

# Experimental Investigation on Separation of Water in Crude Oil Emulsions Using an Oil-Soluble Demulsifier

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**ABSTRACT:** The formation of unwanted oil emulsions during the production, transportation, and processing of crude oil is a major challenging issue. This causes serious technical problems, subsequently, huge financial losses, which indicate the importance of their separation. The present work investigated the influence of an efficient oil-soluble demulsifier and temperature on the Demulsification Efficiency (DE) of water-in-crude oil emulsions through the bottle test method. The Central Composite Design (CCD) based on Response Surface Methodology (RSM) was applied to design the experiments and optimize the demulsification process. Based on the experimental results, a reduced quadratic model was developed using CCD. In addition, the analysis of variance (ANOVA) was used to evaluate the significance of the developed model and operational parameters. It was found that the P-value of the DE model was less than 0.0001, which confirms the considerable significance of the developed model. Moreover,  $R^2$ ,  $adj-R^2$ , and  $pred-R^2$  were 98.89, 98.15, and 94.34%, which indicates the high accuracy of the proposed model. The result showed that the effect of the demulsifier at low temperatures (25-50 °C) was significantly weak on the separation efficiency of the studied emulsions. In this case, the maximum water removal from the oil emulsions reached approximately less than 50%. In addition, the results demonstrated that the maximum interaction effect between parameters was observed by adding 20-25 ppm of the demulsifier at 75 °C. Moreover, the demulsification efficiency was obtained by more than 75%. Meanwhile, the subsequent addition of the demulsifier to the crude oil emulsions at concentrations greater than 25 ppm has almost not changed the efficiency of the process. Finally, the numerical optimization results obtained by CCD indicated that the maximum separation efficiency of 80.65% was achieved under the following optimal conditions: demulsifier dosage at 25 ppm and temperature at 75 °C.

**KEYWORDS:** Demulsifier; Water-in-crude oil emulsions; Demulsification efficiency; Optimization; Central composite design (CCD).

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## INTRODUCTION

Water-in-oil emulsions are formed during the process of crude oil exploitation and transportation [1, 2]. Some materials in crude oil, such as asphaltenes, resins, waxes, and solid particles, can form a film layer at the interface of water and oil, which increases the stability of formed emulsions [3-6]. Also, the type of water and oil and their size in the emulsion define the stability, which strongly affects the phase separation [7]. The separation of water from oil is of great industrial importance, as well as environmental protection. This separation is carried out by electrical, chemical, thermal, and mechanical methods [8-10]. Among these methods, chemical demulsification (use of demulsifying agents) in the petroleum industry is widely used. *Ebrahimzadeh Rajaei et al.* [11] emphasized that the application of a demulsifier is widely used to separate water and oil at the field level. It is completed by adding a small amount of demulsifiers into the emulsions. Using demulsifiers eliminates hydrophobic emulsifying agents and allows water droplets to stick together, helping to separate water from oil [12-16]. The chemical structure and dosage of the demulsifier determine the stability level of the emulsions and separation performance [17]. The emulsion stability can be analyzed by determining various parameters. *Touzouirt et al.* [18] evaluated the physical stability of emulsion by studying elasticity and storage modules. In work [19], it was concluded that the stability of the emulsion is dependent on the salinity, pH, time, and temperature. Thus, these parameters are very important in the analysis of demulsification efficiency.

Effective concentrations of demulsifiers are determined by the ratio of their polar and non-polar frequencies, which determines their Hydrophilic-Lipophilic Balance (HLB) [20-22]. The HLB is an effective tool for estimating the demulsification efficiency. There is a range of 0 to 20 for this value. HLB above 10 indicates that the surfactant is hydrophilic and has a high affinity for the water phase, while HLB below 10 indicates that it is lipophilic (hydrophobic) and is attracted to the oil phase [23]. In addition, surfactants can also act as stabilizers for W/O and O/W emulsions if the HLB value is less than 8 or greater than 14, respectively. Therefore, chemicals with intermediate HLBs could only destabilize the crude oil emulsions effectively [23]. *Esmaili et al.* [24] reported the application of various surfactants with different HLBs in the preparation of water emulsion. They observed

that the most stable emulsions could be formed under specific values of HLB. Demulsifiers with a large conditional HLB group number are the most effective in the demulsification of stable water in oil emulsions.

During demulsification, water-in-oil emulsions undergo several steps prior to being separated into water and oil phases, including flocculation, coalescence, and finally, phase separation or sedimentation [25]. As a result of flocculation, water droplets in crude oil emulsion clump together and form aggregates (form clusters) [26]. Coalescence is a critical step in demulsification and can be described as an irreversible process in which several drops of water are merged into a larger one. As a result, phase separation or sedimentation could occur under the influence of gravity [27]. In addition, a high flocculation rate, high interfacial tension, water cut, the lack of physically strong films, a low interfacial velocity, and a high temperature is crucial for efficient coalescence [28]. Moreover, sedimentation occurs due to the density difference between oil and water. In this case, water droplets settle down at the bottom of the emulsion during the continuous oil phase [29].

An effective demulsifier should separate water from oil at the lowest concentration at a minimum cost. At high temperatures, the chemical reaction at the interface between water and oil occurs at a higher rate. As a result, lower demulsifier concentrations will be required [30]. On the other hand, by heating the emulsion due to the reduction in its viscosity, a larger amount of chemicals can be mixed with the emulsion, which can increase the separation efficiency [31, 32]. Depending on the quantitative composition of natural stabilizers in oil, the destruction of Water in Oil (W/O) emulsions in the demulsification processes can occur at different temperatures [33]. It should be noted that the natural emulsifiers in crude oil have specific functional groups, which are adsorbed at the interface of water and oil, and create a stable layer. The mechanism of the demulsifier is to break this layer [12, 30]. In general, the required concentration of demulsifiers is a function of various factors such as temperature, pressure, wash water ratio, pH, and mixing rate [34-38].

*Vafajoo et al.* [38] evaluated the effect of demulsifying agent concentration, temperature, and pH on the desalting efficiency of an Iranian crude oil emulsion. They indicated that by increasing the concentration of the demulsifier, the required temperature for an effective

**Table 1: The properties of the crude oil**

Specification	Unit	Value	Test Method
Specific gravity @ 15.6 °C	---	0.879	ASTM D5002
API gravity	°API	29.47	ASTM D5002
Kinematic viscosity @ 40 °C	mm <sup>2</sup> /s	14.3	ASTM D445
	°C	-18	ASTM D5853
Pour point	wt %	4.4	IP 143
Asphaltene content	wt %	5.6	BP 237
Wax content			

**Table 2: The composition of ingredients of the applied demulsifier**

CAS Registry Number (RN)	Substance Name
64742-94-5	Heavy aromatic naphtha
1330-20-7	Xylene
67-56-1	Methanol

dewatering process had been decreased to a specific value. In work [39], the authors investigated the dehydration of the crude oil emulsion in the presence of three different ionic liquids as demulsifying agents by conducting bottle tests. They used RSM to evaluate the results of laboratory tests in order to analyze the influence of demulsifier concentration, temperature, pH, and water content on dehydration performance. Yonguep & Chowdhury [40] applied CCD made by RSM to optimize separation efficiency using next various demulsifiers: I) CTAB-cetyltrimethylammonium bromide; II) TTAC-trimethyltetradecyl ammonium chloride. The authors investigated different conditions of operational factors and confirmed the developed models by analysis of variance using the F-test and P-values. They noticed that the effect of demulsifier concentration on separation efficiency was stronger than other factors studied. Furthermore, the highest separation efficiency at an optimum demulsifier concentration of 850 gr/L was determined to be 82.6% and 80% for demulsifiers of CTAB and TTAC. In work by [34], the demulsification analysis was completed with the use of propargyl-alcohol and triethylene-glycol by bottle tests at various demulsifier concentrations, temperatures, and sitting periods. They proposed an efficient model employing RSM in order to calculate the optimal values of factors for the most efficient demulsification process.

Based on the completed literature, we concluded that various parameters could influence the demulsification process, among which the type and concentration of the chemical demulsifier, the temperature of the process, and the ratio of freshwater are the most important factors

that affect the separation of W/O emulsions. Moreover, since each oil has unique properties, the effect of a certain demulsifier on the demulsification efficiency of various crude oils can be different and should be determined experimentally. Therefore, in this work, the influence of an oil-soluble demulsifier at various temperatures on the efficiency of water phase separation from an Iranian crude oil emulsion was investigated. To this end, water-in-oil emulsions were first prepared by adding freshwater to the crude oil sample. Then the demulsification operation was analyzed by the bottle test method. The novelty of the work lies in the fact that the used demulsifier is first applied to the used oil. Accordingly, the interaction effect of the applied demulsifier and temperature on the demulsification process of the studied crude oil emulsions was not previously investigated. In addition, a new model has been developed that can predict the demulsification efficiency as a function of temperature and concentration. Besides, the CCD based on RSM was utilized in order to design the laboratory tests, identify the effect of parameters, and optimize the crude oil demulsification process with the help of the Design-Expert® V13 program.

## THEORETICAL SECTION

### Materials

In this study, Iranian crude oil from the Sarvstan-Saadatabad oilfields was applied. The properties of the used crude oil are presented in Table 1. The used oil sample was characterized by practically high density, and viscosity, as well as increased content of asphaltenes that predetermine the highly kinetic stability of its emulsions (W/O type). The specific gravity, kinematic viscosity, pour point, asphaltene, and wax contents of the crude oil used in this work have been measured according to ASTM D5002, ASTM D445, ASTM D5853, IP 143, and BP 237, respectively. Moreover, the API gravity of crude oil has been calculated through the following Equation:

$$API = \frac{141.5}{\text{Specific Gravity}} - 131.5 \quad (1)$$

Moreover, a chemical product under the trade name DSS 9280 was utilized as a demulsifying agent for the phase separation in the prepared W/O emulsion samples. The used demulsifier was provided by Energy Semnan Company (Iran) and contained a mixture of substances listed in Table 2 in its formulation. In addition, Table 3 represents the physical and chemical properties of the applied demulsifier.

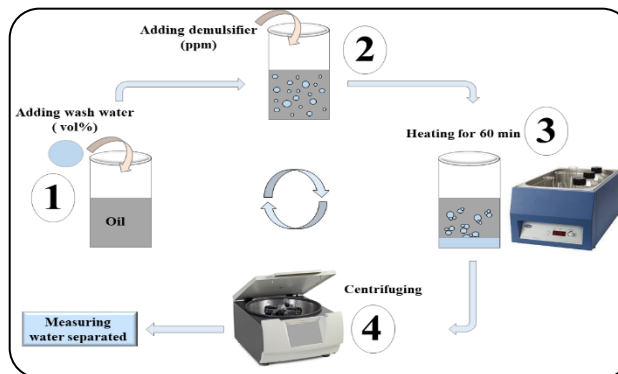
**Table 3: Physical and chemical properties of the used demulsifier**

Property	Value
Appearance	
Form	Liquid
Color	Dark
Odor	Aromatic
Solubility	oil-soluble
Density @ 20 °C, g/cm <sup>3</sup>	0.930 ± 0.05
Viscosity, dynamic @ 20 °C, mPa.s	< 50
Flash point, °C	> 50
Boiling point range, °C	137-143

### Demulsification methodology

The bottle test method has been used to evaluate the amount of water separation in the emulsion samples [34]. For this purpose, the emulsions (W/O type) were first prepared, and then their phases were separated through the bottle test method. Fig. 1 shows the demulsification steps for measuring the amount of water removed from the crude oil emulsions in one cycle of the experiment. As can be seen, to perform each run (experiment), it is necessary to complete a four-step cycle [37]. As shown in the Fig., freshwater (at 5 vol%) is first added to the crude oil and then mixed (homogenized) for a certain time to prepare a stable W/O emulsion without any phase separation (step 1). The stability of the prepared emulsion has been tested in two ways: 1) at room temperature for 48 hours and 2) at room temperature for 60 min by further centrifuging for 15 min. No sign of phase separation was observed at the end, which indicates the high stability of the produced emulsions. Then, the prepared emulsion sample is then poured into a bottle (100 ml) and heated in a water bath heater. After about 5-6 minutes, when the prepared oil emulsion reaches the test temperature, the demulsifier is added to it (step 2). This mixture is then shaken well and placed in a water bath for one hour (step 3). After this time, the separated water is withdrawn from the oil, and its volume is measured. Then, the mixture is taken to a centrifuge tube where it is rotated at 1400 rpm for 15 min (step 4) [37, 41-43]. Afterward, the separated water at the bottom of the tube is also measured. Finally, the total volume of water separated is obtained by determining the water removed from the crude oil in two steps the water bath and centrifuge separations. Additionally, the Demulsification Efficiency (DE) was calculated as follows:

$$DE = \frac{\text{The volume of water separated}}{\text{The initial volume of water in the crude oil emulsions}} \times 100 \quad (2)$$

**Fig. 1: A typical demulsification cycle of the experiment**

### Design of experiments

In this research study, the design of experiments (DOE) and analysis of the obtained results have been performed using the Design-Expert® V13.0.5.0. The CCD of RSM has been utilized for experimental design and optimization of the crude oil demulsification process. The effect of main operating parameters, i.e., demulsifier dosage and temperature, was studied at different levels of low (-1), center (0), and high (+1). Table 4 shows the independent process parameters and their coded levels in the design of experiments. In addition, a total number of 11 experiments, including eight factorial and three center experiment points, have been designed using CCD. In each experiment, the demulsification of the W/O emulsion sample was carried out by the bottle test method, and the amount of removed water was determined. The matrix of the design of experiments and results is depicted in Table 5.

### RESULTS AND DISCUSSION

The effect of demulsifier dosage and temperature on the demulsification of the prepared emulsions by Iranian crude oils has been investigated, and the optimum values of studied variables were determined to achieve the highest demulsification efficiency based on the developed reduced quadratic model using CCD of RSM.

### Analysis of variance (ANOVA)

The analysis of variance (ANOVA) has been applied to determine the significance of the model, individual operating parameters, and their interactions based on the P-values and F-values. In this work, the adequacy of the developed model and the corresponding significance of the parameters were evaluated with a confidence level of 95%.

**Table 4: The experimental levels of independent parameters in the CCD**

Parameter	Variable	Level (coded)			Unit
		Low (-1)	Center (0)	High (+1)	
Demulsifier dosage	A	0	15	30	ppm
Temperature	B	25	50	75	°C

**Table 5: Design of experiments and results of the demulsification process**

Run	Input parameters (coded)		Response
	A Demulsifier dosage	B Temperature	DE
	ppm	°C	%
1	-1.00	1.00	23.00
2	1.00	1.00	83.00
3	0.00	-1.00	23.00
4	1.00	-1.00	23.60
5	0.00	0.00	42.20
6	-1.00	-1.00	0.00
7	0.00	0.00	43.60
8	-1.00	0.00	11.50
9	1.00	0.00	48.00
10	0.00	0.00	45.20
11	0.00	1.00	72.80

Table 6 represents the main results of ANOVA for the demulsification model (DE). Based on the CCD and ANOVA, the following reduced quadratic model was developed to predict the demulsification efficiency:

$$DE = -14.3667 + 1.96689 A + 0.517333 B + 0.0242667 AB - 0.0615259 A^2 \quad (3)$$

It should be noted that P-values below 0.0500 depict that the terms of the proposed model are significant, while values over 0.1000 demonstrate that the terms are not significant [44]. As illustrated in the table, the P-value for the DE model was less than 0.0001 (significantly less than 0.05), which approves that the developed reduced model is statistically significant. In addition, the F-value of 133.39 means the model is significant. The probability that such a large F-value can be caused by noise is only 0.01%. At the same time, as can be seen from Table 6, the following terms namely, demulsifier dosage (A), temperature (B), the interaction of operating parameters (AB), and the quadratic effect of the demulsifier dosage ( $A^2$ ) are significant model terms in the DE model. Moreover, the lack-of-fit test was also used to determine the level of fit of the model for the given set of data. Models with

a non-significant lack-of-fit are suitable for predicting outcomes [34, 40]. As shown in Table 6, the lack-of-fit F-value of “7.2” for the DE model emphasizes that lack-of-fit has not been significantly related to the pure error. As a result, the proposed DE model is in reasonable agreement with experimental data and can be applied to predict demulsification efficiency.

#### Model fit statistics

In this study, the  $R^2$ -statistics, which include  $R^2$  (coefficient of determination), adj- $R^2$  (adjusted coefficient of determination), and pred- $R^2$  (predicted coefficient of determination), as well as the Adequate Precision (AP), were utilized to determine how the developed model fits the experimental data. Meantime, it should be noted that a model, in which the coefficient of determination is greater than 80%, is considered significant [45]. Furthermore, AP is usually applied to examine the ratio of signal-to-noise. A ratio of more than four could be considered satisfactory [39]. The model summary statistics for the DE model are presented in Table 7. As presented in the table, the  $R^2$  for the DE model was determined to be 0.9889, which confirms that the model could explain 98.89% of the variance in the response function. Besides, an AP of 36.680 indicates a sufficient signal, indicating that the model can be used for navigation in design space. Moreover, the pred- $R^2$  value of 0.9434 reasonably agrees with the adj- $R^2$  of 0.9815, since their difference is less than 0.2, indicating a high significance of the DE model [44, 46]. At the same time, the coefficient of variation (CV) for the DE model was 8.99. CV is defined as the ratio between the SD (standard deviation) and the mean. Moreover, the level of dispersion around the mean increases with an increase in CV [47]. In this regard, one can conclude that this low CV value provides strong confirmation of the high reliability of the experiments, and also adequately develops a precision response model [48, 49].

#### Model validation using diagnostics plots

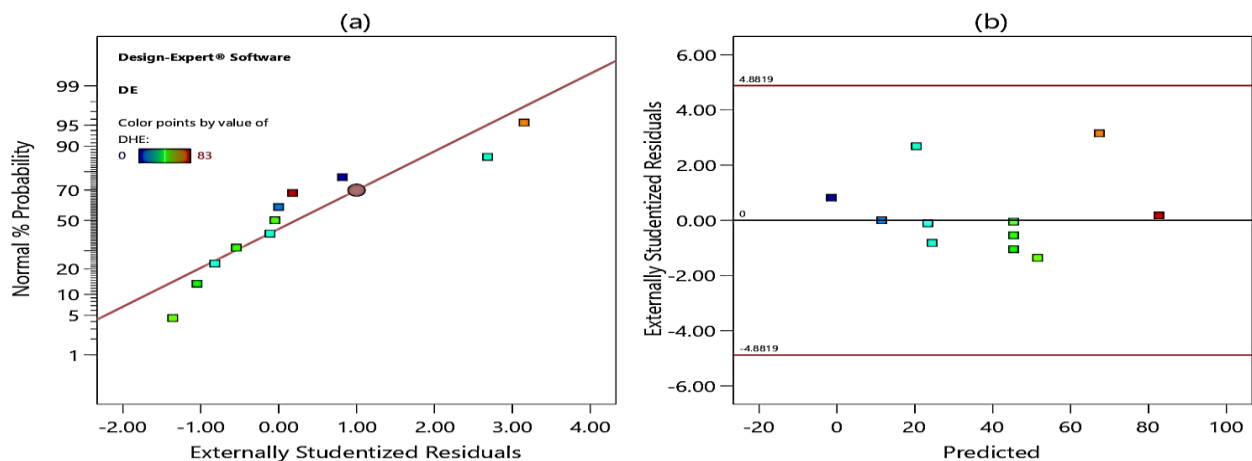
Diagnostic plots are used as one of the main methods to evaluate the adequacy and validity of a developed model. In other words, they are used for checking whether the selected design can provide an adequate approximation of the results to that of the actual experimental data [34, 50]. Fig. 2(a) shows the normal plot of the residuals, and Fig. 2(b) represents the residuals versus the predicted

**Table 6: ANOVA results of the reduced quadratic model for DE**

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	6170.70	4	1542.67	133.39	< 0.0001	significant
A-Demulsifier dosage	2404.00	1	2404.00	207.86	< 0.0001	
B-Temperature	2912.81	1	2912.81	251.86	< 0.0001	
AB	331.24	1	331.24	28.64	0.0017	
A <sup>2</sup>	522.65	1	522.65	45.19	0.0005	
Residual	69.39	6	11.57			not significant
Lack of Fit	64.89	4	16.22	7.20	0.1257	
Pure Error	4.51	2	2.25			
Cor Total	6240.09	10				

**Table 7: Model summary statistics for the DE model**

No	Fit statistics		DE model
1	Coefficient of determination	R <sup>2</sup>	0.9889
2	Adjusted coefficient of determination	adj-R <sup>2</sup>	0.9815
3	Predicted coefficient of determination	pred-R <sup>2</sup>	0.9434
4	Adequate precision	AP	36.680
5	Standard deviation	SD	3.40
6	Coefficient of variation	CV	8.99

**Fig. 2: The normal plot of the residuals (a) and the residuals plot versus predicted (b)**

response for the DE model. As shown in Fig. 2(a), the normal plot demonstrates that the model is adequate due to a normal distribution of the residuals around the straight line. In addition, the residuals versus predicted responses evaluate the assumption of constant variation. As can be seen from Fig. 2(b), the residuals have a random scatter, confirming a constant variation. Fig. 3 illustrates the predicted versus actual values. This Fig. can be considered the most important plot, as it shows a comparison between the predicted data obtained from the model and actual experimental data. As the Fig. depicts, there is an excellent agreement between the predicted values by the developed

DE model and the corresponding actual values.

These observations (from Figs. 2 and 3) confirm the adequacy of the DE model for the prediction of the demulsification of the W/O emulsion samples.

### ***Influence of experimental parameters on the demulsification efficiency***

The influence of the main operational parameters on the DE has been shown in the on-factor, contour, and three-dimensional (3D surface) graphs based on the proposed developed model obtained using CCD. Moreover, in the on-factor graphs, the output response (DE)

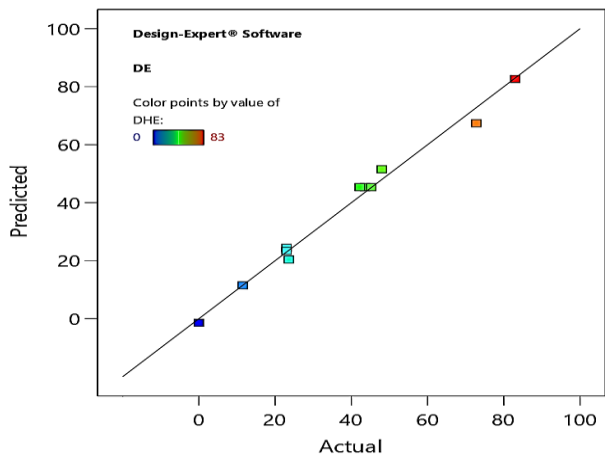


Fig. 3: The predicted versus actual values for the DE model

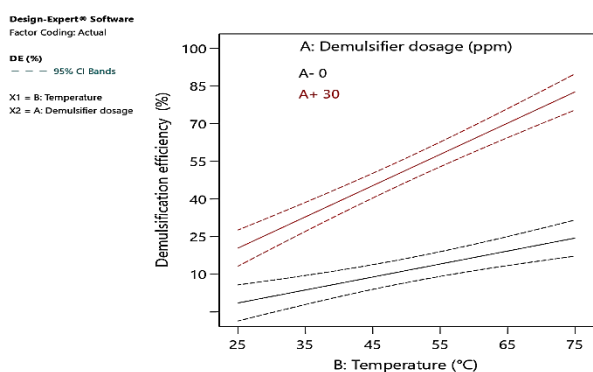


Fig. 4: Effect of the temperature on the DE

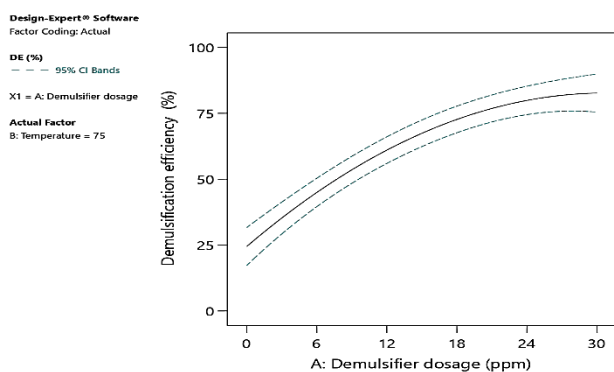


Fig. 5 Effect of the demulsifier dosage on the DE

was maintained as a function of one selected parameter. In contrast, the effect of another parameter was kept at a constant level.

#### Influence of temperature

Fig. 4 shows the effect of temperature on the demulsification process (DE) of crude oil emulsions. Temperature rising has several effects on the separation of

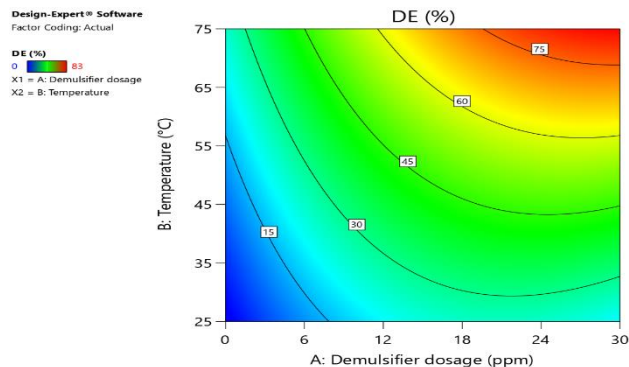
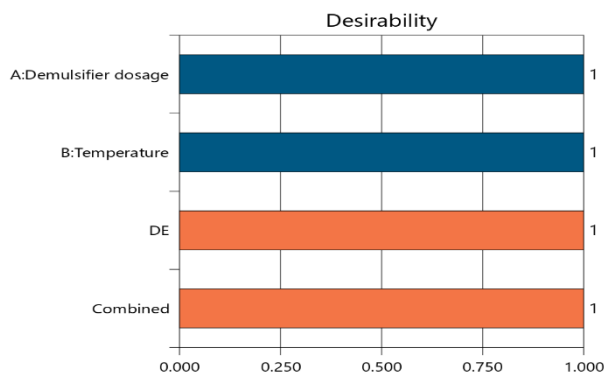
W/O emulsions. Some of them are as follows: a decrease in the viscosity of the continuous oil phase, an increase in the difference between the continuous and dispersed (water) phase of the emulsion, as well as a decrease in the rigidity of the interface. In this case, the quantity of droplet collisions is increased due to the weakening of interfacial film among phases (aqueous and oil), and the droplets could easier coalesce on collision [33, 51]. In Fig. 4, the influence of temperature on separation performance was shown in two different values of demulsifier dosage ( $A=0$  and 30 ppm). As the Fig. demonstrates, in the first case ( $A=0$  ppm), the demulsification efficiency at 25 °C was less than 5%, and an increase in the temperature from 25 to 75 °C increased the demulsification efficiency by only 20%, reaching 25%. Nevertheless, in the second case ( $A=30$  ppm), increasing the temperature has significantly enhanced the separating efficiency. In this case, by increasing the temperature from 25 to 75 °C, the demulsification performance was increased from about 20 to 85% by approximately 65%.

#### Influence of demulsifier dosage

Fig. 5 illustrates the influence of demulsifier dosage on the separation efficiency of W/O emulsions. The applied demulsifier was added to the crude oil emulsions in the range of 0-30 ppm. As shown in this Figure, the addition of the demulsifier to the emulsion samples has constantly enhanced the demulsification efficiency. As can be seen, at a low concentration of demulsifier (less than 12 ppm), the influence of the demulsifier on the demulsification efficiency was low, and the maximum separation was about 50-55%. However, adding 25 ppm of demulsifier, its effect on the separation efficiency was significantly high and could increase demulsification efficiency to a value of more than 80%. The reason for this is the better destabilization of the emulsifiers and the breaking mechanism of the w/o emulsions. It should be noted that the demulsifying agents involve two parts: lipophilic and hydrophilic [52]. The lipophilic part dissolves in the continuous oil phase, and the hydrophilic part dissolves in the dispersed water phase. Thus, by increasing the concentration of the demulsifier in the oil emulsions, the deposition of surfactant molecules at the interface of water and oil phases increases until a sufficient extent has been reached. The interfacial film then becomes thin until it disintegrates and the water droplets coalesce; thereby

**Table 8: Optimal values of parameters for maximum DE**

Parameter	Variable	Unit	Optimal value
Demulsifier dosage	A	ppm	25
Temperature	B	°C	75

**Fig. 6: Effect of the significant interaction variables on the DE****Fig. 7: The desirability of optimal values of parameters for DE**

increasing the efficiency of demulsification. At the same time, as shown in Fig. 5, the addition of the demulsifier to the crude oil emulsion at concentrations higher than 24-25 ppm has almost not increased the efficiency of the process. The justification for this phenomenon is that the demulsifier molecules can start acting as an emulsifier, by increasing in concentration within this distinct range. Moreover, increasing the demulsifier dosage beyond this range (greater than 30 ppm) can even increase emulsion stability and reduce the demulsification efficiency.

#### *Influence of interaction variables*

Fig. 6 shows the interaction between the demulsifier dosage and temperature on the demulsification efficiency. As illustrated in the Fig., an increase in the demulsifier dosage and the temperature has enhanced the separation efficiency. However, upon careful analysis of this

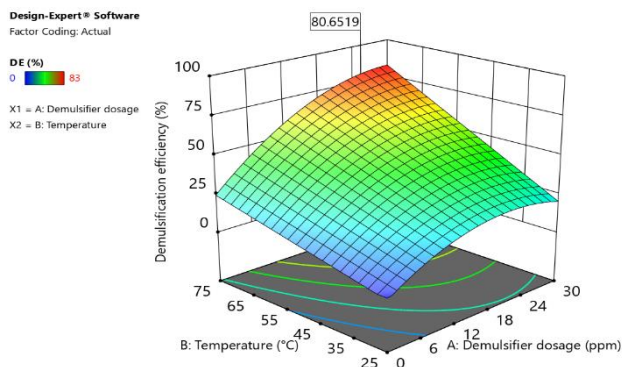
interaction plot, the most important results were observed as follows:

- The effect of demulsifier dosage and temperature at their low levels (A=0 ppm, and B=25 °C) was significantly weak on the demulsification efficiency. In this case, almost no separation was performed.
- The addition of demulsifier from 0 to 30 ppm at a low level of temperature (B=25 °C) had a weak influence on the DE. In this case, the demulsification efficiency was increased only by approximately 20-25%, reaching up to 30%.
- An increase in temperature from 25 to 75 °C at the low level of demulsifier dosage (A=0 ppm) also had a weak effect on separation efficiency. In this case, the maximum DE reached approximately less than 30%.
- The maximum interaction effect between parameters, as can be seen, was observed at the high values of temperature (75 °C), and approximately near the high level of demulsifier dosage (20-25 ppm). As the Figure shows, the demulsification efficiency, in this case, was determined to be over 75%.

#### *Optimization of the demulsification process*

Numerical optimization of the separation of the phases in the emulsions has been completed by using the CCD to achieve maximum demulsification efficiency. Table 8 shows the optimal conditions for the highest DE. As illustrated in this table, the predicted optimum values were as follows: 25 ppm and 75 °C for the demulsifier dosage and temperature. It should be noted that the indicated optimum values of parameters were selected on the basis of desirability, as demonstrated in Fig. 7. In principle, desirability can be viewed as an objective function ranging from zero (least desirable) to one at the goal (most desirable) [44]. In order to optimize a response, a goal must be set. There are five possible "Goals" for responses: "none", "maximum", "minimum", "target", or "in range". The goal of this study was to "maximize" demulsification efficiency. Moreover, the studied parameters at their design range were included in the optimization process. Based on the results obtained, it is evident that in the optimal condition values, as shown in Fig. 7, the desirability was 100%, indicating that the optimal conditions are capable of getting desirable results for Demulsification Efficiency (DE). In addition, Fig. 8 shows the 3D surface plot of numerical optimization for maximum DE.





**Fig. 8:** The 3D-surface plot of numerical optimization for the maximum DE

As shown in this Fig., the maximum demulsification efficiency of W/O emulsions under predicted optimal conditions was determined to be 80.65%. Moreover, the optimum values of operating parameters were retested again in the laboratory, and the obtained results were almost the same as the data predicted by the model.

## CONCLUSIONS

In this work, the influence of demulsifier dosage and temperature on the demulsification process of W/O emulsions was studied using the bottle test method. The CCD based on RSM was utilized to design the experiments and optimize the separation of the phases in the emulsion samples. For this purpose, a reduced quadratic model was developed to predict the Demulsification Efficiency (DE) and optimize the process. It was found that the P-value of the DE model was lower than 0.0001, which confirms the considerable significance of the developed model. Moreover,  $R^2$ ,  $\text{adj-}R^2$ , and  $\text{pred-}R^2$  were 98.89, 98.15, and 94.34%, which indicates the high accuracy of the proposed model. The results showed that the effect of demulsifier dosage and temperature at their low levels ( $A=0$  ppm, and  $B=25$  °C) was significantly weak on the demulsification efficiency. In this case, almost no separation was observed. The addition of a demulsifier from 0 to 30 ppm at a low level of temperature ( $B=25$  °C) had a weak influence on the DE. Under these conditions, the demulsification efficiency was increased only by approximately 20-25%, reaching 30%. Moreover, an increase in temperature from 25 to 75 °C at the low level of demulsifier dosage ( $A=0$  ppm) also had a weak effect on the separation efficiency. In this case, the maximum DE reached approximately less than 30%. The maximum interaction effect between

parameters was observed at the high level of temperature (75 °C) and approximately near the high level of demulsifier dosage (20-25 ppm). In this case, the demulsification efficiency was greater than 75%. Furthermore, the results of numerical optimization of the process indicated that the maximum separation of 80.65% was obtained under the following optimal conditions: demulsifier dosage at 25 ppm and temperature at 75 °C. Additionally, the results showed the high efficiency of the used demulsifier, similar to industrial ones. Comparison of the tested reagent with other demulsifiers is a topic for future work. In addition, the effect of time and pH on the demulsification will be evaluated in our future work. Moreover, more information and suggestions by authors for future works are presented in the next section "Suggestions for future works".

## Suggestions for Future Works

For further research, the authors strongly suggest a number of additional related topics with a focus on heavy and extra heavy oils. Demulsification of such oils is challenging due to their high viscosities, densities, as well as high content of asphaltenes, resins, and other heavy materials, which determine the high stability of emulsions. Therefore, the following main topics are strongly suggested:

- Development of highly efficient composite demulsifiers with different functional groups for demulsification of water-in-extra heavy crude oil emulsions
- Optimization of demulsification process of heavy and extra heavy crude oils using developed composite demulsifiers (along with other common operational parameters involving demulsifier dosage, temperature, wash water ratio, and oil space velocity) on electrostatic desalting (pilot) units.
- Investigation of the influence of low-viscosity petroleum products (like, kerosene or diesel cuts) as a diluent in addition to the effect of the mentioned common operating parameters on electrostatic desalting/dehydration of extra heavy oils and evaluation of its scientific and economic aspects for application and implementation in the industry

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