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Synthesis and Evaluation of Local De-emulsifiers with Field Assessment in Iraqi Oil Fields

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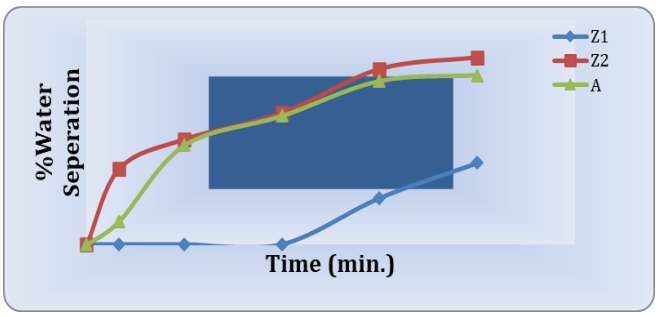
ABSTRACT

De-emulsifiers are one of the important industrial additives used commonly in petroleum industry in order to separate the salt water from crude oil essential the wet crude oil fields in south oil company (B.O.C) in Iraqi fields. De-emulsifiers activities due to the ability of these additives for breaking the thin film between dispersed phase and continuous phase globules in order to obtain two immiscible phase via the adsorption mechanism of the surfactants. In the present study has prepared local demulsifies by synthesis Gemini surfactants bis (Quaternary ammonium salt). The local de-emulsifier was assess in the laboratories of South Oil Company (B.O.C) Comparison with the results of commercial de-emulsifier (A), where the local material efficiency was higher than the important commercial (A) adopted in the B.O.C by bottle Test and later was produced (26) barrels of material prepared and evaluated in AL-SHAMIA Degassing station in Iraqi South Rumaila in (B.O.C). Where, evaluated the local de-emulsifier in the fields and show the positive results, this describes the evaluation of field emulsifying the local material in this study with lost cost of preparation of a one barrel about 500$ in the time that the cost of one barrel of commercial de-emulsifier is 1000$. The assessment was in the conditions of commercial de-emulsifier, depending on the natural of Dehydrator and Desalter in addition of the effective Dose is 25ppm and by 100% separation efficiency in same fresh oil source. The efficiency of local de-emulsifier studied Varity of parameters like: Temperature and the time required to separation function of the Dose. The field evaluation conditions of local de-emulsifier were under control outside of the oils (fresh) of D_2 (Desalter) of isolation units to examine all of the water and salt content of crude oil. This was prepared for export according to the approved evaluation criteria compared with the commercial de-emulsifier imported and used in the oil sector.

GRAPHICAL ABSTRACT



the separation efficiency of de-emulsifiers Z_1&Z_2 compare with commercial de-emulsifier (A) with time at 50°C on south Rumaila Crude oil emulsion treatment in S.O.C Lab

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Introduction

Water in oil emulsion are often observed in oil production, The emulsion stability results from the presence of interfacial barrier preventing coalescence of the dispersed water droplets. This is due to the present of polar components such as asphaltenes, resins, wax and naphthenic acids in the crude oil. Therefore before transporting or refining the oil, it is essential to separate the water for economic and operational reasons [1].

The formation of water-in- oil (w/o) emulsions is a critical issue in industrial applications such as the petroleum sector. In fact, emulsified water can corrode refinery equipment and the water-dissolved salts can poison catalysts in downstream processing facilities [2].

Emulsions can be destabilized by thermal, mechanical, electrical, and chemical methods. The application of chemical demulsifiers is one of the most common strategies applied for resolving w/o emulsions, and it involves the use of amphiphilic molecules which, thanks to their interfacial activity, accelerate the interfacial film rupture, thus promoting the flocculation and coalescence of the water droplets. The main advantage of chemical demulsification relies on the possibility of its easy integration into already existing w/o separation units without the need of equipment shutdown and with relatively small capital costs [3].

The emulsion may contain water cut is about (20-40%) in Iraqi oil reservoir and frequently extremely stable due to the presence in the emulsion of a variety of emulsifiers such as asphaltenes. Iraqi south oil company B.O.C consumption of the commercial de-emulsifiers is between (1200-1500) barrel/month [4].

In this study were prepared Gemini surfactants and selection because of its ability to double in reducing the surface tension due to have two lipophilic chain and two hydrophilic groups from of activated two molecules (Dimeric surfactants) make it the ability to reduce the critical micellization concentration (C.M.C) and the formation of two phases may not be miscible, as is the case in the compounds prepared in the search [5, 6].

The field evaluation depending on the dose used the measured equation (1):

$$Dose = \frac{spent\ \frac{1}{h} \times 1000\ \frac{mil}{l}}{Production\ Capicity\ \frac{m^3}{h}} \qquad (1)$$

Where, the production capacity of AL SHAMIA station was 45000 barrels/day.

The specification of crude oil outside after the treatment by use the prepared local de-emulsifier

- Water content = trace.
- Salt content = 8.2 ptb {ptb(pond/1000 barrel)}.

While the specification of crude oil outside after treatment by used of commercial de-emulsifier is:

Water content = trace.

Salt content = 11.9 ptb.

Material and methods

Material: fresh crude oil from North Rumaila field and South Rumaila field (Quarinat & Shamia) station for field evaluation.

Material evaluation: laboratory-prepared materials of local de-emulsifier leading to barrel of this material.

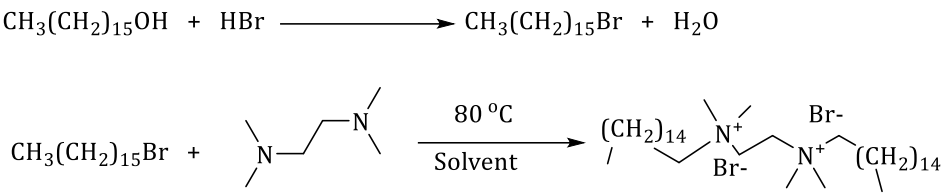
Preparation and characterization of Local De-emulsifier:

Bis-quaternary ammonium salt was prepared in two naked round bottomed flask fitted with separating funnel and condenser. A solution of 1 mole of tetramethylethylenediamine (TMEDA) and 2 mole of cetyl bromide was added drop wise by the separating funnel for 60 min at 50 °C. After the addition, it was completed.

The temperature rise to 80 °C and the reaction was continues for 24 hours. The solvent then evaporated by rotary evaporator. The product is a white solid material, which was dried and the re-crystallized with a mixture of hexane and ethanol (1:1).

The product is soluble in water, xylene and toluene. The yield is 67.5%, with chemical structure $C_{38}H_{82}N_2Br_2$.

The prepared bis(quaternary ammonium) add to one of poly oxy ethylene derivatives and prepare new formula by added suitable solvent and other additives to produce (Z1 & Z2) according to the modification of ratio of ingredients.



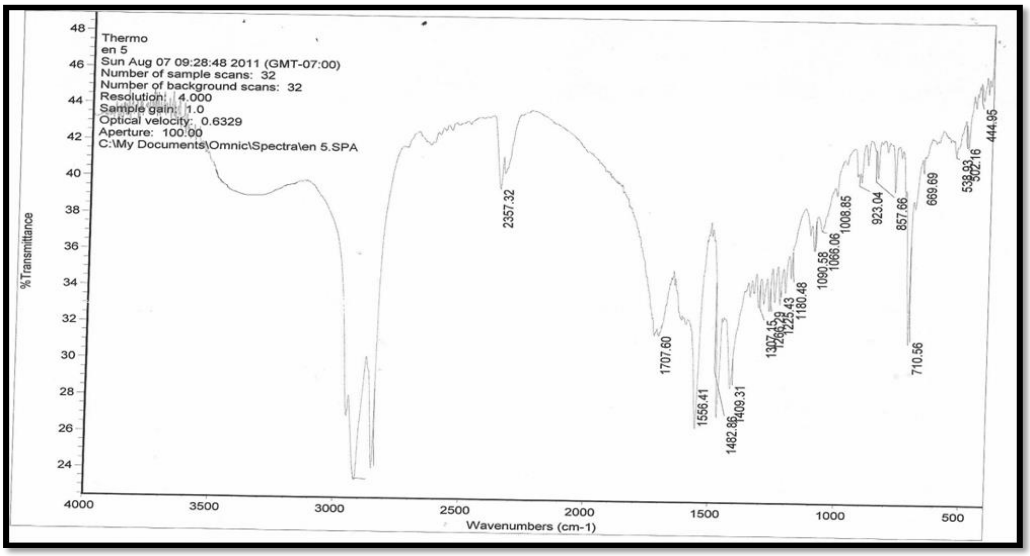


Figure 1: FT-IR of synthesized bis quaternart ammonium salt

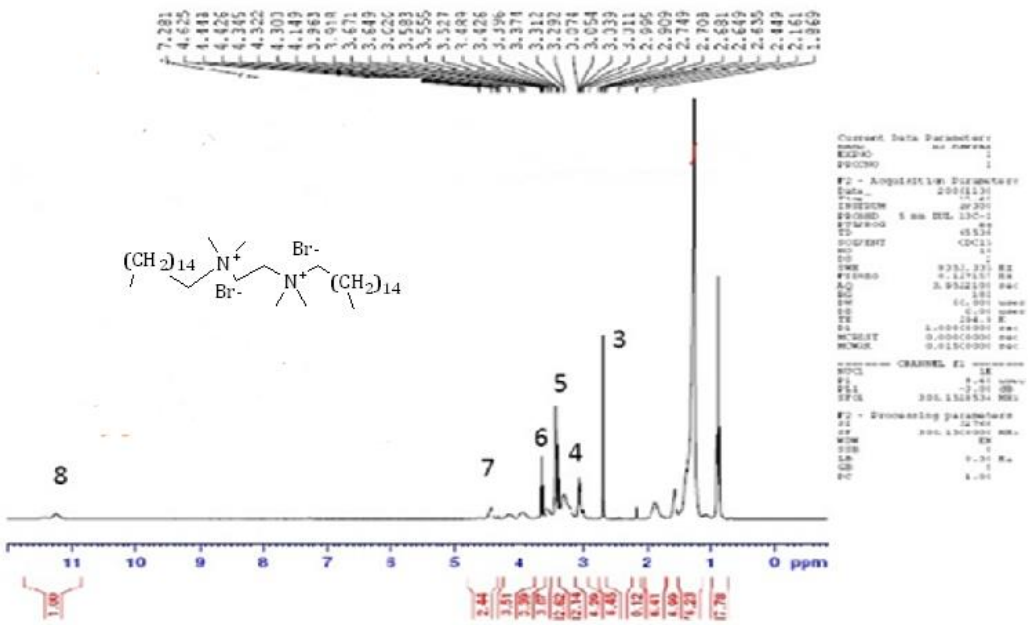


Figure 2: ^{1}H-NMR of synthesized bis quaternary ammonium salt

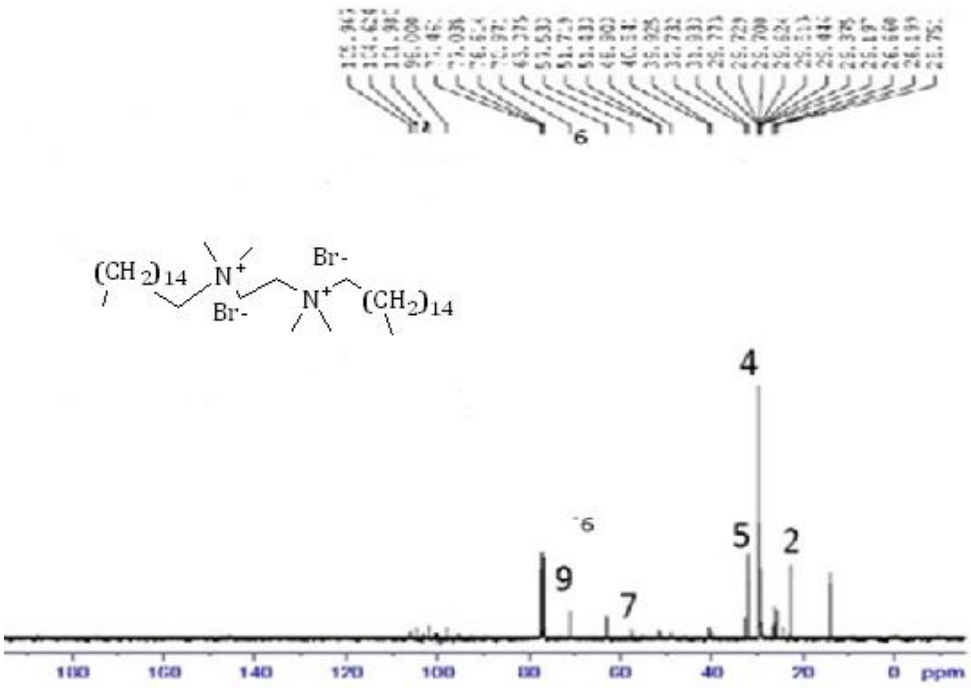


Figure 3: ^{13}C-NMR of synthesized bis quaternary ammonium salt

Evaluation Stages

Laboratory stage using the bottle test and dose in (ppm) while taking a function of temperature and time compared with the important commercial de-emulsifier A & B. As in the tables below (Tables 1, 2, 3 and 4):

Table 1: Represent the local demulsifies efficiency for Crude oil: South Rumaila/ Main pay
Oil/Water Percent (vol.): [oil 84% + Water 16%]
Dose: 100 PPM

Time (Min.)	% Water Separation		
	Z_1	Z_2	A
10	0	40.6	12.5
30	0	56.3	53.1
60	0	70.3	68.8
90	25	93.8	87.5
120	43.8	100	90.6

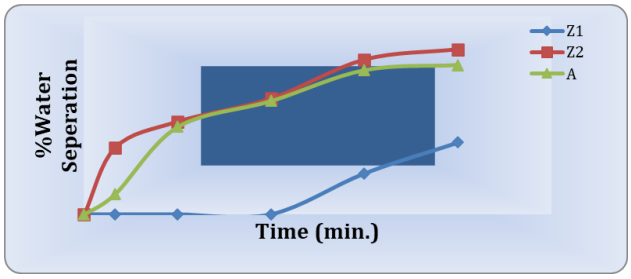


Figure 4: the separation efficiency of de-emulsifiers Z_1&Z_2 compare with commercial de-emulsifier (A) with time at 50°C on south Rumaila Crude oil emulsion treatment in S.O.C Lab

Table 2: Represent the local demulsifies efficiency for Crude oil: North Rumaila
Oil/Water Percent (vol.): 15% [oil 85ml + Water 15ml]
Total volume: 100 cc
Dose: 60 PPM, Temperature= 65°C, Mixing Time= 30 Min /1300 RPM

Time (Min.)	% Water Separation			
	Z_1	Z_2	B	A
30	15	15	13	13
60	15	15	13	13
120	15	15	13	13
240	15	15	13	13

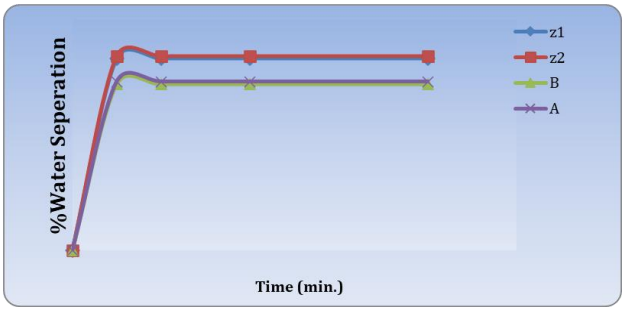


Figure 5: The separation efficiency of prepared de-emulsifiers Z_1&Z_2 compare with commercial A and B with time at 50°C on north Rumaila emulsion in PRDC Lab

Table 3: Represent the local demulsifies efficiency for Crude oil: North Rumayla/ Zubair
Dose: 100 PPM

Time (Min.)	% Water Separation		
	Z_1	Z_2	A
10	34	18.8	25
30	50	50	56.3
60	62.5	96.6	87.5
90	96.9	96.9	93.8
120	96.0	96.9	96.9

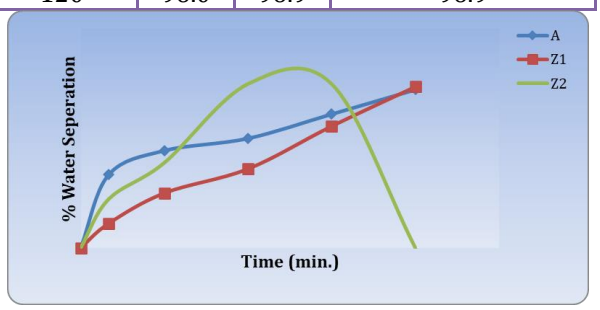


Figure 6: The separation efficiency of prepared de-emulsifiers Z_1&Z_2 compare with commercial A with time at 50°C on north Rumaila Crude oil emulsion/ Zubair location in S.O.C Lab

Table 4: Represent the local demulsifies efficiency for Crude oil: North Rumaila/ Mishrif
Dose: 100 PPM

Time (Min.)	% Water Separation		
	Z_1	Z_2	A
10	13.3	26.7	40
30	30	46.7	53.3
60	43.3	90	60
90	66.7	90	73.3
120	88.3	91.7	86.7

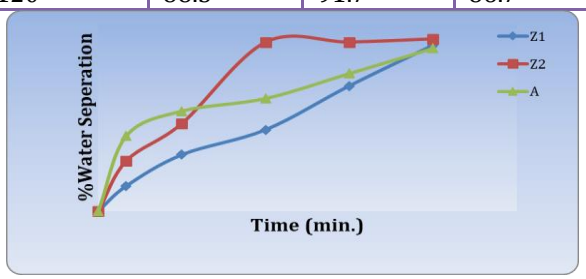


Figure 7: The separation efficiency of prepared de-emulsifiers Z1&Z2 compare with commercial A with time at 50°C on north Rumaila Crude oil emulsion/ Mishrif location in S.O.C.

Result and Dissection

The test results indicators high positive depending on the type of oil and the concentration of the dose, which is directly ejective to the efficiency and the time of separation in addition to study the effect of additives used with prepared local de-emulsifier depending on the integration of structure breakers emulsification of the preservatives and materials increase the stabilizing material and to ensure breaking the film between phases, taking into consideration the factors used in the field and specifically in the site evaluation in the AL SHAMIA station of the south Ramaila Iraqi southern oil company.

According power transformer with a polarity within the buffer in the form of electrostatic field and therefore easy flow phases separated, as well as the degree of reservoir (Main pay, Mishrif, Zubair) where is not used the heating in the AL SHAMIA station), and only evaluation depending on the temperature of the reservoir oil between (45-60 °C), and thus influence the surface tension of the liquid depending on the relationship, which represents the relationship between molar surface and temperature in equation (2).

$$\gamma^{(Mv)^{\frac{2}{3}}} = a - Kt \qquad (2)$$

The selection of Gemini surfactant was according on HLB value scale.

Though the practical results of field proven the prepared in this research Z1 & Z2 are clearly superior in the efficiency of separation and low cost of production per barrel economic compared with commercial de-emulsifier and back over the new chemical formula has proven operating wells containing rations of water cut (20-40)% in operating wells in the evaluation period: Ru(22-24- 53- 61- 82- 101- 107- 109- 112- 124).

The date of inspection field and testing in the ALSHAMIA station 23/August/2011 on the (Blank B) and the rate of salt emerging after treatment using prepared de-emulsifier is (8.2 ptb) and dose (25 ppm) with stabilizing the full contingent of isolation during the period of evaluation and testing field (and the absence of amperage sudden), which indicates the stabilizing material and separation efficiency of the process and table below the shows the staged of examination, temperature, the conditions and the rate of wash water which used in the station.

The study of performances of two local demulsifier and applied in south oil company station which consider a rigid emulsion of crude oil, where from bottle test and field evolution revealed the following:

- The performances of de-emulsifiers increase with increase concentration of de-emulsifier at temperature constant.
- The performances of de-emulsifiers depending on the temperature in field evaluation (morning & night).
- S.O.C can use this material Z1 & Z2 a production line or an additional alternative in the consumption of commercial de-emulsifier.

Conclusion

In this work dehydration of model water in oil emulsion (W/O) containing low water continent by synthesized demulsifer was investigated.

Water in crude oil emulsion has great importance in the oil industry. From experimental results obtained in this research, it can conclude that, the prepared demulsifier is very effective in emulsion breaking.

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Authors' contributions

All authors contributed toward data analysis, drafting and revising the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest

We have no conflicts of interest to disclose.

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