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# Evaluation of the Effectiveness of Synthesized Polymeric Demulsifiers in the Petroleum Sector

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## Abstract

In this study, two new types of polymeric demulsifiers were prepared. Synthesis of polymeric Gemini surfactants depend on ring opening polymerization between ethylene di amine tetra acetic acid di anhydride (EDTA-DA) with di ethylene tri amine once and with glycerol again. FT-IR spectra was measured to determine the functional groups in synthesized polymers, viscosity average molecular weight ( $\overline{M}_v$ ) and critical micelles concentration (CMC) were done. Demulsifiers were applied on emulsions (water in oil) to separate water. The results showed high efficiency in separating water from crude oil.

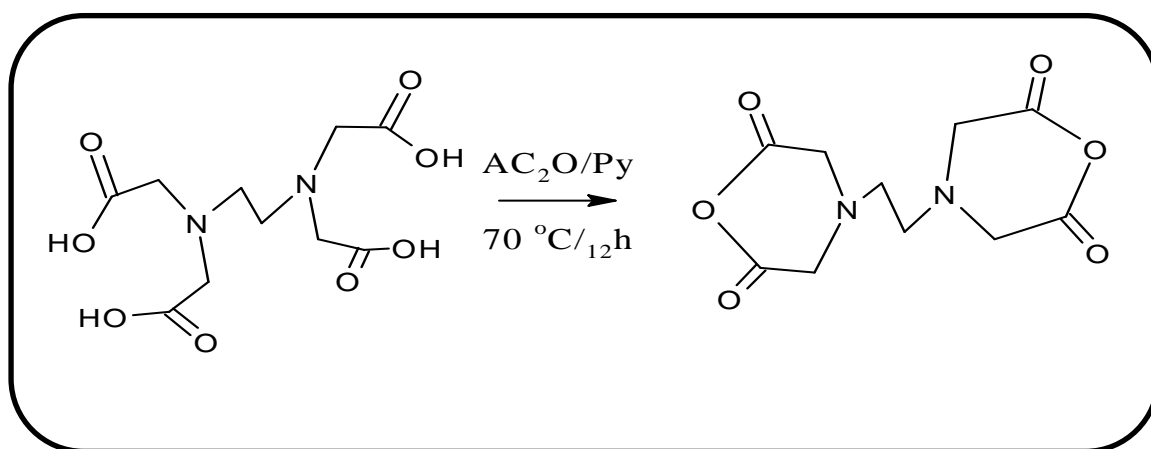
**Keywords:** polymer synthesis, demulsifiers, crude oil treatment, surfactant, ring opening polymerization.

## 1- INTRODUCTION

The emulsion is water in crude oil or vice versa. It phenomena is common in oil sector and can be caused many problems in this field (Martínez-Palou *et al.*, 2011, 2013; Wang *et al.*, 2015; Umar *et al.*, 2018). Treatment of this phenomena is high important in the process of crude oil extraction. The chemical researchers are focusing their efforts to solve this problem by using chemical products called demulsifiers. Demulsifiers or surfactants can be defined as material has the ability to assemble on a surface between two different materials in polarity. The main effect of demulsifier is to reduce the surface tensile between these different material in polarity (Bellanger *et*

*al.*, 2014; Cerrada *et al.*, 2015; Liu *et al.*, 2017; Sunde, Pham and Kwan, 2017; Parker *et al.*, 2018), chemically demulsifiers can be defined as chemical compounds representing the amphiphilic molecules which have two types of chemical characteristics one of her polar and the other is nonpolar therefore have two party a polar party (head) and nonpolar party (tail) (Wang, 2005). The surfactant is characterized by dissolve in the water and organic solvents. Demulsifiers work on balancing effect emulsion factors and reduce the surface tensile for water dirt, it is materials that have ability to configuration system that high stability via the configuration two separate phases non mixed by cracking the ocean membrane is ramblings phase drops, the use of high concentration of demulsifiers leads to create more stable emulsion , it requires that the demulsifier has ability to mobility during the organic phase down to limit the splitter (strong corruption to limit the splitter between water and oil) and it is done fast and suitable system with emulsion would be separated (Al-Sabagh, Kandile and Noor El-Din, 2011; Ojinnaka *et al.*, 2016; Radziuk and Möhwald, 2016; Zolfaghari *et al.*, 2016; Bi *et al.*, 2020).

There are several ways to prepare Polymeric Gemini surfactant vary by domain use, where the characteristics of the outbreak of polymeric or Gemini all on it, where can be used terminal carboxylic groups derived from ethylene di amine tetra acetic acid (EDTA), where the four terminal carboxylic groups can be converted into di anhydride (EDTA-DA) which most effective by the following equation (1-1)(Wattebled and Laschewsky, 2007; Maithufi, Joubert and Klumperman, 2011; Kumar and Tyagi, 2015; Jia *et al.*, 2019).



Equation(1-1):Synthesis of di anhydride (EDTA-DA)

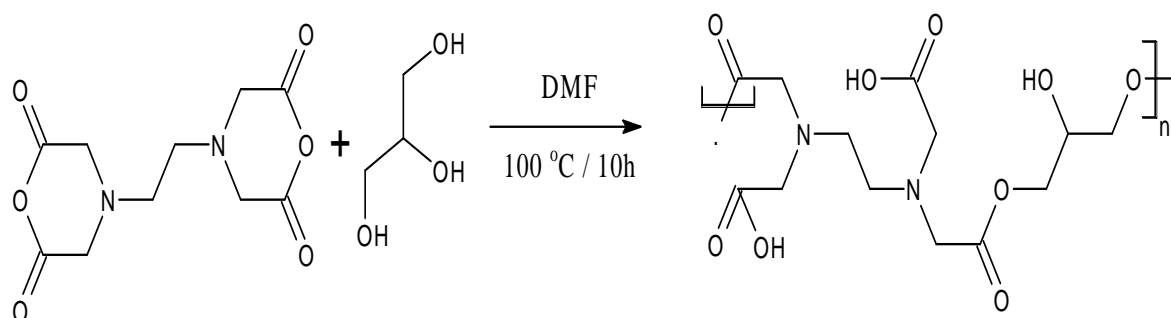
**2- Materials and methods**(Arsalani and Mousavi, 2003):

All materials Ethylene di amine tetra acetic acid EDTA, Acetic anhydride, Pyridine, Di ethylene tri amine, and [1,2-Bis(3-amino propyl amino)ethane]are highly successful. They were purchased from Sigma Aldrich and British Drug House (BDH).

**2-1 preparation of surfactant (F1):**

**Poly{[(2-((carboxymethyl)[2-(2,3-dihydroxypropoxy)-2-oxoethyl]amino)ethyl)(2-oxoethyl)amino]acetic acid}**

2g (0.0078 mole) from prepared (EDTA DA) put in two nick round expand (100 ml ), then a solvent (20 ml) of DMF added to thenick round.It was added 1.67ml (0.023 mole) from Glycerol after dilution it by 2ml DMF and 5ml of methanol.Reflex process was done at temperature 100C° for 10 hours as shown in figure (2-1). The reaction was followed by TLC technique, then the precipitate was filtered and washed with small amounts of ethanol in multiple batches, where a white powder was obtained and the product is weighted 1.75 g.

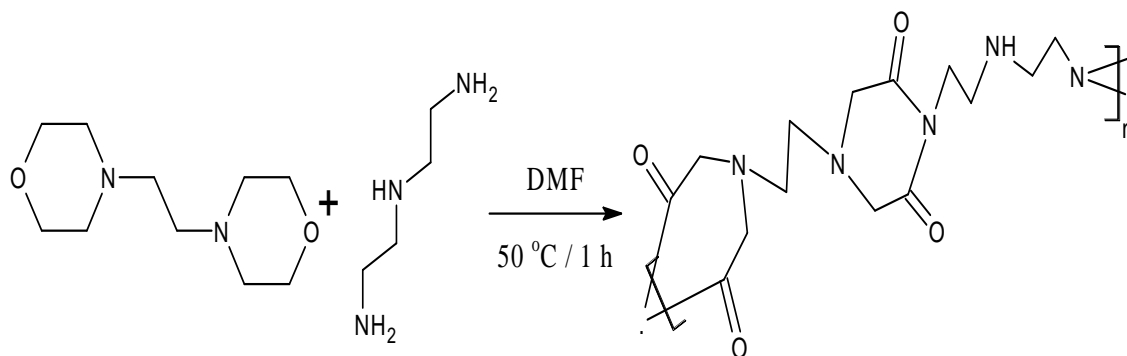


Equation(2-1):Synthesis of surfactant F1.

**2-2 preparation of polymer (F2):**

**poly(2,2'-{[2-(4-{2-[(2-aminoethyl)amino]ethyl)-3,5-dioxopiperazin-1-yl)ethyl]imino}diacetaldehyde)**

2g (0.0078 mole) from synthesized (EDTA DA) put in two nick round (100 ml), add it a solvent (20 ml) DMF then add 2.5 ml (0.023 mole) from [Di ethylene tri amine] after dilution it by 2ml DMF, then take the reflex process with temperature 50C° for 1 hour as shown in equation (2-2) where it is a light brown gelatin precipitate of high viscosity. Then the contents of the round were transferred to a 100 ml baker and the product was washed by ethanol and dried were the result weight is 5.30g.



Equation(2-2):Synthesis of surfactant F2.

Physical properties of synthesized polymeric materials (surfactants) can be placed in table (2-1)

Table (2-1) Physical properties of materials

Comp.	Reaction time	Reaction temperature	Yield %	Color	Physical body
F1	10 h	100 C°	91	Wight	Solid powder
F2	1 h	50 C°	95.6	Light brown	gelatine precipitate

### 2-3 Preparation of Demulsifier:

Two types of Demulsifier were prepared DF1 and DF2 by mixing with the ratio (20g:80ml), The division of this ratio to a smaller ratio was taken (0.2g:0.8ml), Taking (0.1g) of surfactant and (0.05g) of (Castrol oil or coconut oil) and (0.05g) of ammonium chloride and the components melted in toluene solvent and was mixed for making good laboratory Demulsifier.

### 2-4 Measuring the efficiency of the synthesized demulsifier:

Karl Fisher method was used to determine the efficiency of the synthesized demulsifier. Two test tubes 10 ml capacity of each one were taken. Put in 5ml of wet oil which was prepared in laboratory in each test tube. 0.02ml of prepared demulsifier was added to one of the two tested tubes while the second tube left without adding.

The samples are placed in water bath at the temperature (45C°), the volume of separated water was followed up on time (10 ,20 and 30) minute.

### 3- The results and discussion

This section shows the results and their discussion where FTIR was done to determine the composition of synthesis demulsifiers.

#### 3-1 FT-IR spectrum of polymeric demulsifiers

The infrared spectrum of the polymeric demulsifier (F1) gives (OH) carboxylic stretching band at (3322cm-1) and (OH) alcohol stretching band at (3550 cm-1) and two stretching bands for (C=O) ester at (1836 and 1744 cm-1) as shown in figure (3-1).

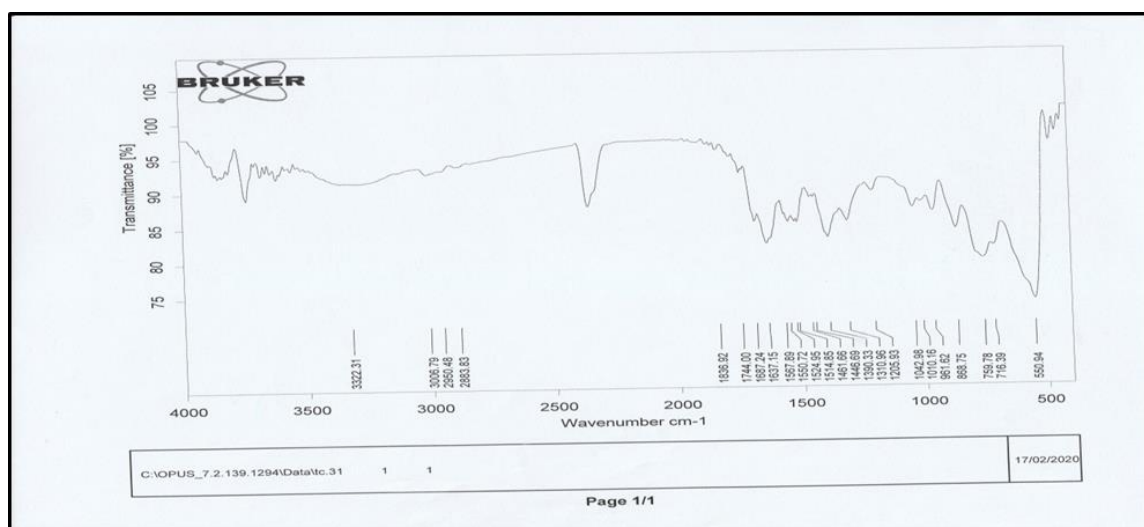


Figure (3-1) FT-IR spectrum of polymer (F1)

The infrared spectrum of the polymeric demulsifier (F2) gives (NH) secondary amine stretching band at (3238 cm-1) and (CH) cyclic stretching band at (3000 cm-1) and two stretching bands for (C=O) amide at (1662 and 1560cm-1) as shown in figure(3-2).

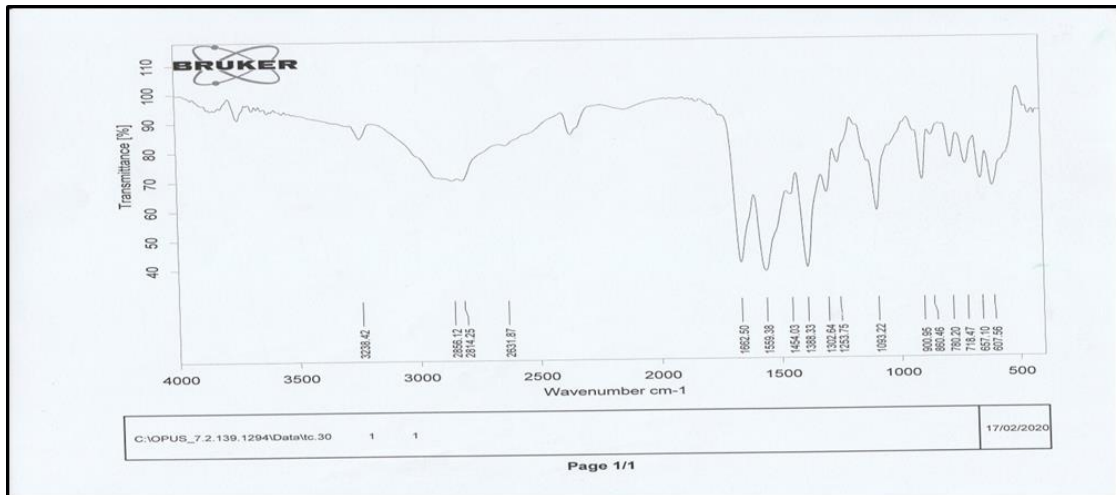


Figure (3-2) FT-IR spectrum of polymeric demulsifier (F2)

**3-2 Determine of viscosity average molecular weight ( $\bar{M}_v$ ):**

A series of solutions were prepared for each of polymers using water as solvent and measurement of the flow time for each it's, where the relative viscosity was calculated by the following equation:

$$\eta_r = t / t_0 \quad \text{----- (1)}$$

Where :

$\eta_r$  = relative viscosity,  $t$  = flow time of solution,  $t_0$  = flow time of solvent

Then calculated the specific viscosity by following equation

$$\eta_{sp} = t / t_0 - 1 = \eta_{r-1} \quad \text{----- (2)}$$

Where:  $\eta_{sp}$  = specific viscosity

Then calculated the reduced viscosity ( $\eta_{sp}/C$ ), Then the intrinsic viscosity value was extracted by drawing a graph between ( $\eta_{sp}/C$ ) with ( $C$ )

$$\eta_{sp}/C \quad \text{----- (3)}$$

Where :

$\eta$ = intrinsic viscosity, C= concentration (g/100ml)

Then a Mark&Houwink equation has been applied:

$$[\eta] = K \cdot \overline{M}_v^\alpha \quad \text{----- (4)}$$

Where :

$\overline{M}_v$ = viscosity average molecular weight.

K ,  $\alpha$  = The constants depend on the type of polymer and solvent and temperature.

Where the data included in the below table (3-1):

Polymers (surfactants)	Intrinsic viscosity ( $\eta$ ) Where $k=0.0002$ and $\alpha=0.76$	Viscosity average molecular weight( $\overline{M}_v$ )
F1	0.3	15103
F2	0.36	19197

### 3-3 Determine of CMC by conductivity method:

A different dilute concentrations was used of prepared surfactant (0.02-0.2g) and the values were recorded by electrical conductivity (G) for prepared solutions at (25C°) , the values were converted to the specific conductivity (L) through the relationship (5) and plot with the change in concentration and extraction of CMC from plot as shown in figures ((3) and (4)).

$$L=K G \quad \text{-----(5)}$$

Where :

L= specific conductivity. K=cell constant. G= electrical conductivity.

Where we note that the conductivity is changing linear with the concentration increasing because an increase in released amphiphilic number in the solution to



reach a critical micelles concentration point (CMC) . Then the change is big because of the increase in the number of free ions in the solution.

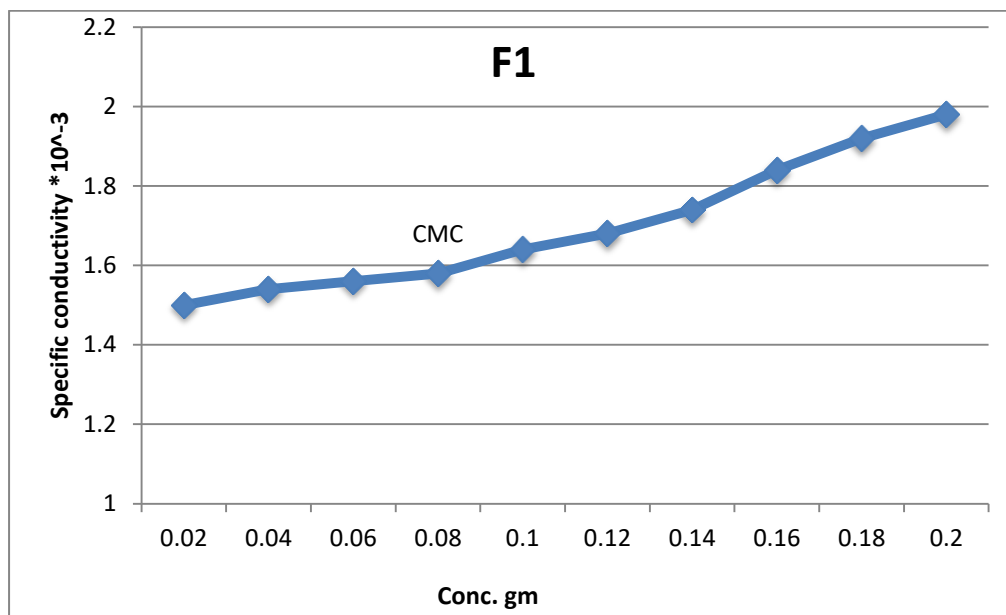


Figure (3) critical micelles concentration of surfactant (F1)

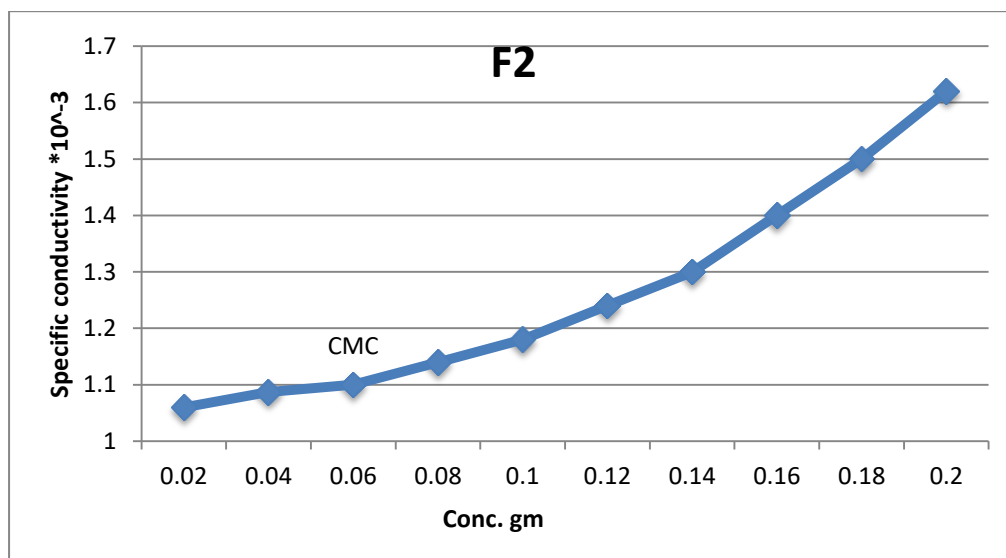


Figure (4) critical micelles concentration of surfactant (F2)

### 3-4 Prepared Demulsifiers:

Demulsifiers were prepared (DF1 and DF2) depending on pre-prepared surfactant (F1 and F2) respectively, Demulsifiers were prepared on the basis of combination and added reached by previous studies so that it is approaching to commercial Demulsifiers are (0.2g:0.8ml) were mixing (0.1g) of surfactant with

(0.05g) of heavy natural oil (castor oil) and (0.05) of ammonium chloride (NH<sub>4</sub>Cl) were added to (0.8ml) of toluene solvent .

Studied and evaluation the separation efficiency of prepared demulsifier materials on the wet crude oil and find out the effective quantity for the full separation process by setting the total content of water in wet crude oil. where the separation efficiency depends on the chemical structure and additions used , and study of the optimal conditions for separation operation of water from emulsion.

The results of the separation were compared with theoretical results for the commercial demulsifier (RP6000) was the importer for the same purpose.

**3-5 Separation efficiency of prepared demulsifier:**

This study has been by certified method , where the separation efficiency was measured by making time as a body vs. the size of separated water at concentration (50 , 100 ppm) and temperature is constant and calculated the percentage of separation (E%) by the following relationship .

$$E\% = V1_{(ml)} / V2_{(ml)} * 100 \quad \text{----- (6)}$$

Where :

E%= percentage of the separation

V1= size of separated water by prepared Demulsifier.

V2= size of separated water by commercial demulsifier (theoretical).

Table (3-2) size of water separation by prepared Demulsifiers at 50 ppm

<b>Time (min)</b>	<b>DF1 (V<sub>H2O</sub>)ml</b>	<b>DF2 (V<sub>H2O</sub>)ml</b>
<b>10</b>	0.5	0.6
<b>20</b>	0.8	0.9
<b>30</b>	1.2	1.3

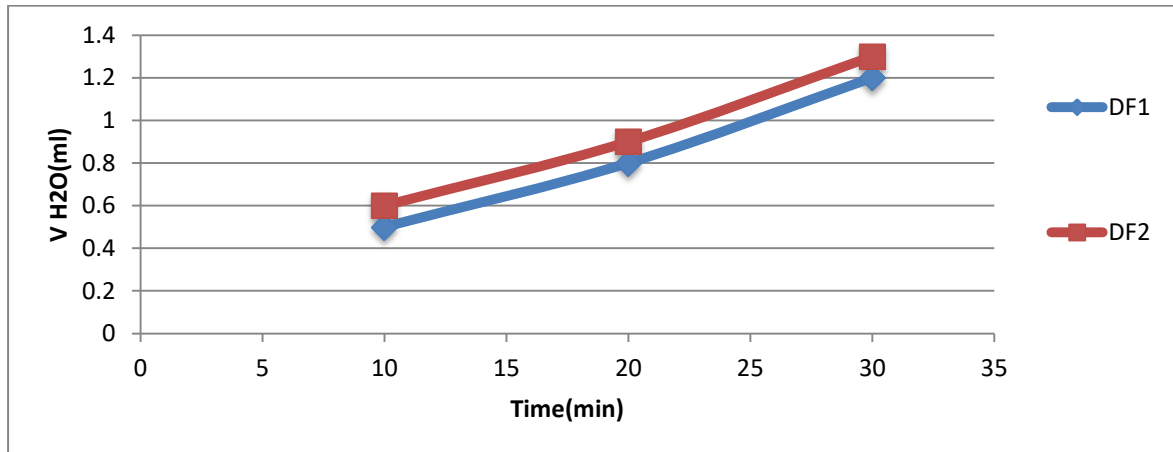


Figure (5) Size of water separation with time by prepared Demulsifier at 50 ppm

Table (3-3) Efficiency of separation by prepared Demulsifiers at 50 ppm

Time (min)	E% DF1	E% DF2
10	62.5	75
20	80	90
30	92.3	100

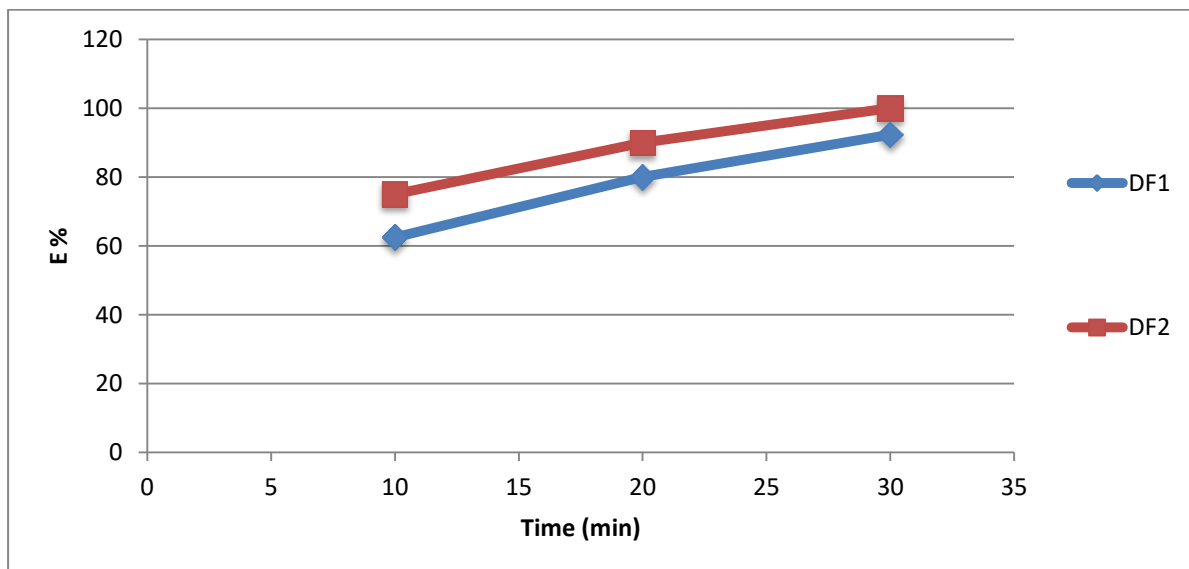


Figure (6) Efficiency of separation with time by prepared Demulsifier at 50 ppm

Table (3-4) size of water separation by prepared Demulsifiers at 100 ppm

Time (min)	DF1 (V <sub>H2O</sub> )ml	DF2 (V <sub>H2O</sub> )ml

<b>10</b>	0.7	0.8
<b>20</b>	1.0	1.2
<b>30</b>	1.3	1.5

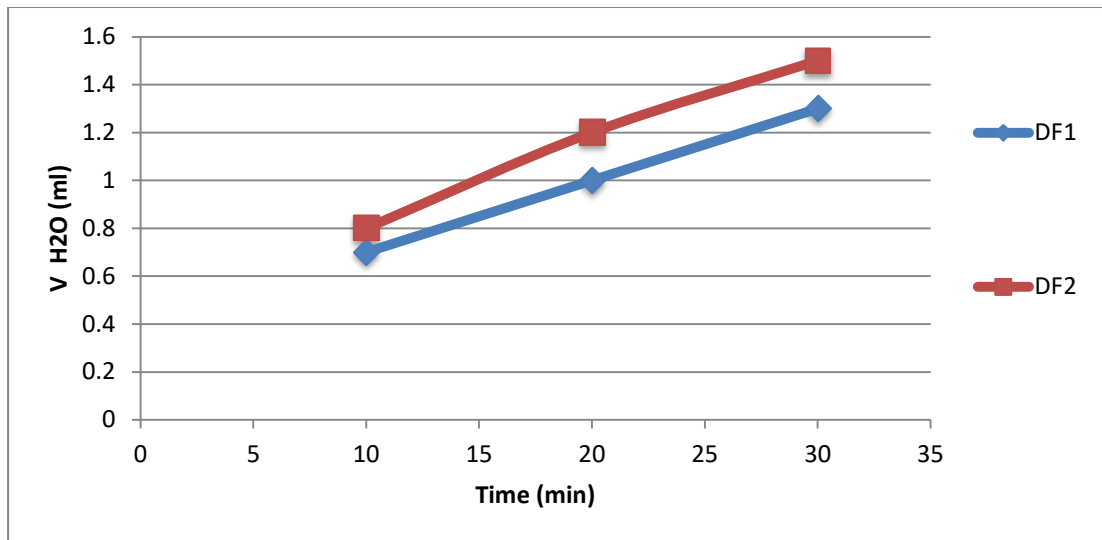


Figure (7) Size of water separation with time by prepared Demulsifier at 100 ppm

Table (3-5) Efficiency of separation by prepared Demulsifiers at 100 ppm

<b>Time (min)</b>	<b>E% DF1</b>	<b>E% DF2</b>
<b>10</b>	87.5	100
<b>20</b>	90.9	109.1
<b>30</b>	86.6	100

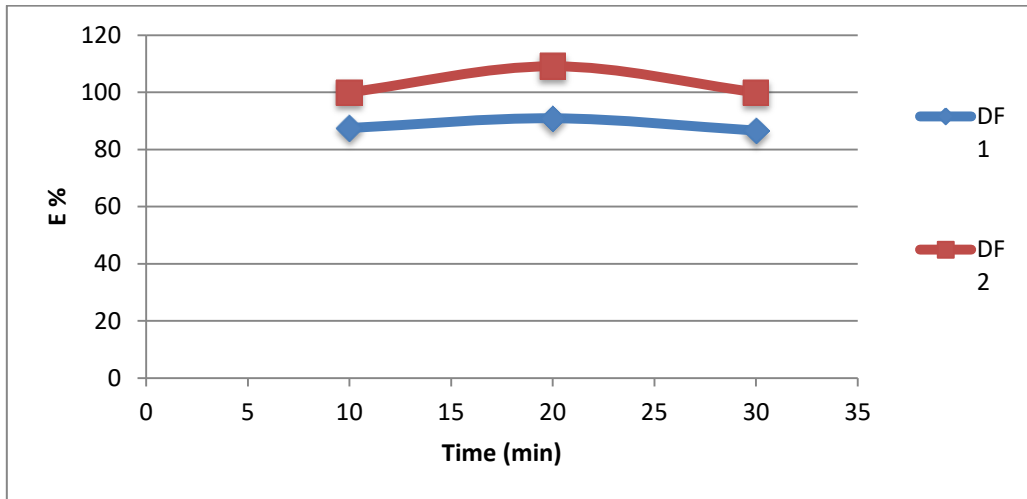
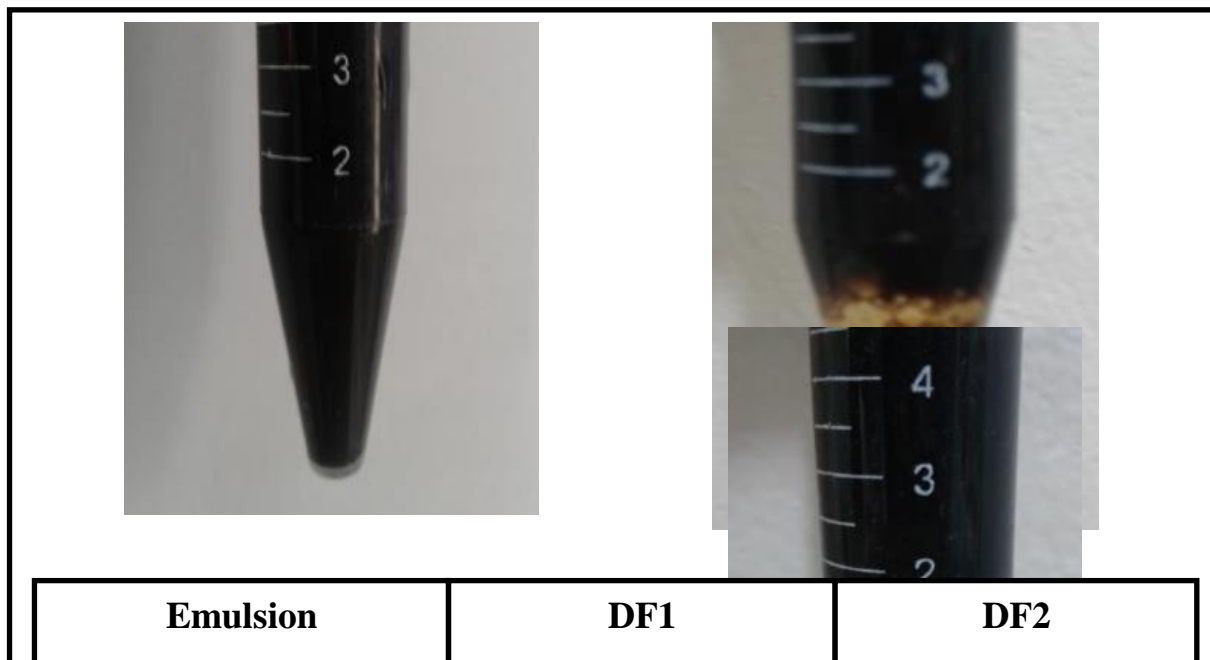


Figure (8) Efficiency of separation with time by prepared Demulsifier at 100 ppm



**13-Conclusion:**

- 1- The study showed the possibility of using polymeric gemini surfactant from (EDTA-DA with multi amine or multi alcohol compounds) polymerization by ring opening to produce very good demulsifier .
- 2- The study proved that the prepared demulsifier used less effect on crude oil properties compare with commercial demulsifier because its tend to milt more in water phase , Where it is disposed with water.

- 3- The study gave a high efficiency of the prepared Demulsifier in dealing with the problem of oil emulsion.
- 4- The prepared materials have a simple chemical composition in comparison with commercial products, this has a great economic return.

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