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Research note

Influence of Salinity, Surfactants and Power of Ultrasonic Homogenizer on Droplet Size Distribution of Crude Oil/Water Emulsions

*M. Eftekhardadkhah, S. H. Hashemabadi**
Computational Fluid Dynamics Research Laboratory, School of Chemical Engineering, Iran University of Science and Technology, Iran

Abstract
In this paper, the droplet size distribution of the Tehran refinery crude oil/water emulsions is determined by analyzing the photomicrographs of model emulsions which were taken by microscope. The normal distribution function is fitted to the experimental data in order to reproduce the droplet size distribution (DSD) of the emulsions by using mean diameter and standard deviation. The effect of different parameters such as surfactant concentration, salinity, and the power of homogenizer on the droplet size distribution and mean droplet diameter of the emulsions are determined. The smaller droplet size was observed in high concentrations of surfactant and in the absence of salt, and also in emulsions which were prepared with lower power of homogenizer.

Keywords: *Oil-in-water Emulsions; Droplet Size Distribution (DSD); Surface Tension, Photomicrographs*

1- Introduction

Emulsions consist of two immiscible liquids, one of which is dispersed in the other in the form of droplets [1]. Stability is obtained by using an emulsifying agent or surfactant which is absorbed around the droplet surfaces. Emulsions are fundamental in many applications [2]. The use of emulsions covers a wide range of processes [3 and 4]. Oil-in-water emulsions are used in every step of petroleum production and separation operations, such as de-oiling flotation and hydrocyclone units, crude oil transport facilities and etc [5].

The droplet size distribution has significant influences on the properties of the emulsions such as stability, viscosity, optical appearance [6], and chemical reactivity [7]. Therefore, determination of the droplet size distribution has been the subject of research work by several authors [8-10].

There are different ways to characterize the size distribution of the emulsions using parameters which indicate the dispersion such as mean diameter [11], Sauter diameter [12], and diameter of the largest stable

∗ Corresponding author: hashemabadi@iust.ac.ir

droplet size [8]. One of the most important weak points of using these parameters is that they fail to provide all the information of the system and thus provide only an approach. For achieving accurate information about most characteristic parameters of the emulsions (total distribution of droplet surface, volume or mass) [2], evaluation of the droplet size distribution (DSD) becomes necessary. A wide variety of analytical and empirical distribution functions have commonly been used to estimate the DSD of emulsions. In the present study, the droplet size distribution of the emulsions is determined by analyzing the photomicrographs of model oil-in-water emulsions. The normal distribution function is fitted to the experimental data in order to reproduce the DSD of the emulsions by using mean diameter and standard deviation. The effect of different parameters such as surfactant concentration, salinity, and power of homogenizer on the DSD of the emulsions are determined and discussed.

2- Theoretical background

The normal distribution is a two-parameter family of curves. The first parameter, μ, is the mean, the second, σ, is the standard deviation. The standard normal distribution, $\varphi(x)$ is functionally related to the error function [13]:

$$\mathrm{erf}(x) = 2\varphi(x\sqrt{2}) - 1 \quad (1)$$

The first use of the normal distribution was as a continuous approximation to the binomial. The usual justification for using the normal distribution for modeling is the Central Limit Theorem, which states (roughly) that the sum of independent samples from any distribution with finite mean and variance converges to the normal distribution as the sample size goes to infinity. So the definition of normal distribution is:

$$y = f(x|\mu,\sigma) = \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{-(x-\mu)^2}{2\sigma^2}} \quad (2)$$

To use statistical parameters such as mean and standard deviation reliably, there is a need to have a good estimator for them. The maximum likelihood estimates (MLEs) provide one such estimator. However, an MLE might be biased, which means that its expected value of the parameter might not equal the parameter being estimated. For example, an MLE is biased for estimating the variance of a normal distribution. An unbiased estimator that is commonly used to estimate the parameters of the normal distribution is the minimum variance unbiased estimator (MVUE). The MVUE has the minimum variance of all unbiased estimators of a parameter. The MVUEs of parameters μ and σ for the normal distribution are the sample mean and variance. The sample mean is also the MLE for μ. The following are two common formulas for the mean and variance [13].

$$\sigma^2 = \frac{1}{n}\sum_{i=1}^{n}(x_i - \bar{x})^2 \quad (3)$$

$$\bar{x} = \sum_{i=1}^{n}\frac{x_i}{n} \quad (4)$$

3- Experimental works

3.1- Materials

The emulsions were prepared using Tehran refinery crude oil. The viscosity of the crude oil was 6 mpa.s at 25°C and its density was 850 kg/m^3. The water used throughout the experiments was distilled water. Two different surfactants used for the preparation of emulsions were Triton x-100 and Tween80. These two surfactants were nonionic and manufactured by Merck. Some properties of surfactants are indicated in Table 1. The main reason for using these surfactants is availability, on the other hand, as is shown, the Hydrophilic-Lipophilic Balance (HLB) value for the mentioned emulsifiers is higher than 10, which would correspond to a molecule made up of more hydrophilic components. Therefore the stability of oil-water emulsion can be improved with these emulsifiers.

Table 1. Properties of used surfactants in experimental works

Surfactant	Molar mass (g/mol)	Water solubility	HLB value
Triton x-100 ($C_{14}H_{22}O(C_2H_4O)_n$)	624	Very soluble	13.5
Tween80 ($C_{64}H_{124}O_{26}$)	1310	Very soluble	15

3.2- Procedure

Aqueous surfactant solutions were prepared by adding a known amount of surfactant in 100 ml water. After hand-shaking solutions for approximately 5 min, surface tension measurements were conducted with KSV-SIGMA700 tensiometer. This tensiometer works based on the ring method. The oil/water emulsions were readied by adding a known amount of oil in prepared aqueous solution of surfactant. After 10 min hand-shaking, the emulsions were prepared using an ultrasonic homogenizer (HD 3200 Bandelin). The oil/aqueous solution mixture were sheared together for 2×30 s with a 1 min pause to avoid overheating.

For any given emulsion, the droplet size distribution was determined by analyzing the photomicrographs which were taken with a Hund optical microscope equipped with a high resolution camera.

4- Results and discussion

4.1- Critical micelle concentration (CMC)

The critical micelle concentration (CMC) is defined as the concentration of surfactants above which micelles are spontaneously formed. Upon reaching CMC, any further addition of surfactants will just increase the number of micelles (in the ideal case) and there is no change in solution surface tension. Based on surface tension measurements, the critical micelle concentration (CMC) was determined for both surfactants in the presence and absence of salt (NaCl). Results of surface tension measurements as a function of surfactant concentration for different salinities are illustrated in Fig 1.

It can clearly be seen that the surface tension of solutions decreases with increasing the surfactant concentration. Moreover, it is obvious that the promotion of the NaCl concentration from 0 to 3 and 6% increases the surface tension of the solution at low concentration of the Triton x-100, but the Critical CMC remains constant around 0.00225 ml/100ml solution. In addition, surface tension of the solution with Tween80 is more than the surface tension of the Triton x-100 solution for all surfactant concentrations, but the CMC of the solutions of both surfactants are similar.

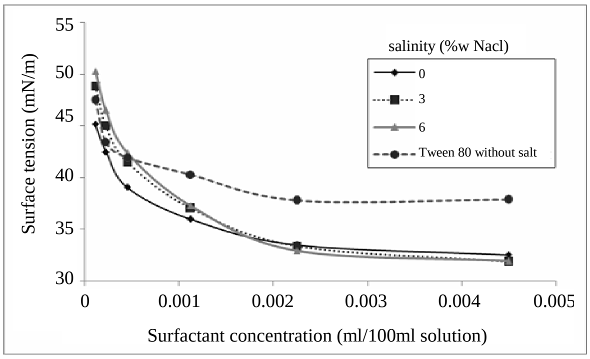
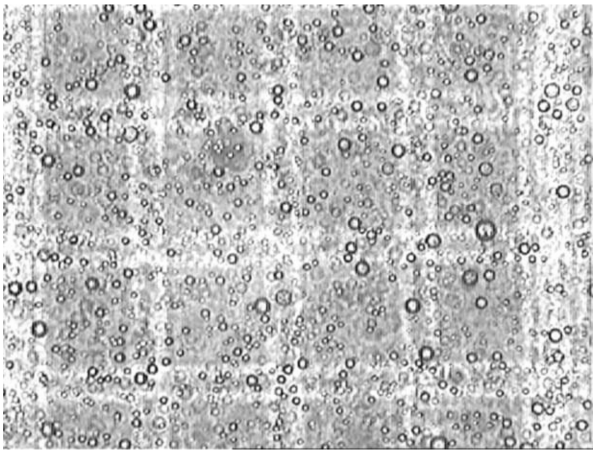


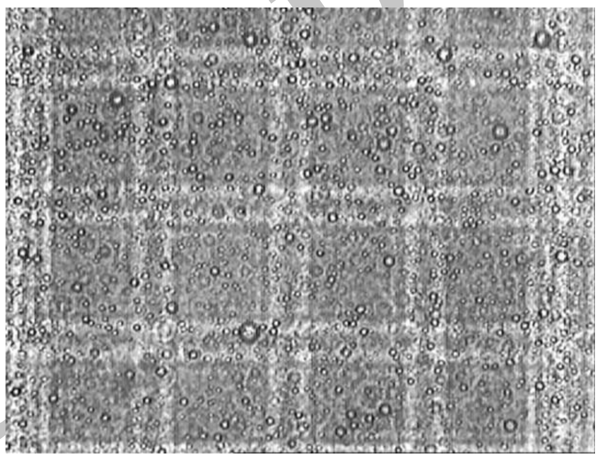
Figure 1. Surface tension of aqueous solutions as a function of surfactant concentration for different salinities.

4.2- Influence of different surfactants on DSD

Figure 2 shows the typical photomicrographs of two sets of emulsions which contain equal amounts of Tween80 and Triton x-100. It can be seen that the emulsions are not monodisperse, i.e. all droplets are not of the same size. It should be mentioned further that the oil droplets in set (a) emulsion (with Triton x-100) are smaller than droplets in set (b) emulsion (with Tween80), because, according to Fig. 1, the ability of Triton x-100 in decreasing the surface tension of the solution is more than the ability of Tween80. Also, this can clearly be seen in Fig. 3 which shows the DSD of the two emulsions. The mean droplet diameter in the emulsion with Tween80 is 3.17 μm and in the emulsion with Triton x-100 is 2.56 μm. Moreover, the proportion of fine droplets (1 -3 μm) in the emulsion which was prepared with Triton x-100 is significantly more than that in the emulsion with Tween80.



(a)



(b)

Figure 2. Photomicrographs of emulsions: (a) Triton x-100 with a concentration of 0.001125 ml/100ml solution; (b) Tween80 with concentration of 0.001125 ml/100ml solution.

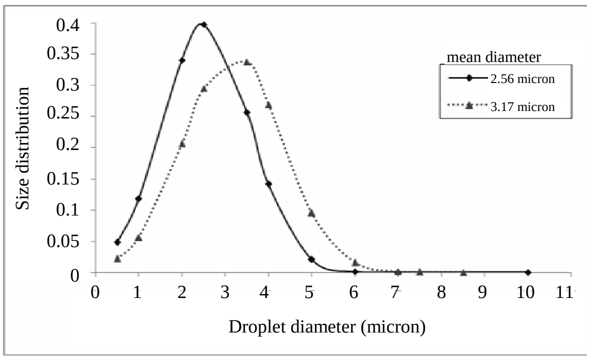


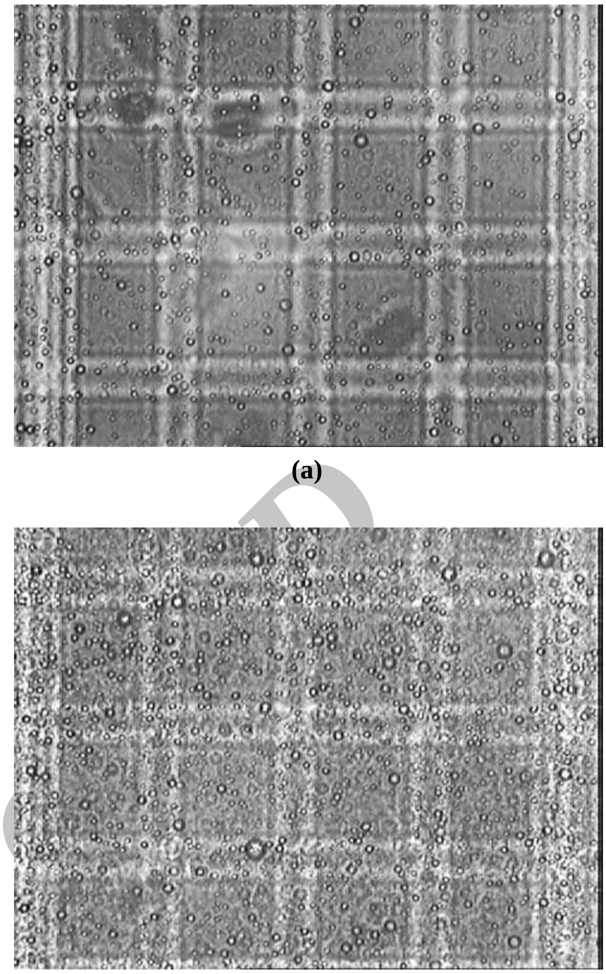
Figure 3. The effect of changing surfactant on the DSD: emulsion with tween80 (dash line); emulsion with Triton x-100 (solid line)

4.3- Effect of surfactant concentration on DSD

The photomicrographs of two sets of emulsions which were prepared with different concentrations of Triton x-100 are shown in Fig. 4. The results illustrate the droplet size decreases with increases in the surfactant concentration. Figure 5 depicts the droplet size distribution as a function of droplet diameter for different surfactant concentration. It is obvious that an increase in Triton x-100 concentration from 0.0001125 ml/ml solution to 0.001125 ml/ml solution decreases the mean diameter of droplets about 19% (from 3.05 to 2.56 μm) due to decreasing the surface tension of the aqueous surfactant solution. In addition, increasing the proportion of fine droplets (less than 3 μm) and also decreasing the proportion of coarse droplets as a result of an increase in Triton x-100 concentration can clearly be seen in Fig. 5.

4.4- Influence of salinity on the DSD

Figure 6 compares the photomicrographs of emulsions which were prepared with different concentrations of Triton x-100 in the presence (3 weight percent) and absence of NaCl. It can obviously be seen that droplets in the presence of NaCl are significantly coarser than droplets in the absence of NaCl. The droplet size distribution of emulsions with and without NaCl is illustrated in Figs. 7-9. Clearly, salinity has a major effect on the DSD of the emulsions. Emulsions with NaCl have more average droplet diameters in comparison with emulsions without NaCl.



(a)

(b)

Figure 4. Photomicrographs of emulsions: (a) Triton x-100 with concentration of 0.0001125 ml/100ml solution; (b) Triton x-100 with concentration of 0.001125 ml/100ml solution.

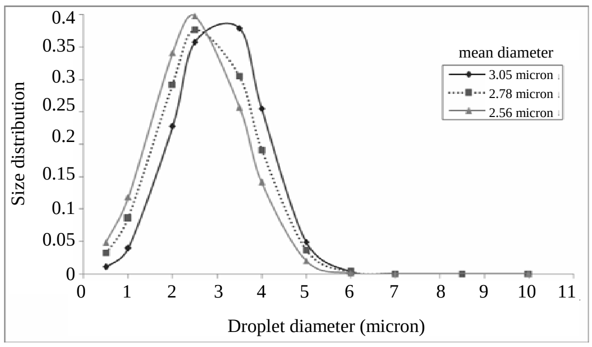


Figure 5. The influence of surfactant concentration on the DSD: concentrations of Triton x-100 are: 0.0001125 ml/100ml solution in black solid line; 0.000225 ml/ml solution in dash line; 0.001125 ml/100ml solution in grey solid line.

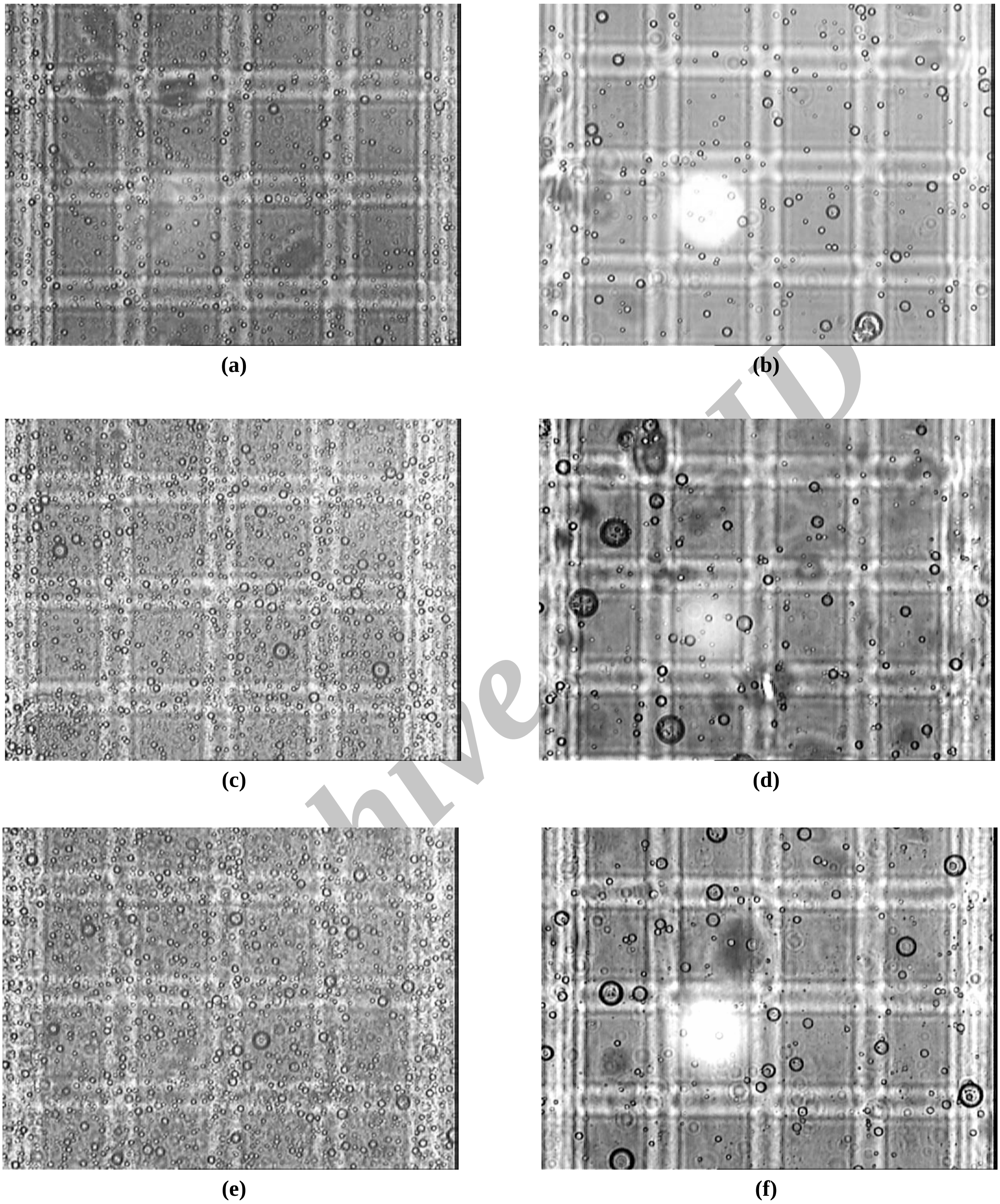


Figure 6. Photomicrographs of emulsions: Triton x-100 with concentration of 0.0001125 ml/100ml solution (a) in the absence of NaCl and (b) in the presence of NaCl; (c) 0.000225 ml/100ml solution in the absence of NaCl and (d) in the presence of NaCl; (e) 0.00045 ml/100ml solution in the absence of NaCl and (f) in the absence of NaCl.

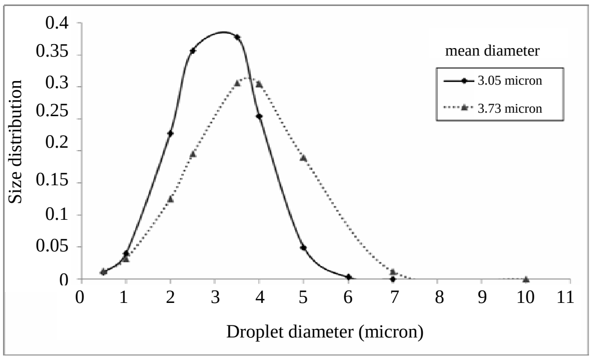


Figure 7. The comparison of the DSD in the presence and absence of salt: emulsion with Triton x-100(0.0001125ml/100ml solution) without NaCl (solid line); with NaCl (dash line)

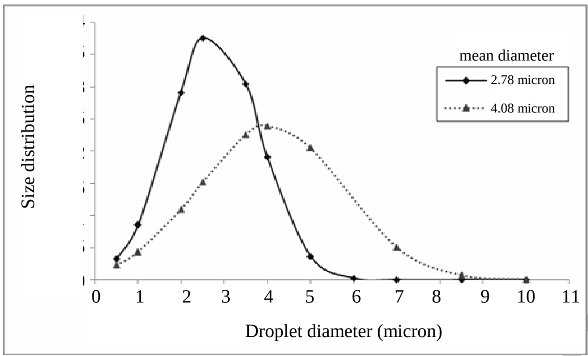


Figure 8. The comparison of the DSD in the presence and absence of salt: emulsion with Triton x-100 (0.000225ml/100ml solution) without NaCl (solid line); with NaCl (dash line)

As presented in Fig. 1, surface tension of aqueous surfactant solution increases in the presence of NaCl. For this reason, the oil-in-water emulsions which were prepared with surfactant solutions containing NaCl have coarser droplets. Moreover, the DSD of the emulsions with NaCl has a lower peak for different surfactant concentrations in comparison with emulsions without NaCl.

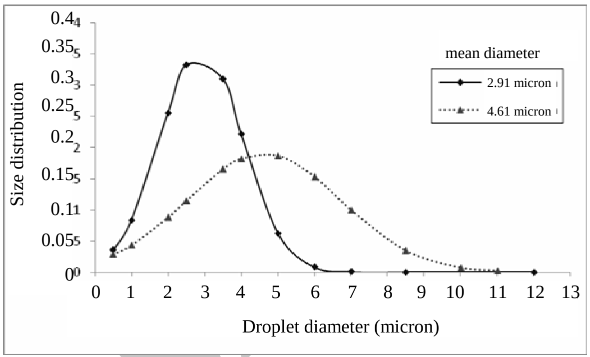
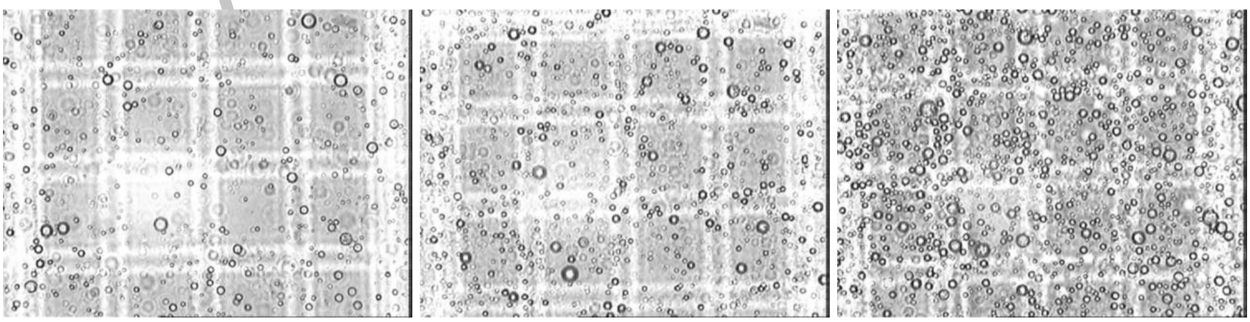


Figure 9. The comparison of the DSD in the presence and absence of salt: emulsion with Triton x-100 (0.00045ml/100ml solution) without NaCl (solid line); with NaCl (dash line)

4.5- Effect of homogenizer power on the DSD

In order to determine the effect of power of the homogenizer on the DSD of the emulsions, 3 sets of emulsion with equal amounts of Triton x-100 were prepared by using various power of homogenizer. Figure 10 shows photomicrographs of these emulsions.



(a) (b) (c)

Figure 10. Photomicrographs of emulsions: Triton x-100 with concentration of 0.00225 ml/100ml solution by shearing with power of (a) 480W; (b) 960W; (c) 2240W

Figure 11 indicates the DSD which is obtained from analyzing the photomicrographs. The calculated mean droplet diameters from the experimental data are as follow: 3.71, 3.42, and 3.35 μm. So, it is clear that increasing the power of shearing aqueous and oil phase together affects the DSD of the emulsions. Consequently, the mean droplet diameter decreases slightly by increasing the power of the homogenizer.

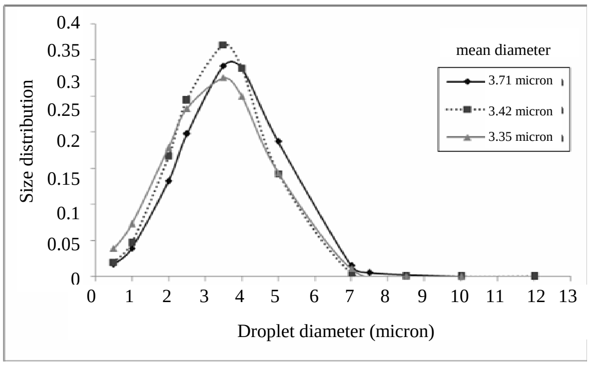


Figure 11. The effect of power of homogenizer on the DSD: emulsions with Triton x-100 (0.00225ml/100ml solution) with 480W power of homogenizer (grey solid line); with 960W power of homogenizer (dash line); with 2240W power of homogenizer (black solid line)

5- Conclusions

In the present study, the droplet size distribution of the Tehran refinery crude oil/water emulsions is determined by analyzing the photomicrographs. Influence of different factors such as surfactant concentration, salinity, and power of homogenizer (for making oil/water emulsion) on the droplet size distribution were discussed. For more convenience in engineering usage, the normal distribution function was fitted to the experimental data in order to reproduce the DSD of the emulsions by using mean diameter and standard deviation. Based on the experimental results and analysis, the following conclusions can be made:

- Triton x-100, in comparison with Tween80, decreased the surface tension of the aqueous solution more. Thus, oil droplets in emulsions which were prepared with the Triton x-100 solution were smaller.
- The mean droplet diameter decreased with increases in the concentration of surfactant due to increases in the surface tension of the surfactant solution.
- Salinity had a major influence on the DSD of the oil-in-water emulsions. NaCl increased the surface tension of the aqueous solution. So, the mean droplet diameter was greater in the presence of NaCl and the DSD was smoother in this condition.
- Changing the power of shearing the oil phase and surfactant solution together in the homogenizer affected the DSD of the dispersions. Increasing the power of the homogenizer decreased the mean drop diameter.

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