EMULSIFICATION OF OIL IN WATER: AS AFFECTED BY ULTRASONIFICATION PERIOD.

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ABSTRACT

Emulsification of oil in water has got a number of industrial as well as medicinal applications, however very little systematic work has been carried out upon it. Therefore, we have considered a very simple system of n-hexane, dispersed in water and tried to understand the mechanism of emulsification by looking into the effect of ultrasonification time over the quality of emulsion. The techniques employed for the purposes were optical microscopic and turbidity measurement. It has been observed that the distribution of size/ number becomes narrowest after 15 minutes of ultrasonification time. However, if the period is further prolonged then the distribution starts widening.

INTRODUCTION

Emulsification is a process of mixing of two or more immiscible liquids, which result in heterogeneous systems, consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets, whose diameters, generally exceeds 0.1 µm. Emulsions are also defined as thermodynamically unstable mixture of two essentially immiscible liquids and are stabilized by a third phase, an emulsifying agent.

A number of mechanical processes are employed to produce emulsion, among them stirring toothed dispersing (often referred to as homogenizing), rotor-stator dispersing colloid milling and high-pressure homogenization and Ultrasonification. Emulsification has been studied for many decades and gathered increasing interest recently. Studies comparing of ultrasonic emulsification with rotor-stator dispersing competitive ultrasound or even superior in terms of droplet size and energetic efficiency. Microfluidisation a type of high-pressure homogenization was found to be more efficient than ultrasound, but less practical with respect to equipment contamination and aseptic processing.

(Bondy and Sollner, 1935; Bechtel *et al.*, 1997; Karbstein and Schubert, 1995; Medina *et al*., 2001; Maa and Hsu, 1999; Richards, 1929; Sergio, *et al* 2006).

Our objective is to study the effect of stirring time and shear rate upon emulsification. In this communication, we have considered n-hexane and emulsified it in water using an ultrasonification technique, it was observed that the ultrasonification method is preferred over the other because of the fact that ultrasonification process is more economical, easy to handle and there is a least chance of introducing any impurity or entrapping air in the system (Baloch *et al.*, 1996; Baloch and Hameed, 2005; Hiememz and Rajagopalsn, 1997; Law and Henry, 1997). It is therefore essential to investigate very simple oil/water system and probe into the detailed mechanism of emulsification and the effect of different parameters on it.

EXPERIMENTAL

Material

The oil used in this study was n-hexane. The n-hexane was obtained from E-Merck, Germany. The oil was double distilled before use. After distillation, it was kept in airtight container at a cool and dry place. Water used for the preparation of emulsion, was freshly double distilled and de-ionized before use.

Preparation of emulsion

A known amount (2 % v/v) of oil was dispersed in water by ultrasonification of the mixture for a fixed period of 5 min, 10 min, 15 min, 20 min, and 25 minutes. The ultrasonic bath used for the purpose was of West Wood Ultrasonic Ltd, Germany

Microscopic measurements

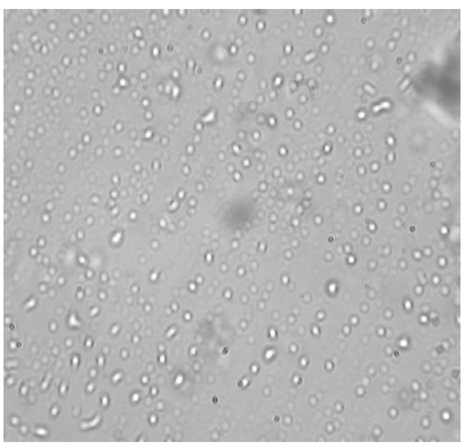
Just after the ultrasonification (with in fraction of second), the emulsion was subjected to microscopic measurements to get the number and size of the droplets. For this purpose an optical Swift M 4000–D microscope fitted with high performance computer controlled digital camera (CCD) was used. It was also equipped with software which directly gave droplet's size, number, its distribution and density etc. Though if we were able to get the size of droplets and their distribution with in a fraction of seconds.

Turbidity Measurement

The turbidity of emulsions was obtained by Turbidity meter model 800 Engineered Systems & Designs, Inc, 119A Sandy Drive USA. The instrument was calibrated with de-ionized water to adjust zero, where as Formozine standard solution of 20 NTU was used for verification. After standardization, the measurement was made.

RESULT AND DISCUSSION

The quality of emulsion, which was prepared through ultrasonification, was monitored, using optical techniques like microscopic, transmittance, turbidity etc. To see the effect of ultrasonification time over quality of emulsion, the oil/water mixture was ultrasonificated for 5, 10, 15, 20 and 25 minutes. For the visual measurement and to see whether the emulsification has taken place and how the droplets are distributed in the emulsion, some micrographs and histograms of the emulsion are presented in Figures 1 & 2 respectively. These figures confirms that with the increase in ultrasonification period the number of droplets increases and their average size decreases and also the degree of dispersity, hence improves the emulsion quality. Further, the degree of dispersity also goes down, concluding that 15 minutes ultrasonification provides better results than smaller and larger period. .



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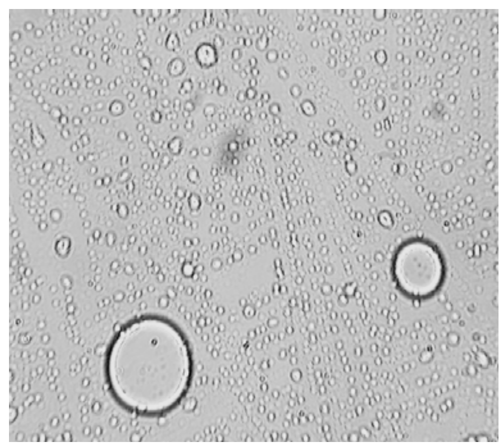

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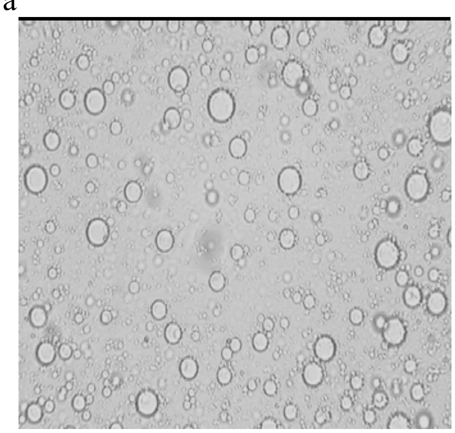

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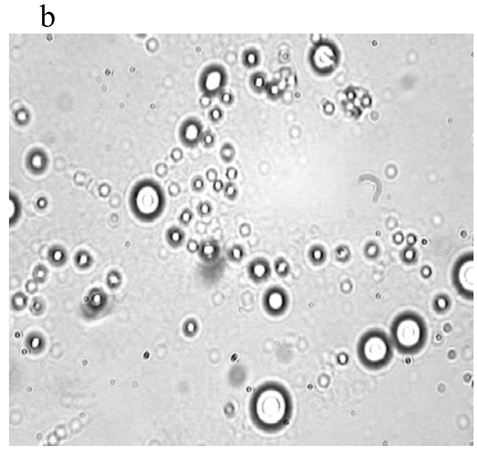

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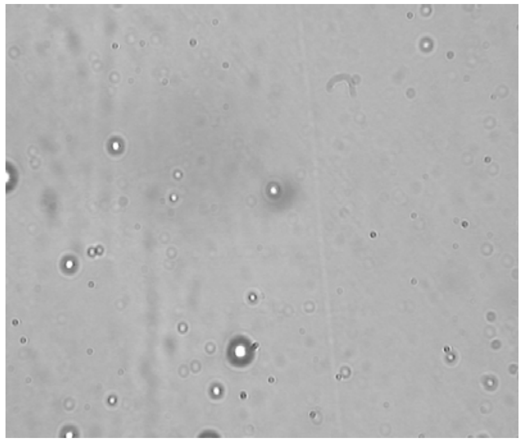

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Figure.1. Micrograph of the emulsion system oil in water emulsified for 5min (a), 10 min (b), 15min (c), 20min (d) and 25min (e).

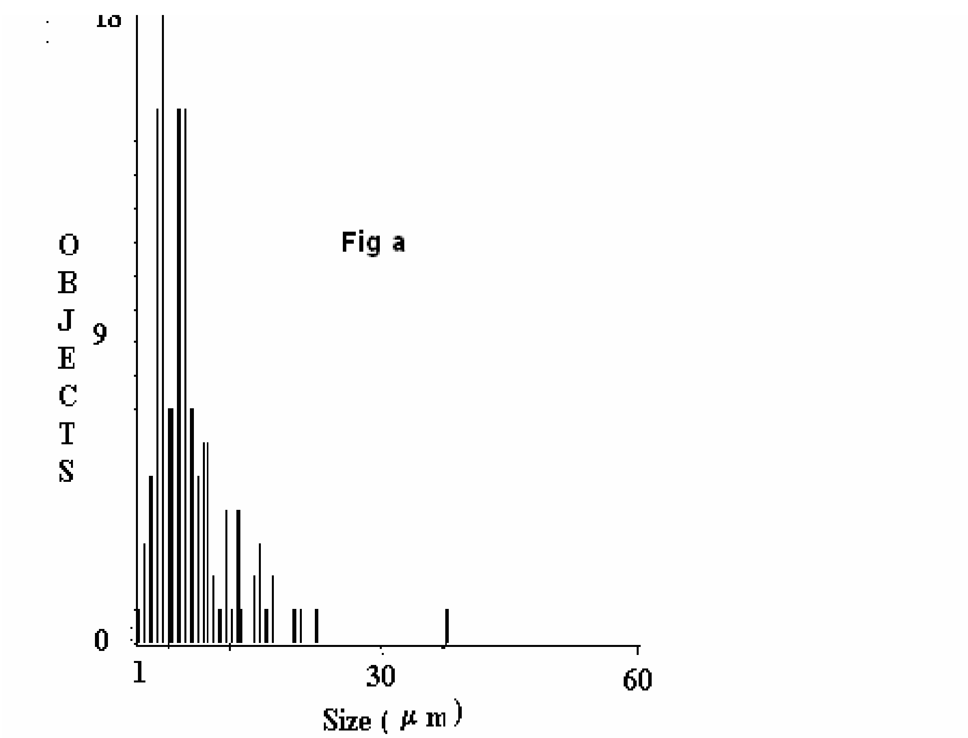


Fig. 2 a: Size distribution of droplets of 2% hexane emulsified for 5min

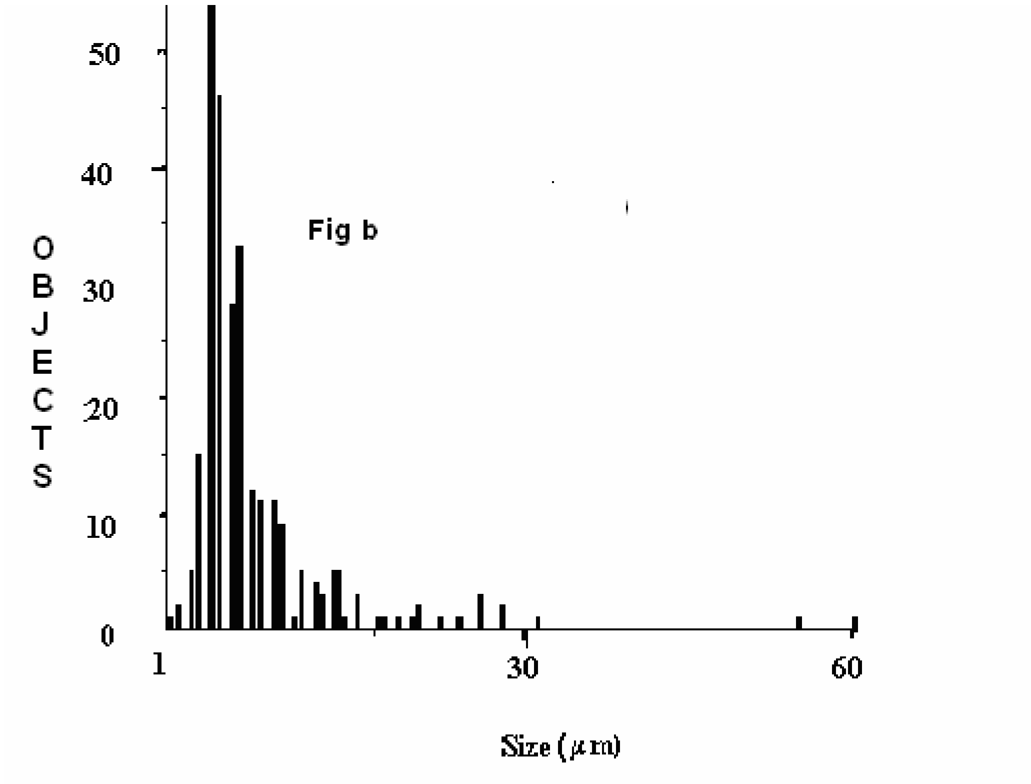


Fig. 2 b: Size distribution of droplets of 2% hexane emulsified for 10min

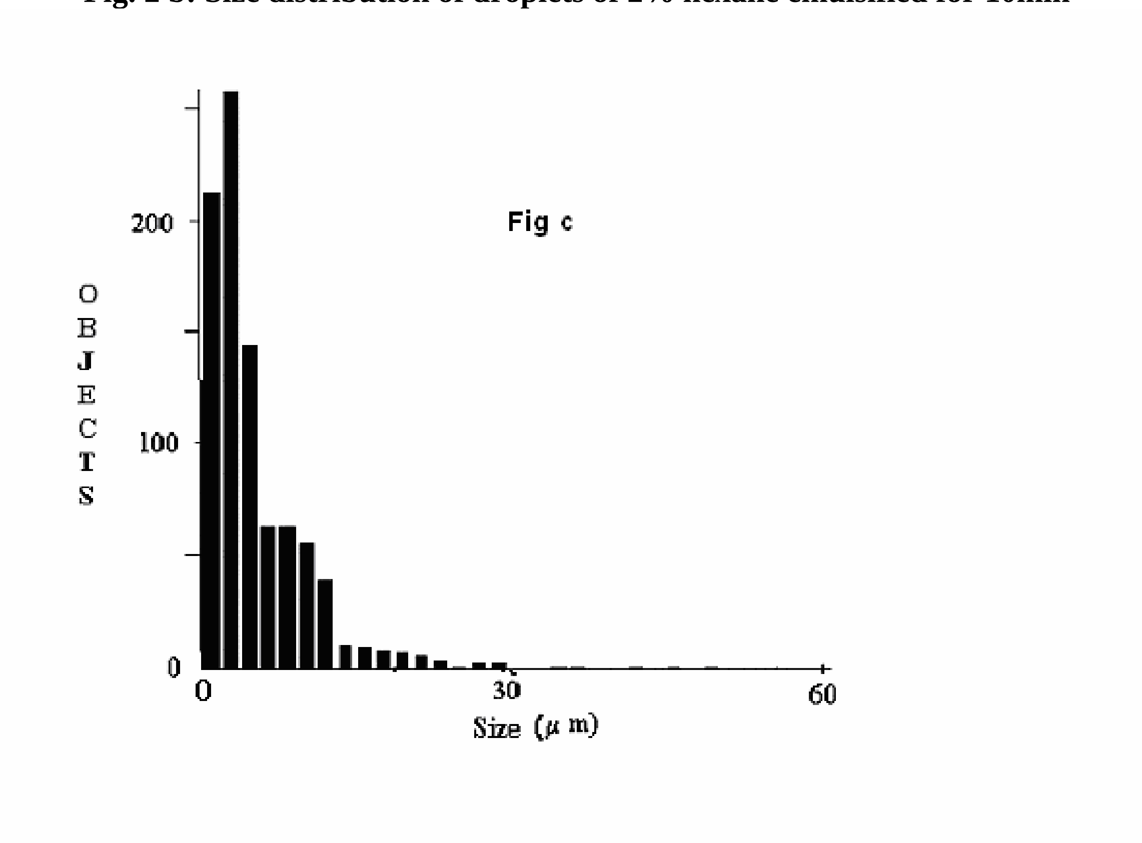


Fig. 2 c: Size distribution of droplets of 2% hexane emulsified for 15 min

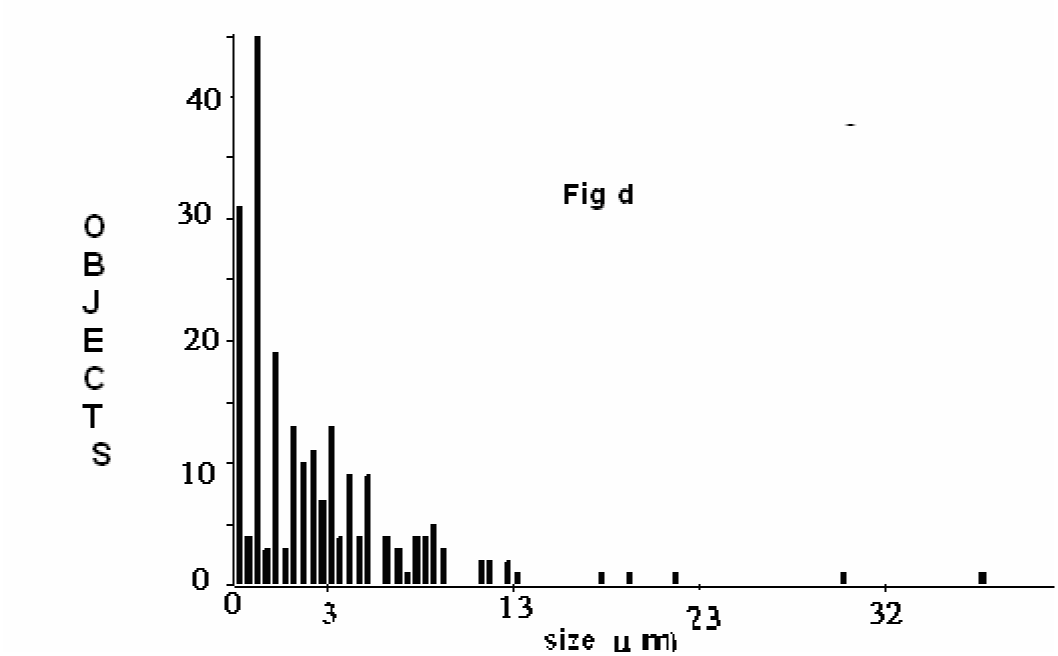


Fig. 2 d: Size distribution of droplets of 2% hexane emulsified for 20 min

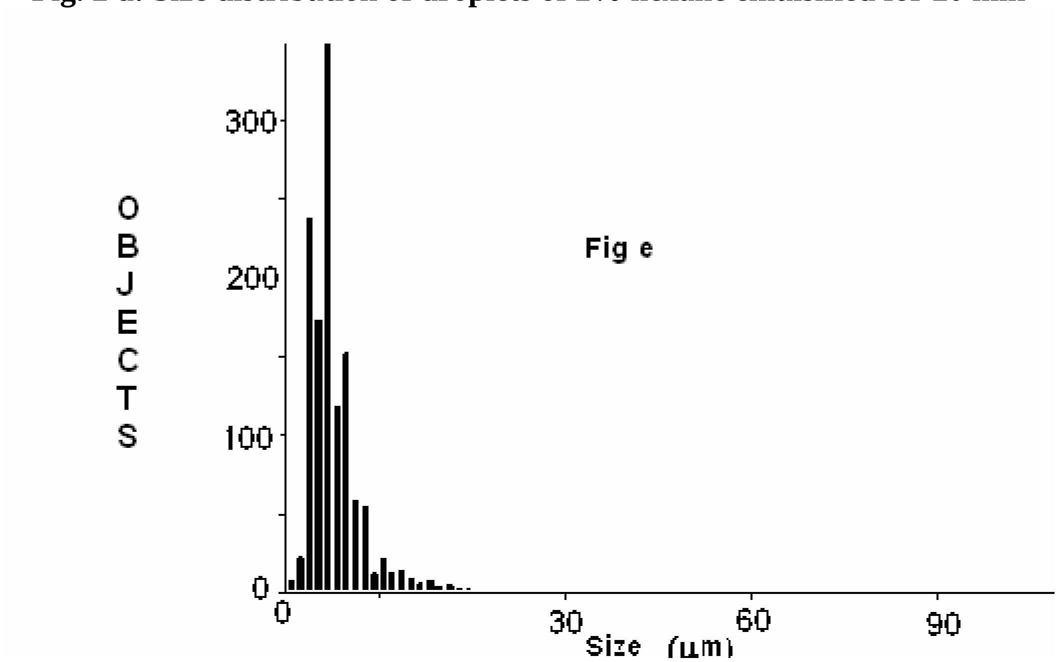


Fig. 2 e. Size distribution of droplets of 2% hexane emulsified for 25min.

The micrographs and histograms show a quite narrow distribution of the droplets and hence we believe that a nice emulsion can be prepared through this ultrasonification. These figures also show integral as well as the differential distribution curves that the emulsion contains narrowly dispersed droplets. The results obtained from micrographs have also been displayed in Figures 3 &

4.These figures also conclude the same as by histograms.

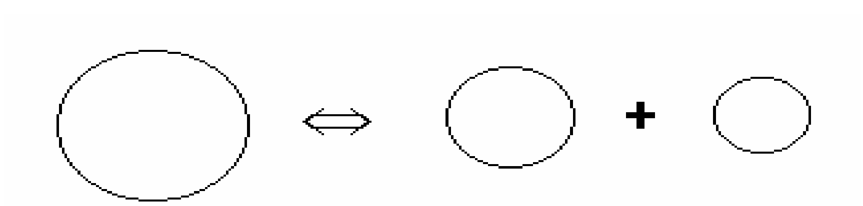
These results are according to the Equation (1) or (2) (Baloch and Hameed, 2005; Levin *et al.,* 1975; Taylor 1934).

$$E = \frac{\eta_B \gamma a(19s+16)}{\sigma(16s+16)} \quad (1)$$

$$E = [\frac{\gamma a(19s+16)}{(\sigma_0 - bc)(16s+16)}][1-\frac{3\Lambda\zeta^2}{2(1+H)(ka)^2}]\eta \quad (2)$$

Here η_B, η, γ, a, σ, σ_0, s, C, b, k and H are viscosity of the continuous phase or medium (water), ,viscosity of dispersed phase or media (oil/water), shear rate, droplets size, interfacial tension with and without the presence of electrolyte or other impurities added to the media, ratio of droplets to medium viscosity, concentration of electrolyte used, number of mole of solute per cm^2 of area in excess of that present in the body of the solution, zeta potential and Debye length respectively (Hiememz and Rajagopalsn, 1997) (Baloch and Hameed, 2005)These equations states that the emulsification will only take place when the shear rate exceeds the critical one. During this experiment, all parameters were kept constant, except emulsification time. The conditions of shear rate higher than the critical one will only favor the process of emulsification leading to decrease in size and increase in number of droplets with time, as well as increase in fraction of oil emulsified.

During this process, however, the de-emulsification may also be taking place simultaneously. The overall impact will therefore depend upon the applied shear forces generating shear rate. If the shear rate is above the critical value emulsion will be formed (Baloch and Hameed, 2005). Otherwise de-emulsification can take place. This process can be presented as shown in Scheme 1.



Scheme 1. A schematic representation of the emulsification and de-emulsification process which may take place during ultrasonification.

Further to it, when a mixture of two immiscible liquid is subjected to ultrasonification it is emulsified if the shear rate is over certain value or coalescence takes places. These results are according to expectation and Equation (3) provided by Taylor (Taylor, 1934).

According to his statement the critical shear rate, γ_c is a function of the ratio of droplet to medium viscosity, *s*, interfacial tension, *σ,* and inversely proportional to droplet viscosity, η_A, and size of the droplets, *a*.

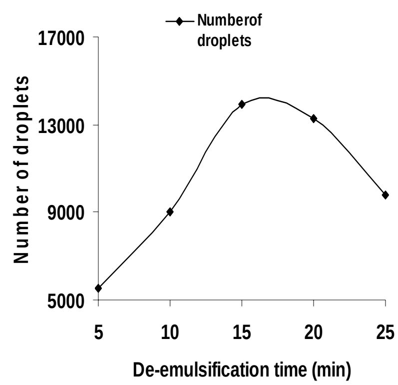


Fig. 3. Variation in average number of emulsion as a function of Ultrasonification time.

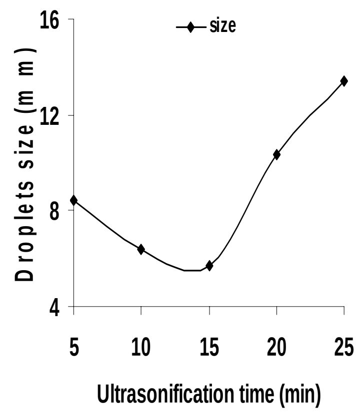


Fig. 4. Variation in size of droplets of Emulsion as a function of ultrasonification time

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The average number and average size of the droplets obtained in this way are displayed in Figure 3 as a function of time for oil content (2% hexane). The Figure 4 also confirms the same trend; the number increases whereas size of droplets goes down with the time of ultrasonification. Further the size and number of droplets vary in the following order kerosene oil > n-decane > n-heptane > n- hexane and as n-hexane > n-heptane > kerosene oil > n- decane (Baloch and Hameed, 2005

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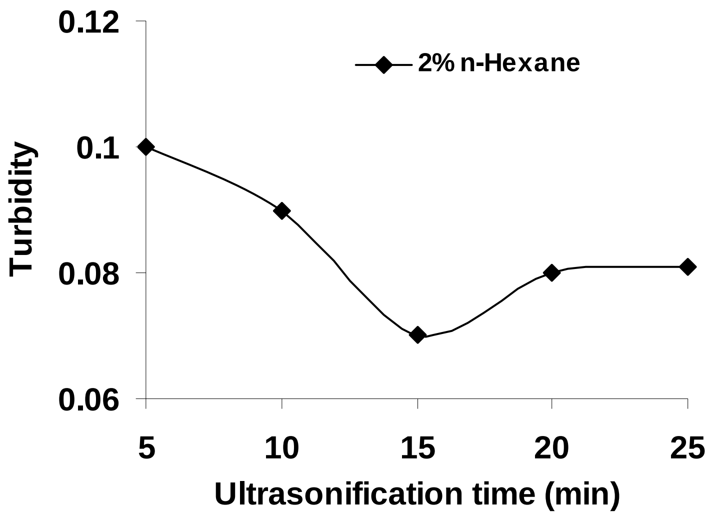

Fig 5. Variation in turbidity of emulsion as a function of ultrasonification time.

The result obtained by the turbidity of n-hexane was measured via spectrophotometer/ turbidity meter, just after the ultrasonification is over. The result so obtained is plotted versus time in Figure 5. As it is obvious from the figure, turbidity first decreases with increase in ultrasonification time. This is due to the fact that the size of the droplets decrease and number increases with the increase in ultrasonification time. This decrease in turbidity is due to the fact that the system has a small droplet size (Baloch *et al.,* 1996).

Another important factor which is to be noted is the decrease in size, if the volume of the dispersed liquid is constant. Keeping in view these facts, we can conclude from Figure 5 that the droplets size decreases and the number increases with the stirring time, this is what one expects from Equation (4).

$$\ln n^0/n = k \gamma t \quad (4)$$

Where

n^0 = Initial number of droplets

n = Number of droplets at time t

γ = Shear rate

k = Instrumental constant

Such trend has been also observed by (Ohtake *et al*., 1987).

CONCLUSION

Study of the stability of the emulsion against time, concludes that longer the ultrasonification period smaller the droplets size and hence lower the coalescence rate. Turbidity was measured as a function of time and shows that it decreases with the increase in ultrasonification time. This also means that the emulsification performed for longer time needs longer duration for coalescence. These observations also support our earlier finding that the ultrasonification time plays an important role in quality of emulsion.

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