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The measurement of droplet size distribution of water-oil emulsion through NMR method

Arash Amani[1], Ali Reza Solaimany Nazar[1,*], Hasan Sabzyan[2], Gholamhassan Azimi[2]

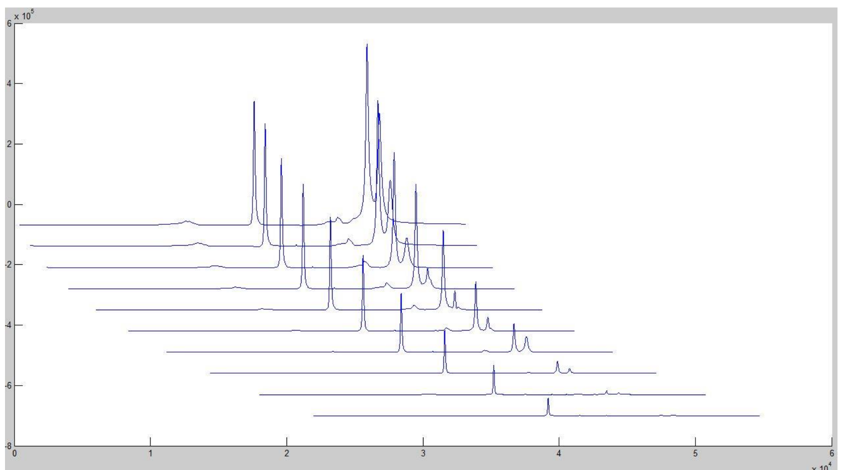
[1]*Department of Chemical Engineering, University of Isfahan, Isfahan, Iran*

[2]*Department of Chemistry, University of Isfahan, Isfahan, Iran*

HIGHLIGHTS

- Average water droplet size in water-oil emulsions were measured by applying NMR technique.
- Effect of type and concentration of demulsifier on average water droplet size was investigated.
- Influence of water volume ratio, water salinity and mixing speed was also evaluated.
- Water/oil volume ratio and water salinity increased the average droplet size.

GRAPHICAL ABSTRACT



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ABSTRACT

The effects of water/oil volume ratio, type and concentration of demulsifier, water salinity and mixing speed on the average water droplets size in water-oil emulsion are evaluated at different times through NMR measurements. The type and concentration of demulsifier have the greatest effects on the average droplets size with 38% and 31.5%, respectively. The water/oil volume ratio, water salinity and mixing speed are significant factors with 13.1%, 7.5% and 5.71%, respectively. The commercial demulsifier Break 6754 has the greater influence on the average droplets size compared to the acrylic acid. The water droplets size increases upon increasing the concentration of demulsifier, the water volume ratio and the salinity of water and decreases upon increasing the mixing speed.

* *Corresponding author. Tel.:+ 98 3137934027; fax:+ 98 3137934031*
E-mail address: asolaimany@eng.ui.ac.ir

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1. Introduction

The water in oil emulsions are formed during the production process, transportation and crude oil refining [1]. Generally, formation of emulsionsis undesirable in oil and petrochemical industry. The dispersed water occupies some of the volume of the oil processing equipment and pipelines and increases the operational costs of processing. Moreover, the physical properties of oil changes substantially due to the emulsion formation [2]. The mechanism of emulsion formation and its stability is almost the same in different industries; therefore, the study of emulsion behavior and factors affecting its stability is beneficial. The droplet size distribution of the emulsion is an important and effective factor on the emulsion stability. There exist several techniques to measure the size of the emulsion droplets having their advantaged and disadvantaged [3,4]. Economical consideration, reliability and the ease of the measurement method are the criteria for the technique selection.

Microscopic imaging method can be used to determine the shape, size, lateral surface and the volume of particles and droplets within a system. The advantage of this method is direct imaging of particles, while in other method, particles sizesare derived indirectly using different size distribution functions with parameters which values are optimized based on measurements on known samples. Direct microscopic imaging method has its own limitations, especially for turbid and dark color samples, as well as opaque concentrated emulsions appearing as cloudy, where do not allow the light to pass through the sample.

Nuclear magnetic resonance (NMR) has been used to measure mainly because of its simple preparation of sample step. The entire sample can be analyzed within a relatively short experiment time. Also there is no limitation for the turbid, dark color or concentrated emulsion samples. NMR has so far been used to measure the weak field coefficient [5], determine the droplet size distribution in oil-in-water and water-in-oil emulsions [6,7]. Houlingsworth et al. [8] proposed a method for measuring droplet size distribution by NMR which reduces the experiment time effectively (from 5-20 minutes to 3-10 seconds per sample). By using this method they succeed to measure silicon oil emulsion droplet size distribution dynamically for water-in-silicon oil samples. This method also allows measurements in non-equilibrium systems.

Van der Tuuk et al. [9] combined the previous methods including Carr-Purcell-Meimboom-Gill (CPMG) pulse sequence, pulsed field gradient (PFG) and simulated echo (STE) and proposed a new method for determining the droplet size distribution by NMR. In this method also the short observation time model [10] and slightly modified method of Parker and Rees are combined to develop a new method for calculating the droplet size distribution of crude oil emulsions.

In this article, NMR relaxation time and measurements of diffusion coefficient of the dispersed phase are used to determine the water-in-oil samples droplet size distributions. The effect of type and concentration of demulsifier, volume water/oil ratio, water salinity and mixing speed on the average droplets size are investigated.

2. Theory

The droplet size distribution is determined through two different methods depending on the sizes range of droplets.

2.1. Large droplet size

If the square root of the average of molecular penetration length inside the droplet is much smaller than the radius of the drop i.e. $(tD_0)^{\frac{1}{2}} \ll \bar{R}$ the short observation time model is used [10]. In short observation time, only a small fraction of molecules within the droplet feels droplet wall. Ignoring this fraction of molecules, Mitra et al. [10] showed that the deviation of the observed diffusivity at time t from the liquid bulk diffusivity within the droplet is expressed as:

$$\frac{D(t)}{D_0} = 1 - \frac{4}{9\sqrt{\pi}}\sqrt{D_0 t}\left(\frac{s}{v}\right) + Q(P,R,T) \tag{1}$$

where, D(t) is the diffusion coefficient of the molecules trapped in the droplets at time t, D_0 is bulk diffusion coefficient of the bulk of dispersed phase, $\left(\frac{s}{v}\right)$ is the surface to volume ratio of the droplets, and Q(P,R,T) is a parameter related to the curvature of the droplet surface. For short times, the Q(P,R,T) parameter is small and thus the $\frac{D(t)}{D_0}$ ratio is related to $\left(\frac{s}{v}\right)$ directly. If values of all other parameters are known the $\left(\frac{s}{v}\right)$ can be obtain from Eq. 1. For a distribution of droplets considered as the average surface-to-volume ratio of all droplets $\left(\frac{S}{V}\right)_{ave}$ and thus, D(t) can be regarded as the average diffusion coefficients of water molecules inside all droplets ($D(t)_{ave}$).

A simple relation connects relaxation time (T_2) to the surface to volume ratio of the droplets [11], i.e.

$$\frac{1}{T_2} = \rho(\frac{S}{V}) \quad (2)$$

where,ρ is the surface relaxation parameter.Averaging above equation for all droplets results in a relation between the average surface to volume ratio of droplets to the average relaxation time, $\left(\frac{1}{T_2}\right)_{ave}$ obtained from relaxation time distribution as follow:

$$\left(\frac{1}{T_2}\right)_{ave} = \rho\left(\frac{S}{V}\right)_{ave} \quad (3)$$

Distribution of the T_2 values is obtained from CPMG inversion recovery (IR) measurements in which the NMR signal attenuation (M^{abs}) is followed with time, and the T_2 values at each NMR frequency is derived from fitting CPMG results to the IR equation [12].

$$\frac{I}{I_0} = exp(-\frac{\tau}{T_2}) \quad (4)$$

The $\left(\frac{1}{T_2}\right)$ values are averaged over the T_2–frequency distribution furthermore to obtain the $\left(\frac{1}{T_2}\right)_{ave}$, the $\left(\frac{S}{V}\right)_{ave}$ value is obtained. By inserting these two values into Eq. 3, the surface relaxation parameter,ρ ,can be calculated. Since the ρ value is constant and does not depend on the droplet size, this value can be used in Eq. 2 to relate the $\left(\frac{1}{T_2}\right)$ to $\left(\frac{S}{V}\right)$ values for any range of droplet size; therefore, the droplet size distribution can be obtained from the T_2–frequency distribution.

2.2. Small droplet size

For small droplet size, the average length diffusion of water molecules is larger than the droplet size. At this condition the measured NMR signal is simplified to:

$$\frac{I}{I_0} = \exp\left(-\frac{1}{5}\gamma^2\delta^2G^2R^2\right) \quad (5)$$

where, G is the applied magnetics field gradient,γ is the gyromagnetic ratio of the nucleus, δ is the width of the gradient pulse and R is the droplet radius.This equation can be used to derive the average value of droplet size distribution, $\overline{R}$, by following the NMR signal.The average radius can be used to calculate $\left(\frac{S}{V}\right)_{ave}$ assuming perfect sphere shape for droplets using

$$\left(\frac{S}{V}\right)_{ave} = \frac{3}{\overline{R}} \quad (6)$$

The $\left(\frac{1}{T_2}\right)_{ave}$ is obtained through the same procedure described.

3. Materials and methods

3.1. Materials

In this study, a mixture of 50% crude oil and 50% diesel is used for sample preparation. The crude oil is mixed with dieselreduce its high viscosity which prevented its delivery into the NMR tube. Note that the dilution diesel sample is the product of the same crude oil fed in the Isfahan refinery. The viscosity and density of the crude oil and diesel used are reported in Table 1.Viscosity measurement is carried out in accordance with ASTM D7042 using a Stabinger viscometer (SV300 model).Aqueous phase re-distillated deionized water is used to prepare the sample with purity 99.99%. NaCl is provided by Merck, Germany. In this study two different demulsifier types are used that the first is Break 6754 commercial demulsifier produced by Ahwaz oil Company, Iran and the second demulsifier is acrylic acid with a laboratory purity of Merck, Germany.

3.2. Methods

3.2.1. Water in oil preparation

Small amounts of clay and the other insoluble solid particles can be suspended during the production and transportation of crude oil. These solids can affect the water droplets distribution in water-oil emulsions; therefore, the solids must be removed from the oil samples.To ensure a complete separation of the particles at first the oil samples are centrifuged by a centrifuge machine at 8000 rpm for 30 minutes and next is filtrated by syringe filters made of regenerated cellulose.

The procedure of water in oil samples preparation consists of three steps: 1- An aqueous solution with

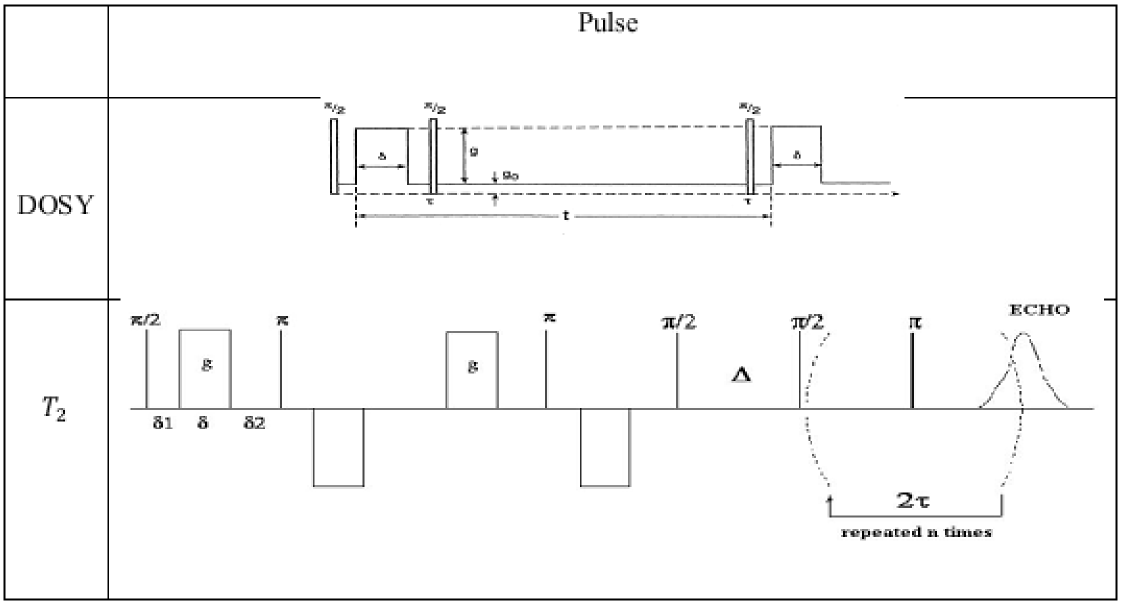

Fig.1. The pulse sequence used for the DOSY and T_2 measurements.

Table1.
API degree, density and kinematic viscosity (all at 25 °C) of the crude oil and the diesel samples used in this study.

Sample	Degree API	Density (g/ml)	kinematic viscosity (mm^2/s)
Crude oil	28.22	0.886	53.4
Diesel	61.28	0.734	3.48

consists of three steps: 1- An aqueous solution with a desired dissolved NaCl in distillated water is prepared. 2- A mixture of 50% crude oil and 50% diesel sample is mixed with the aqueous solution 3- A known volume of a sample demulsifier is added to the sample. In all experiments a mechanical stirrer is applied during mixing processes, for five and one minutes at steps 2 and 3, respectively.

3.2.2. NMR measurements

A 400MHz FT NMR product of Bruker Company is applied in this study. The water in oil emulsion samples are used in the NMR experiments immediately after preparation.The pulse sequence related to DOSY and T2 measurements are presented in Fig. 1. A 5 ml of the prepared sample is charged inside the NMR tube and the sample placed inside the machine for performing the spectroscopy measurements. A period about 5 minutes is needed to reach a thermal equilibrium inside the sample and the spectroscopy on the samples is started. The spectrums of the sample emulsion are shown in Fig. 2 at different times (τ). A typical T_2 distribution obtained in the whole frequency range of the NMR spectra is shown in Fig. 3. In this figure the vertical axis represents the ratio of the numbers of T_2 with a same size to the total counted T_2 and the horizontal axis is chosen somehow that the T_2 distribution has normal shape.

3.3. Experimental Design

The experimental design and the analysis of experiments are adopted through Taguchi method [13] and the average size of water droplets is considered as the experiment response after a long time to achieve the final average size. The experiments are designed using L18 standard orthogonal array. The studied factors and their levels are presented in Table 2. The experiments are conducted as per the experimental layout given in Table 2.

4. Results and discussion

The effects of type and concentration of demulsifier, the water volume ratio, the water salinity, and the mixing speed on the average water droplets size are investigated.

4.1. Analysis of Variance (ANOVA)

The analysis of variance (ANOVA) is used to recognize the significant factors among all the process parameters which are affecting the output quality characteristics using the quantities such as degrees

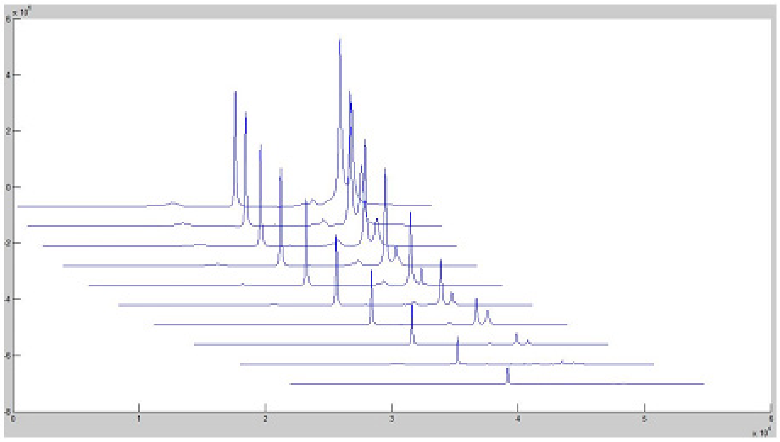

Fig. 2. Typical NMR spectra at different times.

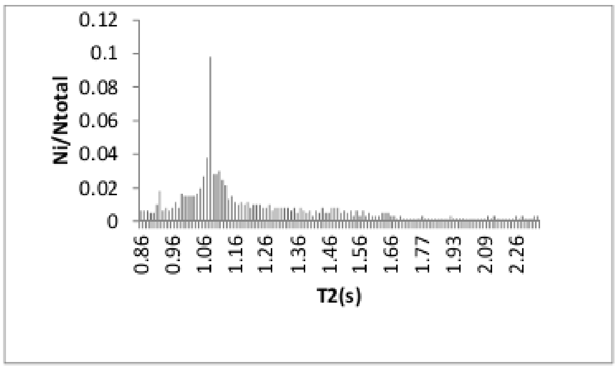

Fig. 3. T_2 distribution related to water/oil emulsion at 30% water/oil volume ratio.

Table 2.
NMR Experimental results with design tests in Taguchi method at different levels.

Number of experiment	Type of demulsifier (TD)	Demulsifier concentration (CD) (ppm)	Water/Oil volume ratio (W) (%)	Mixing speed (N) (rpm)	Salinity (S) (g/lit)	Average water droplet size (micrometer)
1	1	10	10	800	25	155
2	1	10	20	1000	35	180
3	1	10	30	1200	45	214
4	1	50	20	800	25	229
5	1	50	30	1000	35	259
6	1	50	10	1200	45	193
7	1	100	10	800	35	260
8	1	100	20	1000	45	281
9	1	100	30	1200	25	239
10	2	10	30	800	45	170
11	2	10	10	1000	25	98
12	2	10	20	1200	35	109
13	2	50	30	800	35	203
14	2	50	10	1000	45	155
15	2	50	20	1200	25	137
16	2	100	20	800	45	229
17	2	100	30	1000	25	196
18	2	100	10	1200	35	144

of freedom, sum of squares, variance, F-ratio and percent contribution [13]. Table 3 shows the computed results of the ANOVA with 95% confidence level which meanstheresponse value witha p-value lesser than 0.05 is acceptable and indicates that the factor has a significant effect on the average droplets size. The F-ratio and the percent contributions of the various parameters as quantified under the respective columns of Table 3 reveal that type and concentration of demulsifier, water/oil volume ratio, water salinity and mixing speed have significant effects on the average droplets size. The type and concentration of demulsifier factors contribute 38% and 31.5% on the total value, respectively while mixing speed and salinity contribute 5.71% and 7.5%, respectively and the water/oil volume ratio has contributed 13.1% on the total value.The interactions between type of demulsifier and concentration of demulsifier have no significant effect on the response in the studied range of levels.

4.2. Effect of type of demulsifier on the average droplets size

Among all the five factors, the most significant factor is the type of demulsifier, and this factor contributes to 38% on the average droplets size. The counter line diagram of the type of demulsifier on the average droplets size is shown in Fig. 4. The demulsifier has greater influence on the resistant layers around droplets; these layers are destroyed during droplets collisions favoring faster droplets coagulation. Since the demulsifier molecules migrate to the layers between droplets and oil media and adsorb on the interfacial surfaces, the layers are destructed by reaction or dissolution mechanisms within the aqueous or oil phases; hence, a rapid coagulation of droplets is resulted. Due to the lack of information about the formula and the other properties of the commercial demulsifier it is not possible to compare the demulsifier performances through their molecular structures.

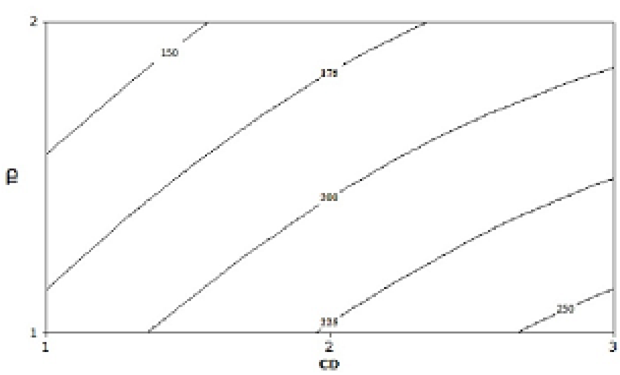

Fig. 4. Contour diagram of average water droplet size in terms of demulsifier types and concentration of demulsifier.

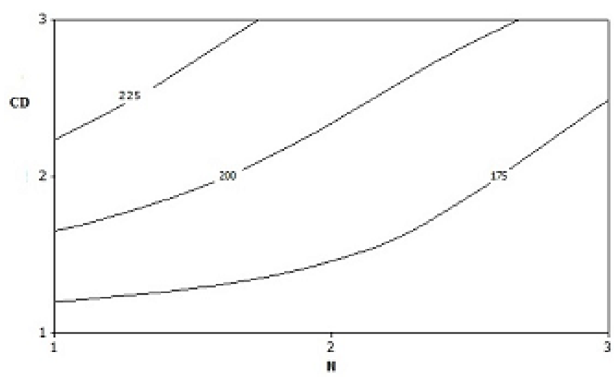

Fig. 5. Contour diagram of average water droplet size in terms of the concentration of demulsifier and mixing speed.

Table 3.
Variance estimation of average water droplet size as response

Factor	Degrees of freedom	Mean squared error	Sum of squared errors corrected	F ratio	P value	Contribution percent
TD	1	17986.7	17986.7	151.01	0	38
CD	2	15075.4	7537.7	63.28	0	31.5
W	2	3762.1	1881.1	15.79	0.004	13.1
N	2	2950.8	1457.4	12.39	0.007	5.71
S	2	6401.8	3200.9	26.87	0.001	7.5
TD*CD	2	130.1	65.1	0.55	0.605	-
Residual error	6	714.7	119.1	-	-	4.19
Total	17	47021.6	-	-	-	100

4.3. Effect of demulsifier concentration

A key factor affecting the average droplets size is the demulsifier concentration. The significant effect of this factor on the output response is shown in Fig. 5. With increasing the demulsifier concentration, the demulsifier molecules numbers between the interface of water droplets increase and the protective layers around the droplets weaken rapidly and break. Therefore, the coagulation rate of droplets increases and larger droplets are formed; hence, the average diameter of droplets increases.

4.4. Effect of salinity on the average droplets size

The water salinity effect on the average water droplet size is evaluated and as shown in Fig. 6, the average droplets size increases with an increase of the water salinity. As water density increases with increasing salinity, the differential density between water droplets and the continuous phase oil is increased; therefore, assists the separation of the oil and water phases and enhances the water droplets coagulation process. Moreover, the existence of small amount of salt or other dissolved solids in the water reduces drastically surface tension which is affective on the droplets coagulation. From another point of view, an increase in the salinity yields to increase the concentration of ions with opposite charges on the surface of water droplets; hence, the faster coagulation of droplets is achieved.

4.5. Effect of water/oil volume ratio on the average droplets size

The result of water/oil volume ratio effect on the average droplets size is shown in Fig. 7. It can be observed from the figure that changes in this factor value will cause a significant effect on the output response.This effect is attributed to an increase in the droplets numbers per unit volume at higher volume ratio of water; consequently, increases the collision probability among the droplets and the larger droplets are formed.

4.6. The effect of mixing speed on the average droplets size

The effect of mixing speed on the average droplets size is shown in Fig. 8. With increasing mixing speed the average droplets size decreases. An increase in the mixing speed causes the droplets become smaller due to the applied shear and both the coagulation induced by Brownian motion and sedimentation are reduced.

4.7. Optimum conditions

One of the purposes of statistical analysis and experimental design is to determine the optimum operation conditions for the process. Here, the purpose is to achieve a larger average size of the droplets. The optimum conditions for the average droplets size according to the mean effect diagrams are illustrated in Fig. 9. The appropriate demulsifier is Break 6754. The optimum conditions of demulsifier concentration, water volume ratio, mixing speed, and salinity are 100 ppm, 30%, 800 rpm and 45gr/liter, respectively.

5. Conclusions

In this study the average water droplet size in

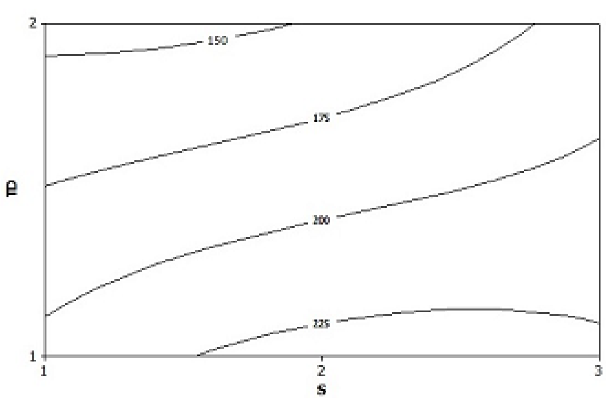

Fig. 6. Counter diagram of average water droplet size change in terms of the demulsifier types and water salinity.

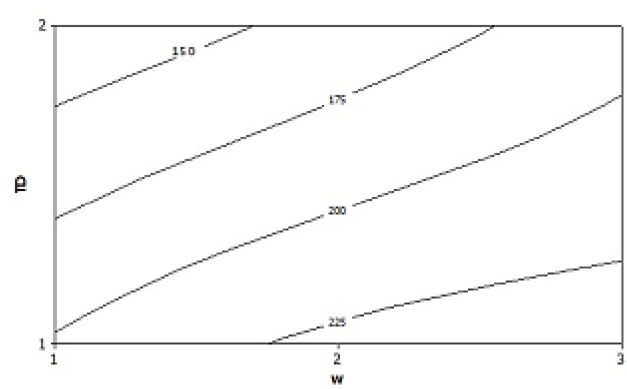

Fig. 7. Counter diagram of average water droplet size in terms of demulsifier types and water/oil volume ratio.

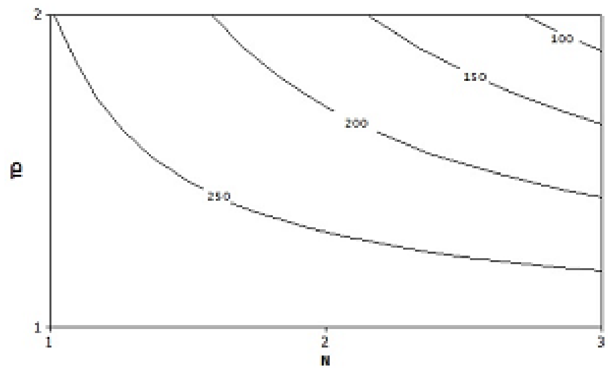

Fig. 8. Counter diagram of average water droplet size in terms of demulsifier types and mixing speed.

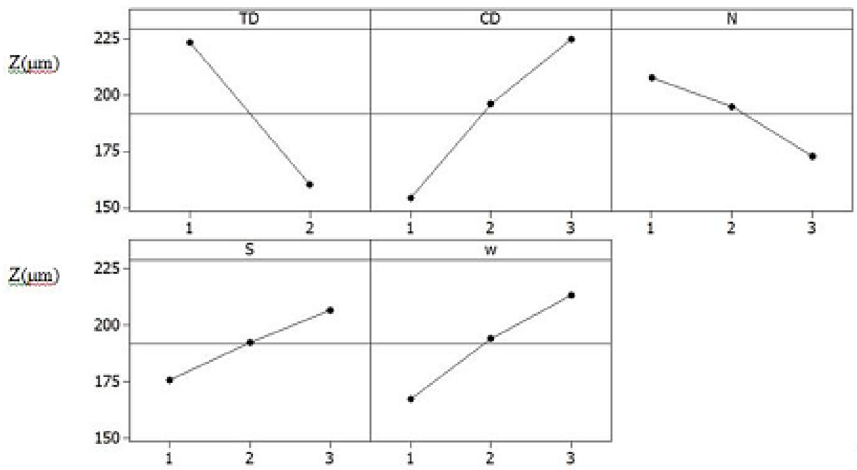

Fig. 9. The main effects diagrams

water-oil emulsions are measured by applying NMR technique in order to evaluate the dependency of the emulsions stability in terms of the operating factors. The effect of type and concentration of demulsifier, water volume ratio, water salinity and mixing speedon the average water droplet size are studied. The demulsifier Break 6754 in compare to acrylic acid has a more impact on the average droplets size and leads to larger average droplets size. The average water droplet size increases with increasing the concentration of demulsifier. Increasing the water/oil volume ratio and water salinity increase the average droplets size, while the mixing speed has an opposite effect.

References

[1] I. B. Ivanov, P. A. Kralchevsky, Stability of emulsions under equilibrium and dynamic conditions, Colloids Surf. A: Physicochem. Eng. Asp., 128 (1997) 155-175.

[2] M. Fingas, B. Fieldhouse, M. Bobra, E. Tennyson, The physics and chemistry of emulsions. Environment Canada and Consult chem, Ottawa, Canada and US Minerals Management Service, Herndon, Virginia, 1993.

[3] D. B. Curtis, M. Aycibin, M. A. Young, V. H. Grassian, P. D. Kleiber, Simultaneous measurement of light-scattering properties and particle size distribution for aerosols: Application to ammonium sulfate and quartz aerosol particles, Atmos. Environ. 41 (2007) 4748-4758.

[4] S. Chodankar, V. K. Aswal, P. A. Hassan, A. G. Wagh, Structure of protein–surfactant complexes as studied by small-angle neutron scattering and dynamic light scattering, Physica B: Condens. Matter. 398 (2007) 112-117.

[5] D. S. Parker, W.J. Kaufman, D. Jenkins, Floc breakup in turbulent flocculation processes, J. Sanitary Eng. Div. 98 (1972) 79-99.

[6] P. S. Denkova, S. Tcholakova, N. D. Denkov, K. D. Danov, B. Campbell, C. Shawl, D. Kim, Evaluation of the precision of drop-size determination in oil/water emulsions by low-resolution NMR spectroscopy, Langmuir, 20 (2004) 11402-11413.

[7] C. P. Aichele, M. Flaum, T. Jiang, G. J. Hirasaki, W. G. Chapman, Water in oil emulsion droplet size characterization using a pulsed field gradient with diffusion editing (PFG-DE) NMR technique, J. Colloid interface Sci. 315 (2007) 607-619.

[8] K.G. Hollingsworth, A.J. Sederman, C. Buckley, L.F. Gladden, M.L. Johns, Fast emulsion droplet sizing using NMR self-diffusion measurements, J. Colloid Interface Sci. 274 (2004), 244-250.
[9] N. van der Tuuk Opedal, G. Sørland, J. Sjöblom, Methods for droplet size distribution determination of water-in-oil emulsions using low-field NMR, Diffusion Fundamentals 7 (2009) 1-29.
[10] P.P. Mitra, P.N. Sen, L.M. Schwartz, Short-time behavior of the diffusion coefficient as a geometrical probe of porous media, Phys. Rev. B, 47 (1993) 8565.
[11] M.D. Hurlimann, K.G. Helmer, L.L. Latour, C.H. Sotak, Restricted diffusion in sedimentary rocks. Determination of surface-area-to-volume ratio and surface relativity, J. Magn. Reson. A 111 (1994) 169-178.
[12] K.S. Mendelson, M.H. Cohen, The effect of grain anisotropy on the electrical properties of sedimentary rocks, Geophys. 47 (1982) 257-263.
[13] R. Roy, Design of experiments using the Taguchi approach, New York: Wiley, 2001.