with HLB 9 had the highest creaming ratio, thus creamed the most. HLB 12 had the least creaming ratio, thus creamed the least. The lowest creaming ratio is a desirable property in emulsion products as it shows stability. Therefore, the optimum HLB for this emulsion is HLB 12.

 The difference in amounts of Tween 80 (HLB 4.3; a more hydrophilic surfactant) and Span 80 (HLB 15.0; a more lipophilic surfactant) have made a difference in the amount of creaming an emulsion undergoes. As the HLB value was increased, the amount of Tween 80 was also increased. Tween 80 tends to form an o/w emulsion, thus increasing the strength of the interfacial film between the oil and water phases; however this is only true up to a certain point, the optimal HLB value i.e. HLB 12. Thus, there needs to be a suitable balance of both surfactants to produce the most stable interfacial film between the two phases.

Experiment C – The effect of increasing the viscosity of the continuous phase on emulsion stability

Viscosity measurements:
The table shows the time taken for the ball to drop between the two levels. It was measured three times and the mean was taken:

[Methylcellulose] %w/v	Density kg/m^3	Time taken for ball to drop between the two levels (seconds)			
		Reading 1	Reading 2	Reading 3	Mean
3	1011	17.34	18.38	16.84	17.52
4	1012	35.03	35.87	36.35	35.75
6	1016	173	142	149	154.67

The viscosity can be found by rearranging Equation (2), from Stoke's Law, for viscosity, η:

$$\eta = \frac{2gr^2 (\rho_d - \rho_c)}{9v} \qquad \text{Equation (3)}$$

where $r = 0.00122$m
   $\rho_d = 1150$ kg/m^3
   ρ_c = as in the table above
   v = distance/time between the two levels on the viscometer tube (0.152m apart)
   $g = 10$ m/s^2

The calculated viscosities are illustrated in the following table:

[Methylcellulose] %w/v	Viscosity of medium (Pas)
3	0.053
4	0.107
6	0.446

The results show that increasing the viscosity of methylcellulose increases the viscosity of the medium. The time taken for the ball to fall between the two levels increases as the concentration of Methylcellulose was increased. From Stoke's Law, there is a decrease in the velocity of creaming. This is because increasing the viscosity of the medium decreases the mobility of the disperse phase droplets. This reduces the amount of collisions that would occur between the droplets, hence decreasing the chances of coalescence.

Experiment D – The effect of homogenisation on emulsion stability

After four days, the extent of creaming was determined by the ratio of volume that creamed against the total volume of the emulsion. This is illustrated in the table below:

[Methylcellulose] %w/v		Creaming volume (ml)	Total volume (ml)	Creaming ratio
3	Unhomogenised	9	64	0.141
	Homogenised	3	25	0.120
4	Unhomogenised	9	50	0.180
	Homogenised	7	34	0.206
6	Unhomogenised	4	46	0.0870
	Homogenised	4	32	0.125

Methylcellulose 3% w/v
The particle size of the homogenised emulsion was bigger than that of the unhomogenised emulsion. This was a very surprising result, as the size of the globules was expected to decrease after homogenisation. This was due to the emulsion not mixed well enough during preparation, thus homogenisation did not have an effect.

However, the creaming ratio of this emulsion decreased after homogenisation. This was expected as the decrease of globule size increases the number of disperse phase droplets in the continuous phase, and increases the surface area onto which the emulsion works, which, in turn, increases the stability of the emulsion, hence the decrease in the extent of creaming.

Methylcellulose 4% w/v
The particle size of the homogenised emulsion was smaller than that of the unhomogenised emulsion. This was an expected result.

The creaming ratio of this emulsion increased slightly after homogenisation. This is another revelation since the disperse phase droplet size decreased after homogenisation. There was not a sufficient volume of the emulsion to retrieve an accurate reading of the various volumes that were required to determine the creaming ratio.

Methylcellulose 6% w/v
There was a decrease in particle size after homogenisation. This was an expected result as homogenisation decreases the particle size of emulsions.

The creaming ratio of this emulsion had a slight increase in the creaming ratio. This may be due to the same causes as mentioned above.

Conclusion

Most of the aims set out at the beginning of the practical were met:

- The unknown emulsion was found to be of the oil-in-water system.

- The optimum HLB for an emulsion was found to be HLB 12.

- The viscosity of the continuous medium was measured using a falling sphere viscometer and the effect of increasing the viscosity of the continuous phase was found to increase the stability of the emulsion as there is a decrease in the creaming ratio.

- The effect of reducing the size of the disperse phase droplets on emulsion stability was not sufficiently found out due to experimental errors. These trends did not comply with the previous experiment.

There are many ways in which these experimental errors could be improved to give a more accurate and sound result.

- The small volumes of emulsion made it difficult to accurately read the creaming volume, thus creating anomalies in the trends. The volume of emulsion should then be increased.
- Homogenisation should be carried out for a longer time period. This would have ensured a decrease in the size of the disperse phase droplets.
- The emulsions may have been disturbed during the time they were left to stand to allow for creaming. This would have disrupted the disperse phase droplets, thus, producing misleading results.

In addition, there can be further investigations that would assist understanding of emulsions:
- Demonstration of phase inversion (demulsification) – from an oil-in-water to a water-in-oil system.
- Measuring coalescence of disperse phase droplets in both oil-in-water and water-in-oil systems.
- Introduction of other emulsifying agents – macromolecules/polymers and finely divided solid particles.
- Test the limits of emulsion stability/instability – charge, electrolyte, changes in pH, oxidation.