Synthesis and evaluation of demulsifier in crude oil treatment

Conference Paper · January 2022

DOI: 10.1063/5.0091943

2 authors:

Ali Ali
University of Thi-Qar
14 PUBLICATIONS **11** CITATIONS
SEE PROFILE

Ali Abdulhakeem Naghmash
University of Basrah
4 PUBLICATIONS **6** CITATIONS
SEE PROFILE

Synthesis and evaluation of demulsifier in crude oil treatment

Cite as: AIP Conference Proceedings **2443**, 030040 (2022); https://doi.org/10.1063/5.0091943
Published Online: 11 July 2022

Ali Abdulkhabeer Ali and Ali Abdulhakeem Naghmash

Synthesis and Evaluation of Demulsifier in Crude Oil Treatment

Ali Abdulkhabeer Ali[1 a)], Ali Abdulhakeem Naghmash[2 b)]

[1] *Chemistry department, college of science / marshes research center, University of Thi-Qar, Thi-Qar governorate, Iraq*
[2] *Chemistry department, college of science, University of Basra, Basra governorate, Iraq*

[a)] Corresponding author: aranru79@utq.edu.iq
[b)] alihakeem222111@gmail.com

Abstract The aim of this paper is to create a new polymeric Gemini surfactant as a demulsifier was synthesized in this paper. It was used to break the emulsion type w/o which has two parts, one of which is polar (water) and the other nonpolar (crude oil). Ring opening polymerization method used to prepare demulsifier by the reaction between Phthalic anhydride and 1,2-Bis(3-amino propyl amino) ethane. Physical properties of Nasiriya crude such as specific gravity, density, viscosity, water content and sediment and sulfur content have been performed in the laboratory. FT-IR spectra was measured for the diagnosis of active groups in the polymer, viscosity average molecular weight ($\overline{Mv}$) of polymer was 3558 at k=0.0002 and α=0.76. Critical Micelles Concentration (CMC) of polymer was determined by conductivity method. The conductivity of synthetic polymer is found linearly proportional to the increase in the concentration of polymer. Thermal stability analysis of synthesized polymer (TGA and DTA curves) showed that polymer has high thermal stability. Karl Fisher method was used to determine the best value for separating water from crude oil was 73.3% at 100 ppm after 30 minutes.

INTRODUCTION

Generally, crude oil's physical and chemical properties are influenced by impurities. These impurities like asphalt, resin, water, waxes and naphthenic acids can accumulate at the interface between crude oil and water [1,2]. These components have the potential to trigger emulsions, which is a major problem in the crude oil industry. Water in oil W/O and oil in water O/W emulsions are the two types of emulsions. The first is commonly produced during the extraction of crude oil. So, for oil pipeline flow and refinery processes, oil free of impurities, especially water, is required.. Demulsifiers can be defined chemically as amphiphilic chemical molecules with two types of chemical features, one polar and the other nonpolar. A polar party represents the head, while a nonpolar party represents the tail [3,4]. Demulsification is a method of removing emulsions from crude oil by using chemical demulsifiers to reduce the stability of the thin film rate between two immiscible liquids. Chemical demulsifiers' primary function has been determined to be changing interfacial rheological characterizations and destabilizing the stability of surfactant emulsion thin films. Polymeric demulsifiers use the concept of adsorption at the oil-water interface to displace the interfacial thin film formed between the oil and water interface. Chemical demulsifiers include polymeric Gemini surfactants. It can be prepared in a variety of ways, depending on the intended use[5,6,7] .

Castor oil was used in this project as a heavy oil. It is a high-density natural oil with numerous benefits, including the ability to prevent ignition and ensure the safety of storage and transportation, as well as an effect on increased flow and viscosity of demulsifiers, improved separation performance, and increased linkage with crude oil [8,9].

Proceedings of the 2nd International Conference on Petroleum Technology and Petrochemicals - 2021
AIP Conf. Proc. 2443, 030040-1–030040-7; https://doi.org/10.1063/5.0091943
Published by AIP Publishing. 978-0-7354-4344-0/$30.00

MATERIAL AND METHODS

All experiments were done with Nasiriya crude oil as shown in (Table 1).

TABLE 1. physical properties of Nasiriya crude oil used in this paper

Property	Standard methods	Nasiriya Crude oil
Specific Gravity at 60 F^0	ASTM D-287	0.8972
Density	ASTM D-287	0.8975
API	ASTM D-287	26.2
Sulfur content wt%	ASTM D-4294	4.1
Kinematic Viscosity cSt @70 F^0	ASTM D-445	47.33
Water Content and sediment	ASTM D-4007	0.05

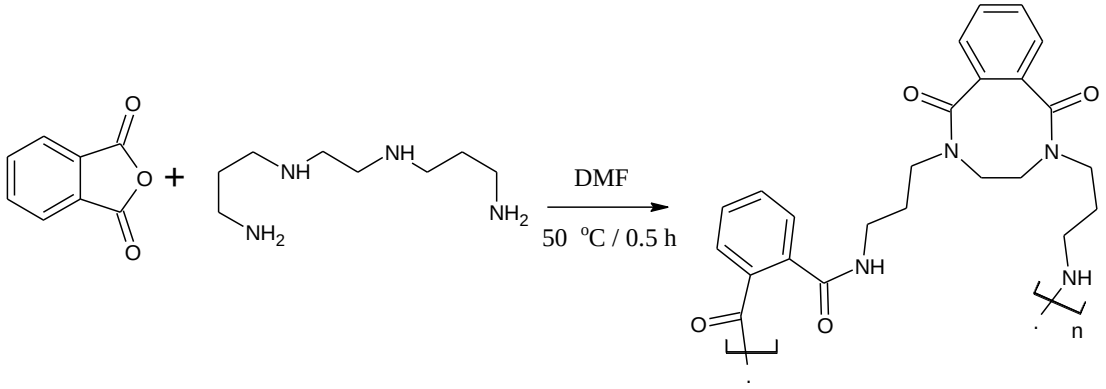
All chemical materials Phthalic anhydride, N,N-Di methyl form amide(DMF), ethanol, [1,2-Bis(3-amino propyl amino)ethane]are very successful, they were purchased from British Drug House (BDH) and Sigma Aldrich.

Wet crude oil preparation

Water in crude oil emulsion had been prepared by adding distilled water 15 vol% to crude oil 85% with mixing by mechanical mixture for two hours at 30 C^0 [10].

Preparation of poly{N-[3-({2-[(3-aminopropyl)amino]ethyl}amino)propyl]-2-formyl benzamide}

0.0067 mole (1g) of Phthalic anhydride was putting in two nicks round size (100) ml. (20) ml of DMF solvent was added to the nick round. (1.44) ml (0.0134) mole of diluted [1,2-Bis(3-amino propyl amino)ethane] by 2ml DMF was added as shown in scheme (1). Reflex process was completed at temperature 50C° for 30 min. Light brown gelatin precipitate of high viscosity was got. The contents in the round were transferred to a 100 ml baker. The obtained product was 3.075 g. after washing it by ethanol and drying process. Physical properties of the final product is shown in the table (2).



SCHEME 1. Synthesis of polymeric surfactant.

TABLE 2 Physical properties of polymeric demulsifier

Reaction time	Reaction temperature	Yield %	color	Physical body
0.5 hour	50 C°	90.7	Light brown	gelatin precipitate

Demulsifier preparation

Demulsifier was prepared by mixing (0.1g) of surfactant, (0.05g) of Castrol oil and 0.05g of ammonium chloride, which was used to make the water phase more polar. The components was disolved in toluene solvent . The mixture was stirrered mechnicaly in the lab for 30 min at 35C^0[11,12].

Evaluation of the demulsifier efficiency

The efficiency of synthesized demulsifier was determined by Karl Fisher method. Two test tubes of (10) ml capacity were taken. (5) ml of prepared laboratary wet crude oil was put in each test tube. (0.02) ml of synthesized demulsifier was added to one of the two test tubes, while the second tube left without adding. The samples were placed in water bath at temperature (45)C°. The separated water volume was followed up on time (10 ,20 and 30) minute [13,14].

The results and discussion

This section shows the results and their discussion. FTIR spectrum was done to determine the composition of the synthesized demulsifier.

FT-IR spectrum of polymeric surfactant

Diagnosis of the demulsifier composition by FTIR spectrum showed disappearance amine bands and appearance a (NH) amide stretching band at (3293 cm^{-1}) and two stretching bands for (C=O) amide at (1654 and 1603 cm^{-1}) as shown in figure (1) and table (3).

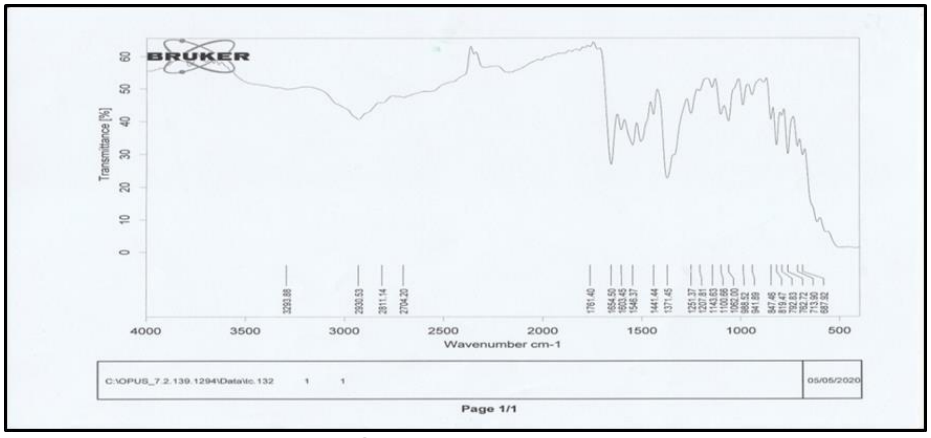


FIGURE 1. FTIR spectrum

TABLE 3. FT-IR spectrum of polymeric surfactant

υNH amide cm^{-1}	**υCH Ar. cm^{-1}**	**υCH Aliph. cm^{-1}**	**υC=O amide cm^{-1}**	υC=C Ar. cm-1	**υC-N cm^{-1}**
3293	3005	2811	1654	1546	1371
			1603	1490	1251

Measurement of viscosity average molecular weight ($\overline{Mv}$)

Numbers of polymeric surfactant solutions were prepared using water as solvent and also as measure of the flow time for each one. Mark&Houwink method was used to calculate the intrinsic viscosity according to the following equation:

$$\eta = K * \overline{Mv}^{\alpha} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where : η= intrinsic viscosity

$\overline{Mv}$= average molecular weight viscosity.

K , α = The constants depend on the type of polymer, solvent and temperature.

Where the $\overline{Mv}$ is 3558 when (k=0.0002 and α=0.76)

Determine of CMC by conductivity method

A different dilute concentrations (20-200)ppm of prepared surfactant were used. The values of prepared surfactant solutions were recorded by electrical conductivity (G) at (25)C°.

The specific conductivity (L) obtained by converting these values by the relationship (2). Critical micelles concentration CMC of surfactant obtained from the plot with the change in concentration as shown in figure (2).

$$L = K * G \text{.....(2)}$$

Where :K=cell constant.

Its noted that the conductivity is changing linearly with increasing in the concentration due to an increase in released amphiphilic number in the solution to reach a critical micelles concentration point (CMC) at (100ppm) . Then the change become large because of the increasing in the number of free ions in the solution.

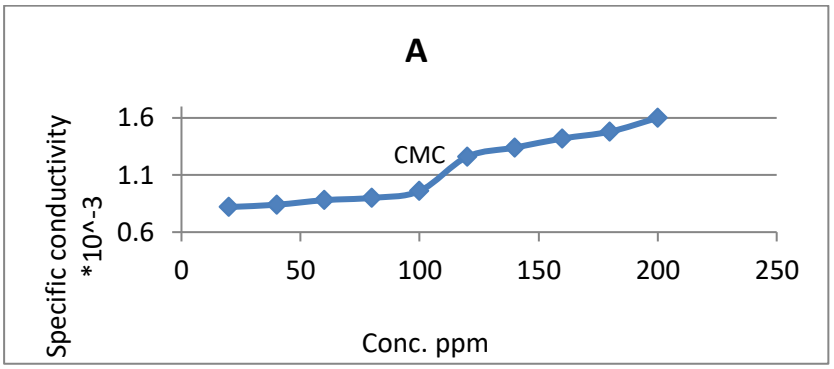


FIGURE 2. critical micelles concentration of surfactant

Thermal stability by weight analysis to polymer

Thermo gravimetric analysis of polymer were done as shown in figure (3). TGA and DTA curves show the losing weight according to the different temperatures. First stage, loss in weight was maximum(37.7%) at temperature (<292.2C°), while in the second stage was maximum loss in weight (7.5%) at temperature (292.2-426.7C°). DTA curve showed weak peak at (352.7C°) and a strong peak at (256.9C°). This explains that the polymer has a high thermal stability [15,16].

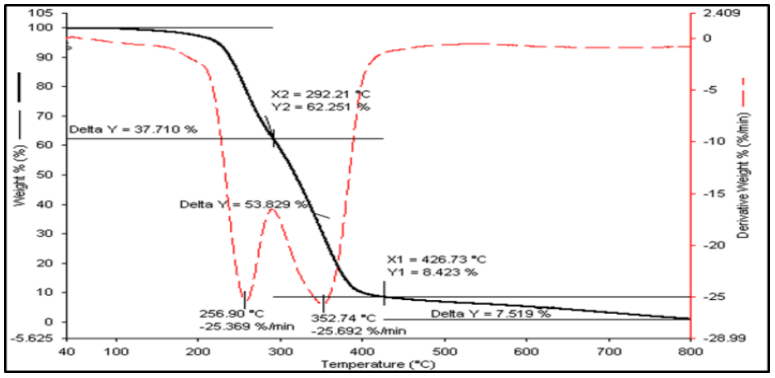


FIGURE 3. TGA and DTA curves of polymer.

Assessment of water Separation efficiency of prepared demulsifier

Efficiency of water separation of prepared demulsifier was Studied and evaluation. The demulsification experiments were achieved in 10 mL test tubes. All filled with the crude oil and water emulsion (w/o emulsion). In each test tube, the demulsifier was added and mixed (3 minute). The gravity separation (GS) of the water phase from the crude oil was permitted to occur. The temperature of test was kept constant at 45 C0 by using a temperature controller in water bath[6]. The doses of demulsifier were 50 and 100 PMM versus time (10, 20 and 30)minute as shown in table (4), while the efficiency of separation was listed in table (5).
The separation percentage (E%) was calculated at constant temperature by the following relationship [13].

$$E\% = \frac{V1(ml)}{V2(ml)} * 100 \quad \text{.....(3)}$$

Where : E%= Percentage of the separation
V1= Volume of the separated water by synthesized demulsifier in this paper.
V2= Volume of the separated water by commercial demulsifier (theoretical).

The effect of demulsifier on the efficiency of water separation over time is illustrated in Figs. 4 and as shown in image (1). Fig. 4 shows linearly an increase in separation of water from crude oil. The best value of separation recorded 73.3% at 100 ppm after 30 min. The separation efficiency of demulsifier back to the activity groups on the long hydrocarbon chain especially, in the terminal carboxylic groups derived from phthalic anhydride in Polymeric Gemini.

TABLE 4. Volume of water separation by prepared demulsifier at (50 , 100)ppm

Time (min)	Demulsifier (V_{H2O})ml at 50 ppm	Demulsifier (V_{H2O})ml at 100 ppm
10	0.2	0.4
20	0.7	0.8
30	0.9	1.1

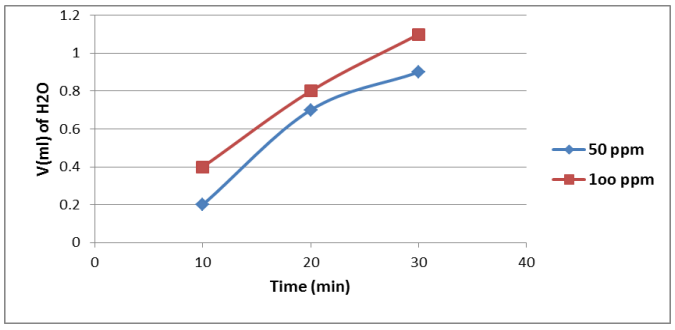
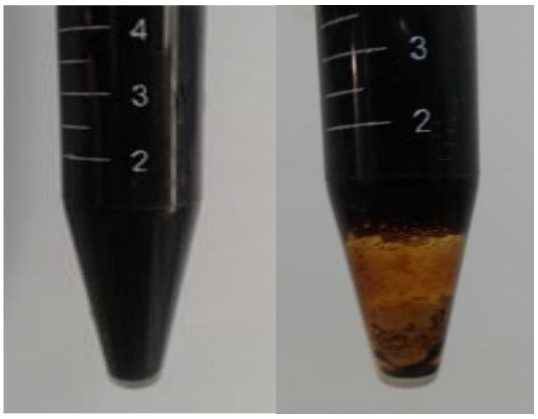


FIGURE 4. Volume of water separation by adding demulsifier at (50,100) ppm

TABLE 5. Efficiency of separation by adding demulsifier at (50,100) ppm

Time (min)	E% Demulsifier at 50ppm	E% Demulsifier at 100ppm
10	25	50
20	70	72.7
30	69.2	73.3



Emulsion of crude of (W/O)

Separation of water by adding demulsifier (100 ppm at 30min)

IMAGE 1. Shows the efficiency process of demulsifier with crude oil.

CONCLUTION

Experimental results of this study showed the possibility of using synthesized demulsifier (polymeric gemini surfactant) which has a simple chemical composition as a good demulsifier with low cost of preparation. High solubility in water is one of the important properties of synthesized demulsifier that is meen it can be easly removal with waste water during the breaking process of crude oil emulsions. Synthesized demulsifier can be worked in large range of temperature according to its high thermal stablity.

ACKNOLODGEMENT

The authors are grateful to the Marshes Research Center at the University of Thi-Qar for providing a laboratory and some equipment.

REFERENCES

1. Biniaz P, Farsi M, Rahimpour MR. *Demulsification of water in oil emulsion using ionic liquids: Statistical modeling and optimization,* Fuel **184**, 325–333(2016).
2. Roostaie T, Farsi M, Rahimpour MR, Biniaz P. *Performance of biodegradable cellulose based agents for demulsification of crude oil: Dehydration capacity and rate*. Sep Purif Technol 1-28(2017).

3. Wang C, Fang S, Duan M, Xiong Y, Ma Y, Chen W. *Synthesis and evaluation of demulsifiers with polyethyleneimine as accepter for treating crude oil emulsions*. Polym Adv Technol 26 **5** 442–448 (2015).
4. Li Z, Geng H, Wang X, Jing B, Liu Y, Tan Y. *Noval tannic acid-based polyether as an effective demulsifier for water-in-aging crude oil emulsions*. Chem Eng J. **354**, 1110–1119 (2018).
5. A.M. Al-Sabagh et al. S*ynthesis and evaluation of some polymeric surfactants for treating crude oil -part 11destablization of Nuturally occurring waterin in oil emulsions by polyalkylphenol formaldehyde amine resins.* Polym. Adv. technol. **13**, 346-352 (2002).
6. Ojinnaka CM, Ajienka JA, Abayeh OJ, Osuji LC, Duru RU. *Formulation of best-fit hydrophile/lipophile balance-dielectric permittivity demulsifiers for treatment of crude oil emulsions.* Egypt J Pet. **25** (4**)** 565–574 (2016).
7. Ali Abdul Hakeem Naghmash and Ali Abdulkhabeer Ali. *Evaluation of the effectiveness of synthesized polymeric demulsifiers in the petroleum sector*. solid state technology **63** (**2)** 1294-1307 (2020).
8. Alves, R. S., Maia, D. L., Fernandes, F. A., Feitosa, F. X., & de Sant'Ana, H. B. *Synthesis and application of castor oil maleate and castor oil maleate-styrene copolymers as demulsifier for water-in-oil emulsions.* Fuel, **269** (2020).
9. Haneen Abdul Wahid Dwesh and Ali Abdulkhabeer Ali *Synthesis of some amides based on oils extracted from castor and linseed seeds, and investigating their anticorrosion, anti-emulsification and activities anti-bacterial*, thesis, University of Thi-Qar-Iraq (2020).
10. Georgius A. Adem, Zaydoon K. Kreamid.P*reparation of Demulsifier of Gemini Surfactant and its application in oil Industry* 86 30-36 (2010).
11. Chen, D., Li, F., Gao, Y., & Yang, M.. Pilot *performance of chemical demulsifier on the demulsification of produced water from polymer/surfactant flooding in the Xinjiang oilfield.* Water, **10** (12**)** 1-9 (2018).
12. Radziuk D, Möhwald H. Ultrasonically treated liquid interfaces for progress in cleaning and separation processes. Phys Chem Chem Phys **18** (10**)** 21–46. (2016).
13. Zolfaghari R,e.t al A. *Demulsification techniques of water-in-oil and oil-in-water emulsions in petroleum industry*. Sep Purif Technol **170**, 377–407 (2016).
14. Bi Y, Tan Z, et al. *The demulsification properties of cationic hyperbranched polyamidoamines for polymer flooding emulsions and microemulsions.* Processes , **8**, (176**)** 1-12 (2020).
15 Al-Taweel SS, et al. *The influence of titanium dioxide nanofiller ratio on morphology and surface properties of* TiO_2 */chitosan nanocomposite. Results Phys.* https://doi.org/10.1016/j.rinp.2019.102296.10229, (2019).
16. Waheeb AS, et al. *Myristica fragrans Shells as Potential Low Cost Bio-Adsorbent for the Efficient Removal of Rose Bengal from Aqueous Solution: Characteristic and Kinetic Study*. Indones J Chem. **20 (**5**)** 1152 (2020).