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Evaluation of the separation efficiency of synthetic polymeric demulsifier for crude oil

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Abstract

One of the major issues confronting the crude oil extraction process is the formation of various types of petroleum emulsions, particularly, water in crude oil emulsions (W/O) due to the presence of water and other natural products in crude oil. Natural product molecules help keep the water/oil interface stable and prevent water droplets from coalescing. In this paper, a polymeric Gemini surfactant was prepared as a demulsifier by condensation polymerization between phthalic anhydride and glycerol. In the laboratory, the physical characterizations of Nasiriya crude oil like water content, specific gravity, sulfur content, density, and viscosity were determined. The viscosity average molecular weight of the polymeric demulsifier was (2653 g/mol) when the constants ($k=0.0002$ and $\alpha=0.76$). The active groups of a synthetic polymer were identified using FT-IR spectra. The authors made a Critical Micelle Concentration (CMC) of the demulsifier. The conductivity of the demulsifier was linearly proportional to the concentration of the demulsifier. The hydrophilic– lipophilic balance (HLB) of polymeric demulsifier was 11.3, which can treat Oil in Water (O/W) emulsions. The different acidity measurements of the polymeric demulsifier were shown to be generally acidic. The best result of water separation from crude oil was at conditions (30 minutes, 100 ppm, PH = 3.9, and the best value of separation efficiency of the demulsifier was 60%.

Key words: Crude oil, Demulsifier, Polymeric Gemini surfactant, , Critical Micelles Concentration (CMC), Phthalic anhydride, Glycerol

1. Introduction

Crude oil is a complex mixture of organic compounds such as alkanes, cycloalkanes, various aromatic hydrocarbons, inorganic chemical compounds, water, and other impurities. It is becoming increasingly relevant in the industry, and obtaining more oil is becoming a challenge. Chemical methods to improve oil recovery are a hot topic for many oil companies looking to get more oil. Problems such as stable crude oil emulsion may occur due to the presence of surfactants, polymers, and natural emulsifiers such as resins and asphaltenes in its structure. The majority of the world's oil fields produce oil, frequently accompanied by necessary water. Many different types of emulsions may form in the same fluids during manufacturing. These emulsions can be oil in water (O/W), water in oil (W/O), or complex emulsions like oil in water in oil (O/W/O) or water in oil in water (W/O/W),

depending on the water, oil, energy in the flow, and oil to water ratios [1,2,3].

It is essential to consider how water and sediment stabilize water-in-oil emulsions to apply the best treatment possible. Creating an elastic or viscous film is the most common method for stabilizing petroleum emulsions. The surfactant effect of the demulsifier was to reduce the surface tensile polarity between these different materials. Demulsifiers are chemical compounds that describe amphiphilic molecules with two types of chemical characteristics, one polar group (head) and the other nonpolar group (tail). They used everything from essential soap to massive polymeric compounds. This is because a combination can break emulsions of hydrophilic and lipophilic molecules. Commercial demulsifiers can be divided into many groups depending on their chemical structure and applications. Three chemicals can be grouped: polymeric surfactants, nanoparticles, and ionic liquids [4,5,6,7]. Polymeric surfactants are

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macromolecules with both hydrophilic and hydrophobic parts. Amphiphilic polymers, micellar polymers, hydrophobically modified polymers, and associative polymers are among the macromolecules classified as polymeric surfactants in the literature [6].

Surfactants categorize according to how they dissociate in water, the most widely accepted and scientifically recognized method. They can divide into five classes: anionic, cationic, nonionic, zwitterionic (amphoteric), and Gemini polymer surfactants. The last one attracts growing attention in academic and industrial fields, consisting of two classical surfactant units joined by a spacer unit. However, according to many studies [2,8,9,10], the Gemini surfactant has been discovered to have many benefits, like superior solution qualities to standard surfactants, lower limiting surface tensions, improved wetting capabilities, and atypical aggregation

morphologies. These benefits make them particularly appealing for catalysis, adsorption uses, analytical separations, solubilization procedures, nanoscale technologies, biotechnology, increased oil recovery, paint additives, and a lower critical micelle concentration (CMC) [10,11,12].

This study treated the emulsion with a synthetic Polymeric Gemini surfactant, a chemical demulsifier. Depending on the field, it can be synthesized in various ways, where polymeric or Gemini outbreak characteristics are all over it, and where terminal carboxylic groups derived from phthalic anhydride can be used [13, 14].

The novelty of this paper is based on the polymer's solubility in water, which allows for the separation of water from crude oil, resulting in oil without water and a demulsifier. The second point is that synthetic polymers are accessible and have acceptable economic value.

Table 1 shows the physical properties of the Nasiriya crude oil used in this study.

Property	Standard methods	Nasiriya Crude oil
Specific Gravity at 60 F ⁰	ASTM D-287	0.8907
Density g/mL	ASTM D-287	0.8898
API	ASTM D-287	27.3
Sulfur content wt%	ASTM D-4294	3.7
Kinematic Viscosity cSt @70 F ⁰	ASTM D-445	47.33
Salt Content, lb/1000/brl	ASTM D-3230	2.5 ^{PTB} / 7.3 ^{PPM}
Water Content and sediment	ASTM D-4007	0.05

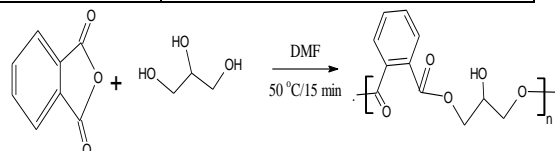
2. Materials and Methods

2-1 Materials

All of the materials have been extremely good. Phthalic anhydride, N, N-Di methyl formamide (DMF), ethanol, and glycerol purchased from Sigma Aldrich and British Drug House (BDH). The characteristics of crude oil from the Nasiriya refinery are tabulated in table 1.

2.2 Synthesis of surfactant poly (2,3-dihydroxypropyl 2-formylbenzoate)

One gram or 0.0067 moles of Phthalic anhydride placed in the round size (100 ml) of two nicks. The nick round received 20 ml of Dimethylformamide (DMF) solvent. The author added 0.977ml (0.0134mole) of glycerol after dilution by 2ml of DMF to the round. The reflux process was carried out at 30°C for 30 minutes. Following solvent evaporation, the final product was a colorless, viscous liquid. Surfactant synthesis can be shown in below scheme (1)



Scheme (1): Synthesis of a polymeric surfactant

2.3 Synthesis of demulsifier

A demulsifier is synthesized by mixing 0.05 grams of both castor oil and ammonium chloride with 0.1 grams of polymeric surfactant. The authors melted all the components in toluene solvent and mixed them.

2.4 Evaluating the demulsifier's efficacy

The efficiency of synthesized demulsifiers was determined using the Karl Fisher method. Two test tubes, each with a capacity of 10 mL, were used. Each test tube received 5ml of synthesized laboratory wet crude oil. One of the two test tubes had 0.2 mL of synthesized demulsifier applied, while the other was left empty. The samples are put in a 45°C water bath.

The amount of separated water was monitored for 10 minutes, 20 minutes, and 30 minutes [15, 16].

3. Results and Discussion

This section contains the results of the FTIR analysis used to determine the composition of the synthetic polymer and a discussion of the results.

3.1 IR spectrum of polymer

Table 2 and Figure 2 display the infrared spectrum of the polymer, which shows disappearance anhydride bands and a stretching band for (OH) alcohol at (3300 cm-1) and two stretching bands for (C=O) ester at (1658 and 1651 cm-1).

Table (2): FT-IR spectrum data of a polymeric surfactant

Comp.	ν OH acid cm ⁻¹	ν OH cohol cm ⁻¹	ν NH amine cm ⁻¹	ν NH amide cm ⁻¹	ν CH Ar. cm ⁻¹	ν CH Cyc. cm ⁻¹	ν CH Aliph. cm ⁻¹	ν C=O amide cm ⁻¹	ν C=O ester cm ⁻¹	ν C=O anhyd. cm ⁻¹	ν C=C Ar. cm ⁻¹	ν C-N cm ⁻¹	ν C-O cm ⁻¹
phol	-----	3300	-----	-----	3030	-----	2932	-----	1658 1651	-----	1598 1454	-----	1285 1030

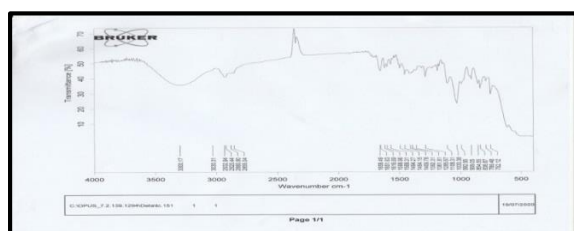


Figure (2) FT-IR spectrum of polymer

3.2 Determine the average molecular weight of viscosity (\overline{M}_v)

A series of solutions of polymeric surfactant were prepared using water as a solvent. The author measured the descent time for each solution. The intrinsic viscosity was measured using the Mark & Houwink method and the equations below [17]:

$$[\eta] = K \cdot \overline{M}_v^\alpha \dots\dots\dots 1$$

Where : η = intrinsic viscosity
 \overline{M}_v = the average molecular weight of viscosity (g/mol)
 K, α = The constants change depending on the polymer, solvent, and temperature.
 Where the (η) and (\overline{M}_v) is(0.08) and (2653 g/mol) respectively, when (k=0.0002 and α =0.76).

3.3 Determine Critical Micelles Concentration (CMC) by conductivity method

The prepared surfactant solutions (20–200) ppm at 25° were used in various dilute concentrations, and the values were recorded using electrical conductivity (G). The values were converted to specific conductivity (L) using the relationship (2), then plotted with changes in

concentration and CMC extracted from the plot as illustrated in Figure (3),Where:

$$L = K G \dots\dots\dots 2$$

L= specific conductivity (s/cm). K=cell constant (cm⁻¹). G= electrical conductivity (s).

As a result of an increase in the released amphiphilic number in the solution hitting a critical micelle concentration point (CMC) of 100 ppm, the conductivity changes linearly as the concentration increases. Then, the improvement is essential due to the rise in the number of free ions in the solution (15). The critical micelle concentration (CMC) is especially crucial to investigate because, at concentrations above this value, surfactant adsorption at the interface becomes minimal, suggesting that the optimal surface or interfacial tension reduction has been reached [18].

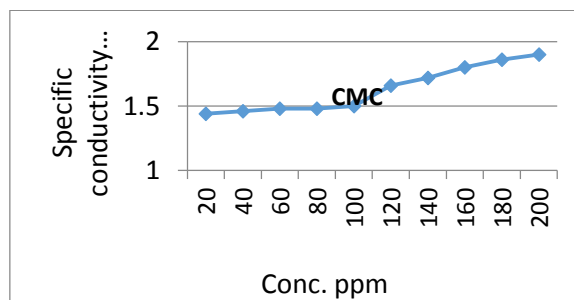


Figure (3): Critical Micelles Concentration of polymeric surfactant.

3.4 Determine the polymeric surfactant's hydrophilic-lipophilic balance (HLB).

The HLB method is beneficial for identifying surfactants based on their intended use. Nonionic

surfactants are used in a variety of applications within the HLB ranges mentioned in Table 3:

Table 3: Surfactant application based on HLB range [8,19]

HLB	Applications	
3.5-6	(W/O)emulsion	lipophilic ↑ ↓ 20
7-9	Wetting agents	
8-18	(O/W) emulsion	
13-15	Detergents	
15-18	Solubilization	

Hydrophilic-Lipophilic Balance (HLB) was calculated by acidity depending on the following equation.

$$HLB = 20(M.wt\ hydrophilic/M.wt\ hydrophobic) \dots 3$$

Where:

M.wt hydrophilic= The hydrophilic groups molecular weight.

M.wt hydrophobic= The hydrophobic groups molecular weight.

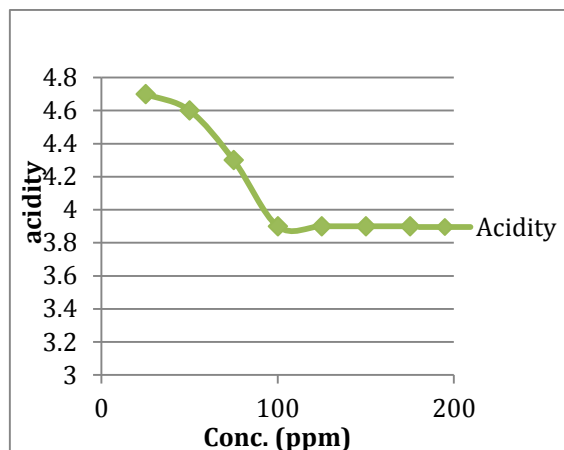
The calculated results of HLB are (11.3). This means it can be used as a demulsifier of (O/W) emulsion type, as shown in the above table (3).

3.5 Acidity measurements of polymeric surfactant

Several measurements by calibrated PH meter were made regarding the nature of the prepared demulsifier. These measurements showed that the polymer is generally acidic despite changes in concentrations, as shown in table (4) and figure (4). Experimental results show the acidity is directly proportional increased with the increase of the demulsifier concentration.

Table(4) shows the relation between the acidity and concentration of demulsifier

Conc. ppm	acidity
25	4.7
50	4.6
75	4.3
100	3.9
125	3.9
150	3.9
175	3.9



Figure(4): Relation between the concentration of polymer and acidity.

3.6 Separation efficacy of prepared demulsifier

Demulsifier separation efficiency of wet crude oil was investigated and evaluated. The chemical structure and additions are used to determine the separation quality. In this paper authors selected the best conditions for separating water from the emulsion. It is noted in the results of many studies that testing the effectiveness of emulsifying breakers is suitable for the first 30 minutes, and after that, the effectiveness is minimal [20,21]. This may be due to the reduction of the effectiveness of the chemical groups in the demulsifier [20]. Based on this, we found the maximum effective time of prepared demulsifier at 30 minutes.

We compared the results of water separation in this study with a commercial demulsifier type Chimec2439 for Basra oil, where water content was 20% [22]. The comparison results showed that the best results of the examination were under conditions (200, 300, and 400) ppm was (67, 77, and 83)% respectively.

The author calculated the separation efficiency by plotting time vs. the size of separated water at different concentrations (50, 100 ppm), as shown in the following table (5) and figure (5).

Table 5: shows the amount of water separated. by a demulsifier at 50,100 ppm.

Time (min)	(V _{H2O})ml at 50ppm	at	(V _{H2O})ml at 100ppm
10	0.2		0.3
20	0.4		0.6
30	0.7		0.9

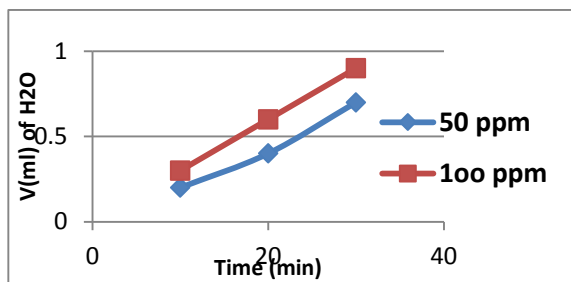


Figure (5): Water separation quantity by prepared demulsifier at 50,100 ppm

When compared to commercial demulsifier Chimec2439, the results of this investigation are promising, especially when considering the tiny dose of synthetic Gemini polymer (50 and 100 PPM) utilized and the short treatment duration (30 minutes).

The following relationship (3) was used to calculate the percentage of separation % at a constant temperature.

$$E\% = V1_{(ml)} / V2_{(ml)} * 100 \dots\dots\dots 4$$

Where :

E% : percentage of the water separation.

V1= volume of the water separation by prepared demulsifier.

V2= volume of separated water by commercial demulsifier.

The influence of the demulsifier on the water separation efficiency versus time is demonstrated in Fig (6) and Table (5) depicts a linear rise in water separation from crude oil. At concentration 100 ppm and time 30 minutes, the best separation value was 60%, while images (1) clearly show the demulsifier's effect on emulsion.

Numerous additional parameters, such as oil characteristics and temperature, that can affect demulsifier activity on crude oil were not addressed in this paper since they would take additional effort and time and could be studied in future work.

Table (5) separation efficiency of prepared demulsifier at 50,100 ppm

Time (min)	E% at 50ppm	E% at 100ppm
10	25	37.5
20	40	54.5
30	53.8	60

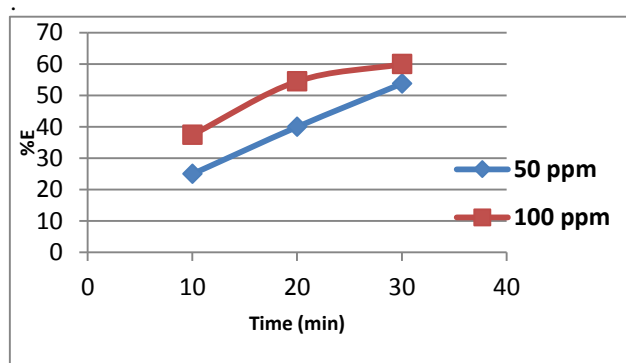
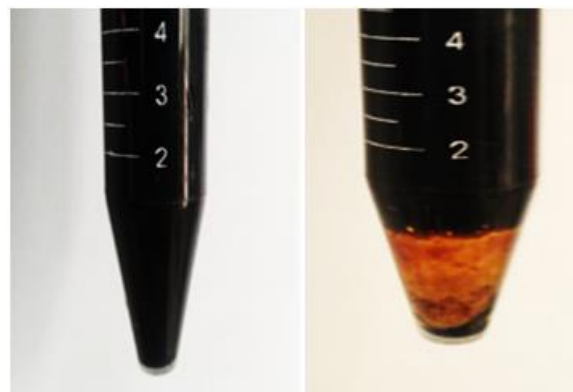


Figure (6) Separation efficiency of prepared demulsifier at 50,100 ppm.



Images 1: Represent A Emulsion, B crude oil after treating by demulsifier at conditions (100 PPM,30 min.).

4. Conclusion

The experimental results demonstrated the feasibility of using a synthesized demulsifier with a simple chemical structure and low cost of synthesis. One of the most critical properties of the synthesized demulsifier in this paper is its high water solubility. This property allows it to easily be removed with wastewater during the demulsification process of emulsions.

5. Conflicts of interest

There are no conflicts to declare.

6. Acknowledgment

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