Effect of Dispersed Phase Viscosity on Stability of Emulsions Produced by a Rotor Stator Homogenizer

Abubakar Mohammed[a*], Sylvia Ijeoma Okoye[b] , Jamilu Salisu[c]

[a] *Department of Chemical Engineering, Modibbo Adama University of Technology Yola, Nigeria.*
[b] *Department of Chemical Engineering, Modibbo Adama University of Technology Yola, Nigeria.*
[c] *Department of Chemical Engineering, Modibbo Adama University of Technology Yola, Nigeria.*

[a]*Email: amajalingo@gmail.com*
[b]*Email: ljkasie99@gmail.com*
[c]*Email: ejamilsalih@yahoo.com*

Abstract

Stability is one of the key quality parameters of emulsion systems, which goes a long way in predicting the shelf life of emulsion products. In this study, the effect of dispersed phase (oil) viscosity on emulsion stability was investigated by preparing oil-in-water emulsion samples of varying linseed and vegetable oil viscosities between 0.022 Pa.s and 4.00 Pa.s. The destabilization characteristics of emulsions prepared emulsions were followed by monitoring changes in droplet sizes and distribution as the emulsions aged. The ageing of the emulsions was accelerated by subjecting the samples to freeze-thaw tests. Polysorbate20 (Tween 20) surfactant was used as the emulsifier and a Silverson L4R mixer was used to provide homogenisation at speed of 7000 rpm. The droplet size analysis was done by laser diffraction. Results from the droplet size distribution analysis showed average droplet sizes increased as the dispersed phase viscosity of the emulsions increased.

Keywords: Emulsion Stability; Dispersed Phase; Homogenization; Laser Diffraction.

----

* Corresponding author.

1. Introduction

Emulsions are thermodynamically unstable and with time they tend to break down and separate into their constituent liquids. One of the most important quality requirements for emulsions is for it to be able to remain stable for the engineered time frame. There are instances, however, where emulsions are engineered to be unstable [1], but this research focuses on stable emulsions. To reduce the rate of instability emulsifiers are normally added to the formulation, they provide stability in emulsions primarily by reducing the interfacial tension at the oil-water interface. The surface tension of water or the interfacial tension between the oil and water can be reduced as much as 50% by adding as little as 0.1% of a surfactant [2]. When the surface or interfacial tension is lowered the oil (dispersed phase) and water (continuous phase) droplets tend to remain homogenous for relatively longer periods, basically resulting in higher stability for the emulsions.

Emulsifiers that are more soluble in the aqueous phase tend to produce oil-in-water (O/W) emulsions while those more soluble in the oil phase tend to produce water-in oil (W/O) emulsions. This basis of emulsion type determination was put forward by Bancroft and is commonly known as Brancroft's rule [3].

Several mechanisms have been known to be responsible for the instability of emulsions; these include creaming, flocculation, coalescence, phase inversion and Ostwald ripening [4]. During normal storage of emulsions, a variety of chemical, and microbiological stresses, in addition to temperature, will also cause the destabilization of the emulsion over time, however such mechanisms would not be considered in this research. Most of these mechanisms are controlled in industries by using additives such as emulsifiers (surfactants).

Numerous studies have been carried out to investigate the effect of droplet size distribution on emulsions stability; it was found in most cases, emulsions with smaller droplet sizes tend to be more stable than those with larger droplet sizes [5-8]. The use of particle size reduction methods to improve stability involves in most cases the use of more energy for mixing or homogenization. With the ever increasing cost of energy it would be worthwhile to look into the effect of other parameters that might affect the droplet size distribution and consequently the stability of the emulsions.

Most of the work done on emulsion stability is derived from the Stokes Law;

$$\upsilon = 2\,r^2\,(\rho - \rho_o)\,g\,/\,9\eta \ [\,9\,]$$

(where, υ is the creaming or settling rate as the case may be, r represents the radius of the droplet radius, ρ the density of the droplet, ρ_o the density of the continuous phase, η the viscosity of the continuous phase and g the local acceleration due to gravity) which considers densities of the dispersed and continuous phases, the droplet size of the dispersed phase and the viscosity of the continuous phase, which all affect the destabilization rate of emulsion systems. This study would however, look into the effects of dispersed phase viscosity on the droplet sizes and distribution of emulsions by using emulsions prepared with oils of different viscosities and then measuring the size distributions after subjecting the emulsion samples to standardized test conditions over a period of time. The choice of emulsification and droplet size analysis techniques adopted in this study were made out of the techniques widely used in industries.

The rotor-stator homogenizers are mostly used in the food, pharmaceutical, cosmetic and petrochemical industries [10]. They come in different sizes; ranging from small hand held types to very large industrial scales. The rotor is housed concentrically inside the stator, some authors refer to the rotor and stator assembly as the mixing head, and some however, refer to the stator as the head [11].

It might seem straight forward to run the rotor-stator at its maximum speed this is however not the case, most operators do not run their machines at its maximum speed for fear of over working it and thus reduce its efficiency and ultimately damaging it. As long as the power draw is within the machine's range, running at the maximum speed is desirable. Droplets breakage normally increases with speed of rotor-stators and residence time until an equilibrium size distribution is reached. When the rotor-stator is operated at certain speeds, a corresponding equilibrium size distribution is attained by the emulsions. When the speed is changed, again a different equilibrium size distribution would be attained. The best possible speed setting for the rotor-stator would be at its maximum; as this would give the optimal size reduction possible with the equipment [12].

1.1. Emulsion stability tests

One of the most important parameters used in observing emulsion stability is changes in the droplet size distribution and concentrations, which are measured as a function of storage time at specified temperatures [13, 14]. Other bulk properties of the emulsion such as rheology and colour etc could be measured as a function of time to determine stability of emulsions; however, interpreting such properties to obtain meaningful information about changes happening at the colloidal level is much more difficult.

Stability tests are often time consuming and a vast amount of research have been carried out to find alternative ways of measuring the stability of emulsions. In one of such studies, particularly in the cosmetic industries, methods were developed to reduce the time for such tests to just about 24 hrs [15]. A number of methods have been developed to accelerate these tests, one of such tests is the freeze-thaw cycle. Freeze-thaw has been widely used as an accelerated test to determine emulsion stability [9]. The emulsion sample is stored at -10°C for 24 hours and then stored at ambient, this constitute a cycle. The procedure continues between 2 to 5 cycles, depending on the end application of the emulsion.

Table 1 lists some of the common stability test used by industries and their time frame.

Salt titration is another method of testing emulsion stability; the emulsion is titrated until it separates. The amount of salt solution titrated can be used to estimate emulsion stability. The use of Turbiscan is another way of determining emulsion stability, which over the years is gaining more ground [9].

1.2. Interpreting droplet size distribution results

The results from droplet size analysis are reported in a number of ways these are internationally recognized;

i. **D(v, 0.5):** This is the size in microns at which 50% of the sample is larger smaller and 50% is larger. It is sometimes referred to as the Mass Median Diameter (MMD) or the median of the distribution.

ii. D(v, 0.1): This is the size of the droplet below which 10% of the sample lies

iii. D(v, 0.9): This is the size of the droplets below which 90% of the sample lies.

iv. D[4, 3]: This is the volume weighted mean or mass moment mean diameter.

v. D[3, 2]: This is the surface weighted mean, sometime referred to as the surface area moment mean diameter or Sauter mean.

The v in some of the expression shows that they are volume distribution. This can be replaced by s, for surface or l, for length depending on the choice of distribution one intends to make measurements. Volume distributions are in most cases used for reporting size distributions [16].

Table 1: Emulsion Stability Tests and Duration

Conditions of storage	Period of storage
Ambient temperature	25^oC for about 3 years or the projected shelf-life of the emulsion product
Elevated temperature	37^oC for about 6 months and $45oC$ for 3 months
Refrigeration	Approximately 4^oC for 3 months
Freeze/thaw cycles	Approximately -10^oC to ambient
Cycling chamber	4^oC to $45oc$ in 48 hours for 1 month
Light exposure	1 month exposure to north-facing day light or light cabinet

2. Materials and Method

2.1 Materials

Materials used in the experiments include; refined and boiled linseed oils of 0.022 and 4.00 Pa.s at 25^oC respectively, vegetable oil of viscosity 0.036 Pa.s also at 25^oC, polysorbate 20 (Tween 20), distilled and deionised water.

2.2 Emulsion preparation

Refined and boiled linseed oils supplied by Hampshire Commodities limited, UK of viscosities of 0.022 and 4.00 Pa.s respectively were first blended by weight in ratios of 1:9, 2:8, 3:7, 4:6 and so on. The viscosities of the blended oils were measured using a Bohlin high resolution C-VOR rheometer at 25^oC. Linseed oil was chosen due to the fact that different grades of linseed oils are available and could be easily blended to get a wide range of oils with similar chemical properties but with different viscosities.

Blended oils of viscosities 0.022, 0.050, 0.134, 0.358, 1.240 and 4.000 Pa.s were then chosen to make O/W emulsion samples with formulations of 15 wt.% oils and 0.5 wt.% polysorbate solution in distilled water. The polysorbate solution was then added to the oils. Adding water to oil involves phase inversion and has been shown to produce emulsions of smaller drop size than when oil is added to water [17]. Polysorbate 20 was chosen due to its having a HLB number of 16.7 making it suitable for preparing O/W emulsions [18].

A Silverson L4R mixer was used to homogenize the samples at 7000 rmp making 6 samples. The duration for homogenization for all the samples was 10 minutes. The samples homogenized were labelled A1, A2, A3, A4, A5 and A6 indicating corresponding to the dispersed phases (oil) viscosities of 0.022, 0.050, 0.134, 0.358, 1.240 and 4.000 Pa.s respectively.

In order to validate the findings of this study, an emulsion samples was prepared using vegetable oil of viscosity 0.036 Pa.s measured at 25°C using the same formulation as those prepared using linseed. The sample was also homogenized at 7000 rpm and labelled D1.

2.3. Droplet size distribution measurements

The droplet size distributions for all the emulsion samples prepared were measured with a Malvern Mastersizer 2000 laser diffraction machine. To measure the droplet size distributions for the emulsion samples standard operating procedures (SOP) was generated. The information required to generate the SOP include the density and refractive index of the dispersed and continuous phases. The refractive index of water is well known to be 1.33, while that for the oils were measured at 25°C with the aid of a refractometer, giving refractive indexes ranging from 1.4818 for the lowest viscosity oil to 1.4904 for the highest viscosity oil. In order to get accurate results SOPs were prepared for all samples by measuring the refractive index of each of the blended linseed oils as well as that of the vegetable oil.

Most errors in measuring droplet size using the Mastersizer is as a result of user errors which arise if wrong parameters are entered, the lens is not properly cleaned or due to poor delivery of samples, for this reason the lens must be kept as clean as possible. In this study, deionised water was used to clean the lens. For detailed information refer to the Mastersizer manual [16].

2.4. Stability tests

The freeze-thaw stability test was used to accelerate the rate of destabilization of all the emulsion samples. The tests were carried out in 3 cycles; the first cycle involved the emulsions being stored at approximately -10°C for 24 hours (achieved with the aid of controlled refrigeration) and then exposing the emulsion samples to ambient temperature for 24 hours, this constituted 1 cycle. At the end of each cycle the droplet size distributions were measured with the Mastersizer 2000 as already described. The emulsions prepared with vegetable oil were also subjected to the same conditions as those prepared with linseed oils.

2.5. Other tests carried out

To determine the extent to which the surfactant reduced the surface tension in water, the surface tension of 0.5wt% polysorbate solution was measured at 25°C with the aid of a Kruss K12 Tensiometer, the Du Nouy ring measurement technique was adopted.

3. Results and Discussion

The droplet size distribution results from emulsions made with vegetable oil are included, with a view of making comparisons with those obtained from emulsions prepared using linseed oils. This was done in order to obtain a more generalized conclusion on the relationship, if any, that exists between the viscosity of the oils (dispersed phase) used and their respective particle size distribution and hence emulsion stability.

3.1. Results of Blending High and Low Viscosity Linseed Oil

The results obtained from blending high and low viscosity linseed oils in different ratios are shown in table 2. A graphical representation of the results is further shown in figure 1. The 0% of boiled linseed indicates a 100% refined linseed oil, 10% boiled represents a 10% boiled and 90% refined and so on.

The results from the blending show an exponential increment in the viscosities as the amount of boiled (higher viscosity) is increased. This could be used as a guide for blending linseed oils that fall within the range of the oils used in this study.

3.2. Droplet size distribution of emulsion samples

Figure 2 shows the results obtained from measuring the droplet size distributions of emulsions prepared at maximum homogenizer speed of 7000 rpm.

Table 2: Blending of High and Low Viscosities of Linseed Oil

% of Blended Linseed Oil	Viscosity (Pa.s)
0	0.022
10	0.029
20	0.050
30	0.087
40	0.134
50	0.250
60	0.358
70	0.665
80	1.240
90	2.145
100	4.000

Figure 2 also shows that emulsion sample with the lower dispersed phase viscosities have narrower size distribution, as opposed to those with higher viscosities. An interesting point worth noting is the size distribution of the emulsion formulated with vegetable oil; it follows a similar pattern to the emulsions formulated with linseed oil.
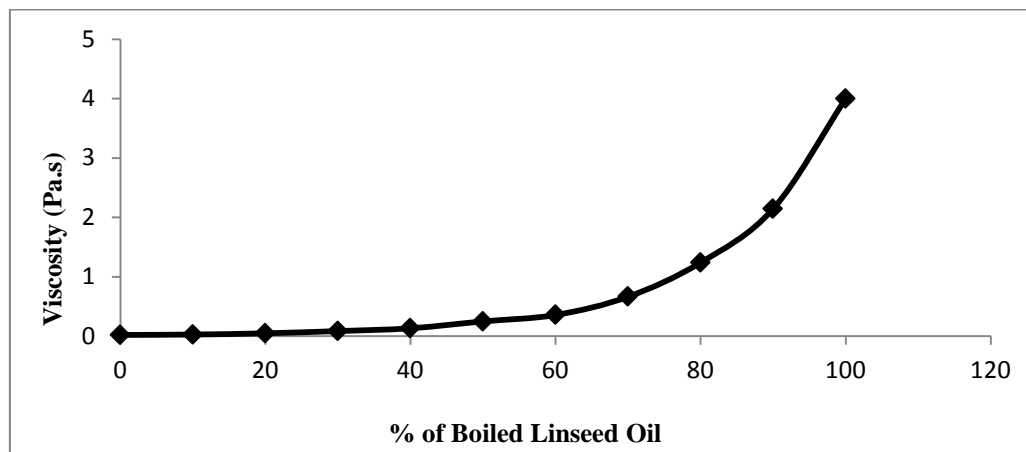

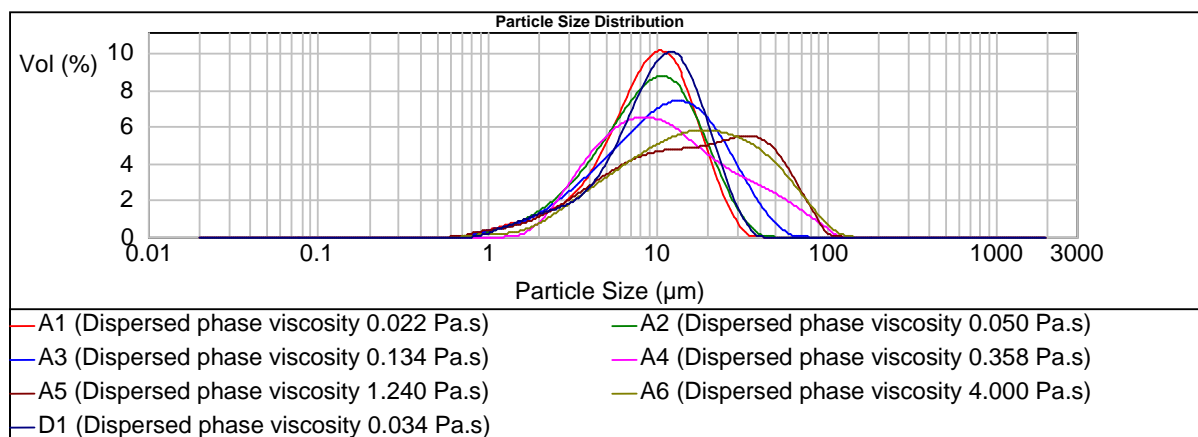**Figure 1:** Graphical representation of blending boiled and refined linseed oils.

Figure 2: Droplet size distribution of emulsion samples homogenised at 7000 rpm

Information extracted from the droplet size distribution obtained from analyzing the emulsion samples are presented in table 3, samples A1 to A6 represents the emulsions produced with linseed oils, while D1 represent the emulsion produced with vegetable oil. The average size of the droplets is reported in terms of the volume weighted mean or mass mean diameter D[4, 3].

From table 2 and figure 3, it can be seen that there is a marked difference between the average droplet sizes in the emulsion sample prepared with the lowest oil viscosity and that prepared with the highest oil viscosity even though the homogenization speeds are the same for all the samples. An increase of about 133% in the average

droplet size as the oil viscosity goes from 0.022 Pa.s to 4.000 Pa.s is quite substantial. It had been gathered from literature that the initial state of an emulsion would have a bearing on its destabilization rate. The average droplet size was used in this study as a measure of the initial state and was followed as the emulsion aged, accelerating the destabilization process via the freeze-thaw method.

Table 3: Volume Weighted Mean Diameters of Emulsions Homogenised at 7000 rpm

Sample	Viscosity of Dispersed Phase (Pa.s)	D[4, 3] (μm)
A1	0.022	10.303
D1	0.034	11.365
A2	0.050	11.422
A3	0.134	13.701
A4	0.358	17.348
A5	1.240	22.885
A6	4.000	23.986

Graphical representation of the variation of droplet size distribution with dispersed phase viscosity is shown in figure 3.
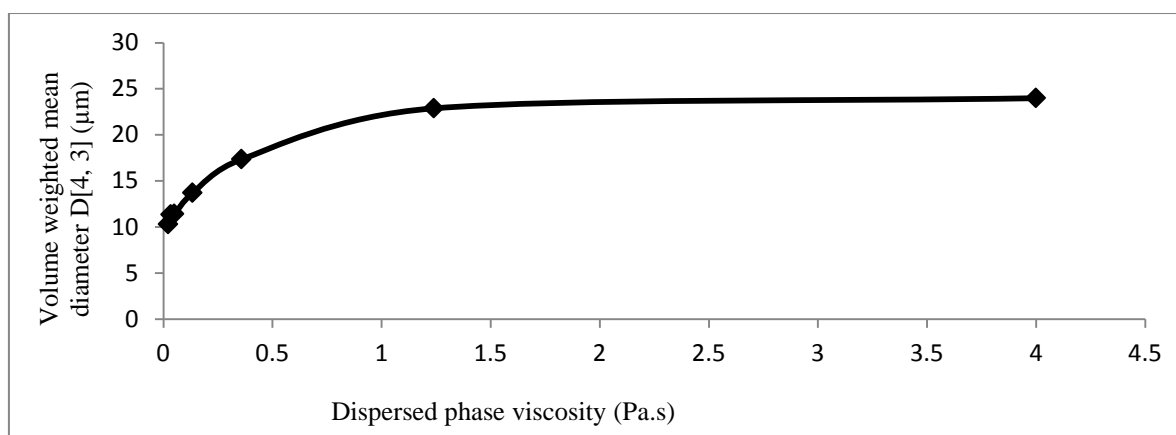

Figure 3: Variation of emulsions average droplet sizes with dispersed phase viscosities at 7000 rpm

3.3. *Variation of Droplet Size Distribution for the Emulsions Homogenised at 7000 rpm after Freeze-Thaw Cycles*

The emulsions having being subjected to freeze-thaw cycle showed changes in their droplet size distributions. Figures 4 and 5 shows the droplet size distribution measured after all the emulsion samples had been subjected to 2 freeze-thaw cycles.

The results obtained from the droplet size analysis showed emulsion samples which were prepared with lower

dispersed phase viscosity with initial smaller droplets corresponding to lower dispersed phase viscosity, destabilized after the first freeze-thaw cycle at a slower rate than the emulsions with higher dispersed phase viscosity. This judgement was based on the average droplet sizes of the emulsions as well as the width of the distributions.
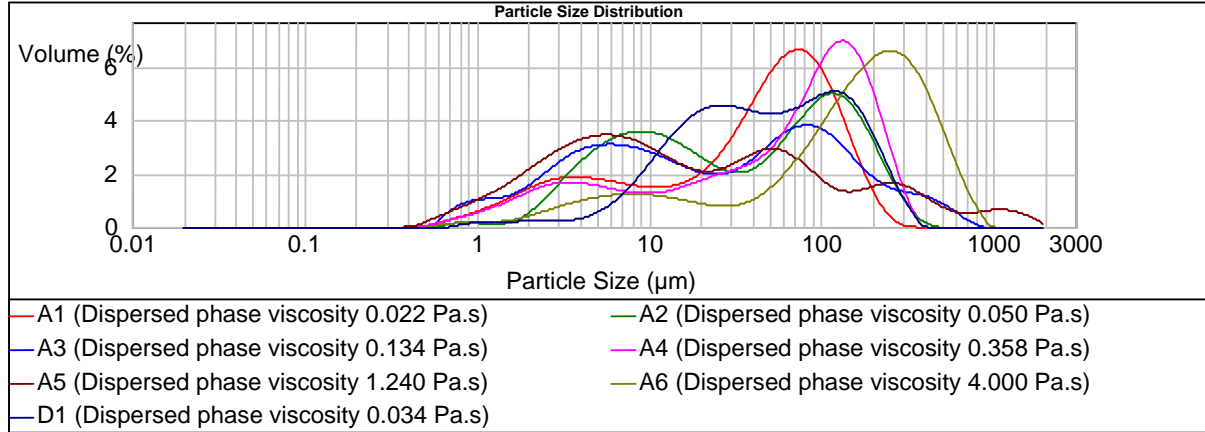

Figure 4: Size distribution of emulsions homogenized at 7000rpm, after first freeze-thaw cycle

The second freeze-thaw cycle produced similar results as the first in terms of the destabilization pattern; this is shown in figure 5.
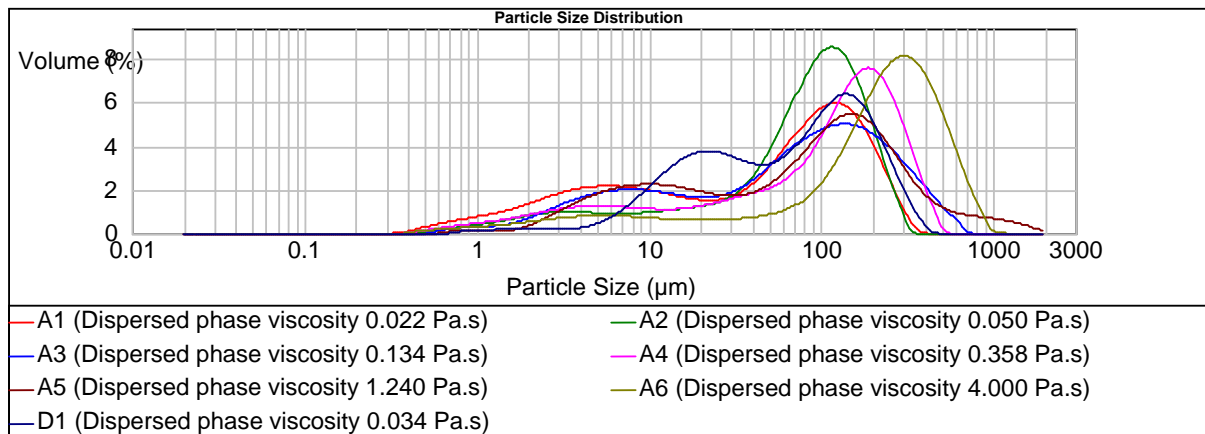

Figure 5: Size distribution of emulsions homogenised at 7000rpm, after second freeze-thaw cycle

Data extracted from the droplet size analysis are presented in table 4, again in terms of average weighted mean diameters D[4, 3].

The results obtained so far tends to suggest that the viscosity if the dispersed phase affects the initial droplet size distribution, which in turn affects the rate of destabilization based on the increase in average sizes of the droplets as shown in table 4 and figure 6. Lower viscosity emulsions produced lower droplet size distribution,

and in turn lower destabilization rates as seen for both linseed and vegetable oil emulsions.

Table 4: Mean diameters of emulsion droplets homogenised at 7000 rpm after freeze-thaw cycles

Sample	Viscosity of Dispersed Phase (Pa.s)	D[4, 3] (μm)	D[4, 3] After First Cycle (μm)	D[4, 3] After Second Cycle (μm)
A1	0.022	10.303	56.099	75.136
D1	0.034	11.365	73.815	92.597
A2	0.050	11.422	66.865	92.299
A3	0.134	13.701	71.643	114.821
A4	0.358	17.348	87.248	131.003
A5	1.240	22.8851	101.326	156.148
A6	4.000	23.986	203.128	255.862

The variation in droplet size distribution as the emulsion ages is further represented in figure 6.
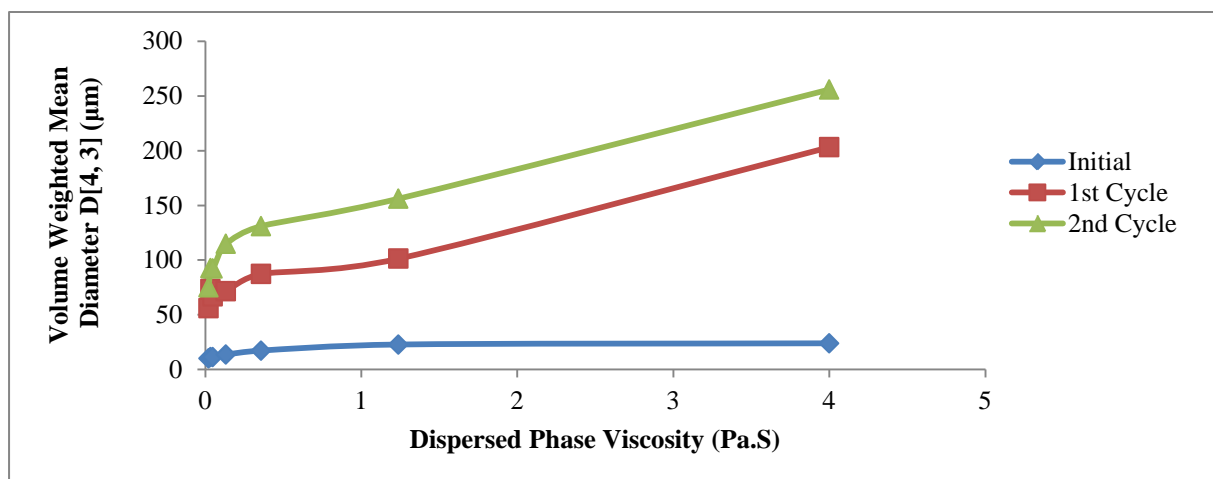

Figure 6: Variation of dispersed phase viscosity with mean diameter after freeze-thaw cycles at homogenization speed of 7000 rpm.

3.4. Effect of Surfactant Concentration on Surface Tension

From literature [2, 5, 6] is had been established that surfactants enhance stability by reducing the surface tension of the aqueous phase. The results from surface tension measurement carried out on 0.5% polysorbate solution at $25^{o}C$ showed a decrease of about 57% in the surface tension of water; that is from about 0.072 N/m to about 0.031N/m. Since the same formulation was used in all cases, the emulsion samples would experience almost the same reduction of surface and interfacial tensions

4. Conclusions drawn from study

The results of the droplets size distribution analysis carried out on all the emulsion samples have shown that not only does homogenization energy affect the average drop sizes, but also the viscosity of the dispersed phase (oils). The viscosity of the dispersed phases on the other hand, showed a direct relationship with droplet sizes; the smaller the dispersed phase viscosity the smaller the average droplet sizes for all emulsion samples used in this study.

This study also showed that emulsions with smaller droplet sizes at the time of production are relatively more stable than those with larger droplets also at the time of production. This conclusion drawn from the fact that all the emulsions were subjected to the same conditions during production and during the stability tests. It should be remembered that the stability criteria used in this study was the rate of change (increase) in droplet sizes of the emulsions as they aged, which were measured at the time of production and during the test period.

It is well known that industries are continually seeking to cut down their energy consumption, given the fact that energy prices are on the increase and to some extent unpredictable. Emulsification using mixers or homogenizers is energy intensive and this study has shown within its limits, one way of using less energy would be to use, where possible oils of low viscosities rather than high viscosities, as the droplet sizes are smaller and the emulsions prepared with them are more stable than those prepared with high viscosities.

5.   Recommendations for further studies

There are certain areas that could be explored in the future, one of such could be using different emulsification methods and to determine if the methods chosen have any effect on the rate of destabilization of the emulsions. It also would be interesting to try developing mathematical models that would be used to predict the stability or otherwise of prepared emulsions.

References

[1] R. Chanamai and D.J McClements ''Dependence of creaming and rheology of monodisperse oil-in-water emulsions on droplet size and concentration.'' Colloids and Surfaces A: Physicochemical and Engineering Aspects. Vol. 172, pp. 79–86, 2000.

[2] I.D. Morrison, and S. Ross, Colloidal Dispersions Suspensions, Emulsions and Foams. New York: John Wiley and Sons, Inc., 2002, pp. 616.

[3] E. Ruckenstein, ''Microemulsions, Macroemulsions, and the Bancroft Rule.'' Langmuir. Vol 12(26),

pp 6351–6353, 1996.

[4] T.F. Tadros. ''Emulsion Science and Technology: A General Introduction'' in Emulsion Science and Technology. T.F. Tadros, Ed. Weinheim: 2009 WILEY-VCH Verlag GmbH & Co. KGaA, 2009, pp. 1-5.

[5] K. Fontenot, and F.J. Schork, ''Sensitivities of Droplet Size and Stability in Monomeric Emulsions.'' Ind.

Eng. Chem. Vol. 32, pp. 373 – 385, 1993.

[6] J. Bibette, et al., ''Stability Criteria for Emulsions.'' American Physical Society, vol. 69(16), pp. 2439 – 2442, 1992.

[7] B. Abismail, et al., ''Emulsification by Ultrasound: Drop Size Distribution and Stability.'' Ultrasonics Sonochemistry, vol. 6 (1999) pp. 75 – 84, 1999.

[8] A.N. Ilia, and A.H. Nour, ''Effect of Viscosity and Droplet Diameter on Water-in-Oil (W/O) Eumlsions : An Experimental Study.'' World Academy of Science, Engineering Technology, vol. 62, pp. 691 – 694, 2010.

[9] ''Emulsion Stability and Testing'': http://www.particlesciences.com/docs/technical_briefs, 2011 [Oct. 11 2013]

[10] F. Brailler, M. Heinche., and P.A. Tanguy, ''CFD Analysis of a Rotor-stator Mixer with Viscous Fluids.'' Chemical Engineering Science, vol. 61, pp. 2888 – 2894, 2006.

[11] A. Utomo, M. Baker, and A.W. Pacek, ''The Effect of Stator Geometry on the Flow Pattern and Energy Dissipation Rate in a Rotor-Stator Mixer.'' Chemical Engineering Research and Design, vol. 87, pp. 533 – 542, 2009.

[12] ''Run Your Rotor/Stator Mixer at Maximum Speed to Optimize Particle Size Reduction'': http://www.mixers.com/insights/m_t_u%2042.pdf , 2010 [Oct 15 2013].

[13] D. Rousseau, ''Fat Crystals and Emulsion Stability - A Review.'' Food Research International, vol. 33, pp. 3 – 14, 2000.

[14] S. Pasalic, and P. Jovanic, ''Modeling of the Emulsion Stability using Fractal Dimensions.'' Chemical Industry and Chemical Engineering Quarterly, vol. 14 (3), pp. 153 – 158, 2008.

[15] V. Andre, et al., Cosmetics and Toiletries Manufacture Worldwide. US: Aston Publishing Group, 1994, pp.102-109.

[16] ''Mastersizer 2000 User Manual'' Malvern Instruments, Mar. 2007.

[17] U.T. Lashmar and J. Beesley, ''Correlation of Rheological Properties of an Oil in Water Emulsion with Manufacturing procedures and Stability.'' International Journal of Pharmaceutics, vol. 91, pp. 59 – 67, 1993.

[18] T. Schmidts, et al., ''Multiple W/O/W Emulsions - Using the Required HLB for Emulsifier Evaluation.'' Colloids and Surface A: Physiocochem. Eng. Aspect, vol. 372, pp. 48 – 54, 2010.