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Using Amides Demulsifiers for Crude Oil Processing

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Abstract

This work evaluated the efficiency of two types of synthesized Amides (demulsifiers) Oleic Ethylene Diamine (OED) and Oleic Methyl Aniline (OMA) in the Laboratory by variating time(5, 10, 15, 20, 25, 30) minute at constant temperature (ºC) and concentration. Both demulsifiers are prepared by the reflux method. Oleic Ethylene Diamine (OED) was prepared by the reaction between Oleic acid and ethylene di amine. Methyl aniline (p-toluidine) was prepared by the reaction between oleic acid and methyl aniline. FTIR and H.NMR spectra were used to diagnose the synthesized demulsifier's structure. A comparison between these types of demulsifiers was made. The photos show the amount of separation between the water and oil phases. Demulsifiers showed high efficiency in the separation process of water from crude oil.
Keywords: Synthesis of amide, Demulsifier, Crude oil, Separation process.

1. Introduction

There are many hydrocarbon and nonhydrocarbon components in crude oil, making it a heterogeneous mixture of substances. Each oil component has its unique chemical makeup, varying in quality and quantity, with just carbon and hydrogen atoms serving as a unifying factor among the majority of molecules present in a mixture [1,2]. When two liquids (water and crude oil) are mixed together, they form an emulsion. A colloidal system is described as the dispersion of one liquid into another that is neither totally dissolved nor miscible. The liquid in which the droplets are scattered is called the dispersion medium. Emulsion systems that use crude oil as the organic phase are popular. The water droplets are widely spread. The term "wet oils" refers to the type of emulsification system that produces oil emulsions, which remain untreated, resulting in issues such as high pumping costs, corrosion of pipes and pumps, poisoning of catalysts for the refinery, low productivity, and other issues [3,4].It is necessary to utilize a demulsifier to remove any salts present in an oil emulsion with a water content ranging from (5-20) %, making it unusable for industrial purposes because they do not meet the criteria of OPEC [5]. Agglomeration adsorption method and removing dense sections are useful methods for demulsifier. A demulsifier is one of the most complicated operations

[6]. Demulsifiers are lowering the surface tension between water and oil; they include two terminal parts hydrophilic and hydrophobic. The hydrophilic refers to the water phase, and the hydrophobic refers to the organic phase. These substances can either be ionic (positive or negative ions) or non-ionic (a surfactant). Demulsifiers, are added to emulsion by mixing chemicals, that should have sufficient substance to function properly [7]. Using demulsifiers method is fast, effective, able to lower oil's viscosity in an emulsion and can separate the emulsion into two separate water and oil components.The demulsifier agent concentration in the droplet must be sufficient to enable propagation expansion at the interface when it is dissolved in the oil phase. [8,9].This work [Oleic Ethylene Diamine (OED) and Oleic Methyl Aniline (OMA)] aims to evaluate the ability of synthesized amid to treat the emulsions as a demulsifier.

2. Materials and Methods
2.1. Chemical materials

The utilized compounds in the investigation are listed in table (1).

2.2. Equipment and Apparatus

Equipment and apparatus have been shown in table (2).

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Table (1): Chemical Materials.

NO.	Material	Supplied company
1	Ethylene diamine	G.C.C(U.K)
2	Xylene	G.C.C(U.K)
3	Silica-gel	G.C.C(U.K)
4	Trichlromethane	BDH(England)
5	Methanol	BDH(England)
6	4-methyl aniline	BDH(England)

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Table (2): Equipment and Apparatus.

NO.	Equipment	Supplied company
1	Balance	Germany-Artoriu,1320
2	Water bath	Thomas Sc.Ap. (England)
3	FT-IR	ShimadzuFT-IR8400S spectrophotometer and Perkin Elmer tonser 27Bruker
4	H-NMR spectra	Bruker DRX System AL 500,125 500, 125MHZ
5	Closed cup flash point	SYd-261
6	Viscometer	U.S.A
7	Hot plate	Gallen Kamp (England)
8	Oven	Gallen Kamp (England)

2.3 Measurements the Physical and Chemical Properties of Crude oil

2.3.1 Density and Specific Gravity
A sample of crude oil is placed in a glass cylinder on a stable place and vertically at a certain temperature. A glass hydrometer listed gently in free and vertical inside a sample and allowed it to sit. Then the specific weight and density was determined according to the method (ASTMD 1298-55) [10].

2.3.2 Viscosity
Viscometer used to determine the viscosity the crude oil according to the method (ASTM D 287 - 64) by pulling (10)ml from a sample into the viscometer and fixed in a water bath at a temperature of 40 ^{0}C for 20 minutes. The processes three times repeated and take the average value [10] . The viscosity is calculated according to the following equation:

$V = C \, t$ ………………(1) whereas : V = viscosity, C = viscosity coefficient, which is a numerical number, that shows the effect of temperature on viscosity. t= time in seconds. (seconds)

2.3.3 Water Content
The percentage of water content was measured according to the method (ASTM D 4006). 100 ml of crude oil were added into 1000 ml of glass beaker. 400 ml of pure xylene were added to it with boiling stone.

The boiling rate of the sample was increased until the percentage of water in the collecting tube was fixed for 5 minutes in a graduated glass tube [10] .

2.3.4 Flash Point
The Pen Sky–Martens closed device (ASTM D 287-64) was used in this examination. The inspection container was cleaned and dried, then filled to the certain mark and placed with the aforementioned device. The material was gradually heated and the thermometer reading determined in each Celsius degree [10] .

2.3.5 Salts Contents
It refers to the salt content expressed in milligrams of NaCl per liter of oil compared to the amount of salt dissolved in water. The salinity ratio was measured using TDS (Total dissolved salts) [10].

2.3.6 Prepare Wet Crude Oil in Laboratory
The wet oil was prepared in the laboratory by mixing (15%) distilled water and (85%) crude oil and using stirring device for a period of 2 hours.

2.3.7 Preparation of Amides
It prepared by the interaction between (12gm) of Ethylen diamine with Oleic acid by using xylene as a solvent. Put 50 ml of xylene in a four neck round bottom flask fitted with electrical stirrer to solve the previous mixture. Oleic acid Added as drops in the

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flask for 1hour at about 110 °C with electrical stirring rate of 600 rpm. The mixture was electrically stirred at about 120 ° C for another 5hr to convert all oil to amide. Complete interaction was detected by Thin Layer Chromatography (TLC) .The solvent was removed by rotary evaporation. The produced oil amide was further purified in a chromatographic column of silica-gel using the mixture of trichlromethane and absolute methanol (V:V=6:1) with a yield of 93.8% the purified oil amide [10].

2.3.8 Demulsification Process

The Demulsification process was accomplished through the use of a volumetric cylinder. In a volumetric cylinder, place 10 mL of the oil emulsion. At 303 K, 500 ppm of prepared amides (OE) were added to the volumetric cylinder. For a period of time, the cylinder was shaken by hand. The maximum time allowed for the demulsification process was 30 minutes. [11].

3.   Results and discussion

Infrared spectrum of Oleic acid was carried out to diagnosis the structure of Oleic acid as shown in Figure (1) and Table (3).

Table (3): Infrared spectrum peaks(FT-IR) of Oliec Acid

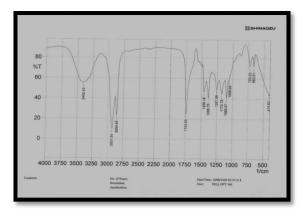| Functional group	Oleic acid
OH	3402.43
C=O	1743.65
CH_2(Aliphatic)	2854.65-2931.80
CH_2 bend	1458.18
CH_3 bend	1388.75
C-O-C	1257.59
C-OH	1172.72

Figure (1): FTIR spectrum of oleic acid.

3.1.   Preparation of Amide (OE)

Amide was prepared by reacting (oleic acid) with the amine (ethylene diamine) in the presence of xylene as a solvent. The mechanism of reaction happen by the Nucleophilic attack of the nitrogen atom in the amine
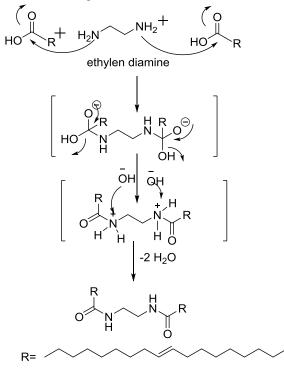
on the carbonyl carbon according to the mechanic shown in scheme 1.

The progress of the reaction was monitored by TLC using a solvent (using the mixture of trichlromethane and absolute Methanol) with a ratio of (6:1) (V:V). The structure of Oleic Ethylene Diamine (OED) was diagnosis by FTIR spectrum and HNMR as shown in Figures (2,3) and Tables (4,5) respectively.
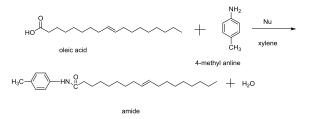
3.2 Synthesis of Oleic Methyl Aniline (OMA)

The second class of amides was synthesized from the amine methyl aniline (p-Toluidine) by reacting oleic acid with methyl aniline in the presence of xylene as a solvent, as illustrated in the scheme (2).
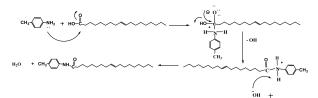
Where the reaction takes place by the Nucleophilic attack of the nitrogen atom in the amine on the carbonyl carbon and the proposed mechanism are shown according to the Scheme 3.

Scheme (1): Mechanism of amid preparation (OE).

Scheme (2): Amid reaction (OMA).

Scheme 3 Mechanism of amid preparation (OMA).

Table 4: Infrared spectrum peaks (FT-IR) Oleic Ethylene Diamine (OED).

Infrared spectrum peaks (FT-IR)	
Functional group	**OE**
N-H (amides)	3456.44
-C=O-NH (amide)	1651.07-1666.50
C-H(alphatic)	2862-2931
CH$_3$ bend	1388.75
CH$_2$ bend	1496.76
C=C aromatic	-----------
C-N	1064.71
C-H(aromatic)	----------

Table 5: H.NMR signals of Oleic Ethylene Diamine (OED).

OE	NMR (ppm)
	8.03 (S, 2H, NH amide), 5.31 (q, 2H, CH=CH), 3.15 (t, 2H, CH2) 2.75 (t, 2H, CH2). 2.00-2.10 (q, 4H, CH2), 1.19 (p, 2H, CH2),1.34 (m, 20H, CH2) 0.87-0.97 (t, 3H, CH3).

Table (6): Infrared spectrum peaks of OMA

Infrared spectrum peaks (FT-IR)	
Functional group	OMA
N-H (amides)	3479.58
-C=O-NH (amide)	1658.78-1689.64
C-H(alphatic)	2854-2931
C-H(aromatic)	3008.95

Table(7): Nuclear magnetic resonance peaks of amide OMA

Nuclear magnetic resonance signals (ppm)	
OMA	8.13-8.30 (S, 1H, NH amide), 7.51 (d-d, 2H, CHaromatic ring), 7.11 (d-d, 2H, CH aromatic ring), 5.31 (q, 2H, CH), 2.72 (t, 2H, CH2), 2.26 (S, 3H, CH3), 1.97 (q, 4H, CH2), 1.45-1.50 (p, 2H, CH2), 1.25 (m, 20H, CH2), 0.86 (t, 3H, CH3).

CH$_3$ bend	1388.75
CH2 bend	1442.75
C=C aromatic	1504.48
C-N	1145

Figure:2 FTIR of Oleic Ethylene diamine (OED).

Figure (3) HNMR of prepared amid.

The progress of the reaction was monitored by TLC using a solvent (using the mixture of trichlromethane and absolute Methanol) with a ratio of (6:1) (V:V).

Infrared spectrum of OMA shows low frequency peak oscillation vibration of the carbonyl group from 1743 cm^{-1} to 1658.76-1689.64 cm^{-1} because of group compensation (NH), it also note the emergence of new a peaks at the frequency (3479.58) due to the vibration of the group (NH). and the compound s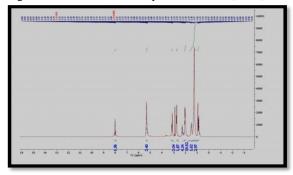howed an absorption pack at the frequency (2931-2854) that due to (CH) aliphatic and absorption pack at the frequency (3008.95) that due to (CH) aromatic and an absorption peak at the frequency (1442.75) due to (CH2) bend, and an absorption peak at the frequency (1095.57) due to (C-N) .Infrared peaks are shown in the table (6).Figure (4) show the infrared spectrum of amide OMA.

Study of the nuclear magnetic resonance spectrum of the compound (OMA) was studied using dimethyl sulfoxide as a solvent and (TMS) as a standard reference, as we note the emergence single a peak due to (NH) amide at the chemical displacement (8.13-8.30) ppm .We note the emergence multiple a peak due

to (CH$_2$) the chain component amide at the chemical displacement (1.25) ppm and appeared signal peak at (2.5) ppm due to the solvent (DMSO) in addition to the   other a peaks nuclear magnetic resonance spectrum indicated in the table (7). The spectrum of the nuclear magnetic resonance of the amide (OMA) is shown in Figure (5).

3.2. Studding time effect on demulsification process

Many scientific papers consider the time factor is significant in evaluating the effectiveness of the demulsifier on crude oil [12,13]. A study has been conducted to determine the influence of time on the efficiency of water separation from wet crude oil due to the relevance of this process in terms of production and economics. As a result, the experiment was carried out to investigate the effect of different time periods on the effectiveness of synthesized amides OE and OMA demulsifiers in the separation of water from crude oil at a temperature of 303 K and a concentration of 500ppm. It was revealed that the separation process for both demulsifiers is proportional to time. The activity of the demulsifier speeds up the separation of the emulsion into two stages. The ability of synthesized amides to separate water from oil by shattering the barrier enclosing the water droplets and making the emulsion non-adsorbent and very stable makes them excellent demulsifiers. This means that the process of separating water from oil is dependent on numerous mechanical principles including agglomeration, adsorption and the capacity to remove dense components [14]. According to the results shown in table (8), both amides provided a good separation amount. But the results of the prepared amide from ethylene diamine gave a better separation efficiency compared with the prepared amide from methyl aniline. This is back to a long hydrocarbon chain in the amide Oleic Ethylene Diamine (OED). The presence of effective groups such as nitrogen atom, oxygen atoms as well as double bonds in the chain contribute increasing the efficiency of separation processes of water from crude oil, and this is lead to the increasing in the hydrophobic characteristic of the molecule and the increase in the surface tension action of the surface activated molecule [14,15].

Each time (5, 10, 15, 20, 25, 30) minute, a photograph of the crude oil sample was taken before

and after treatment to demonstrate the demulsifier's effect on the process of separating the aqueous layer from the organic layer (crude oil), as illustrated in Figures 6 and 7.
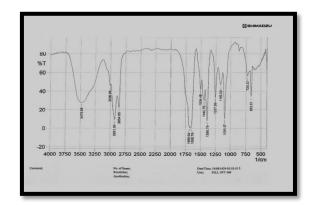

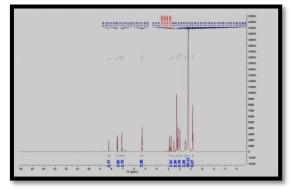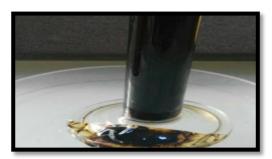Figure (4) Infrared spectrum of the amide OMA

Figure (5) : H- NMR spectrum of OMA

Table (8): Shows the amount of water that has been removed from the crude oil. Concentration of prepared amides (OE) (500) ppm at 5-30 minute intervals at room temperature was done.

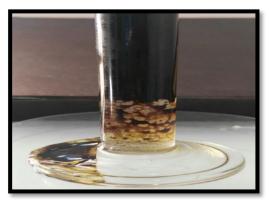| Volume of water separated in (ml)			
TIME(min)	OED	OMA	blank
5	2.4	0.3	-----
10	2.6	0.5	-----
15	2.8	0.6	------
20	2.9	0.9	------
25	3	1.4	-----
30	3.2	1.9	0.1

Figure 6: Iimages (A,B,C,D,E,F) illustrate the steps of the separation process employing (OE) at different intervals times (5,10,15,20,25,30) minute respectively at 303 K.
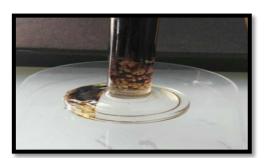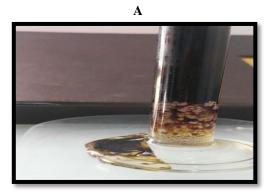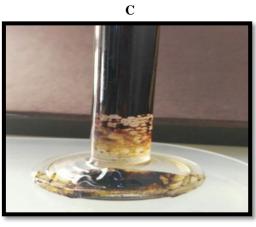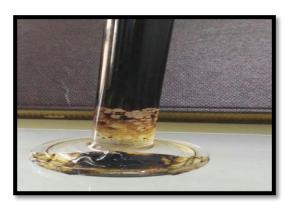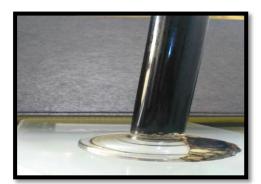
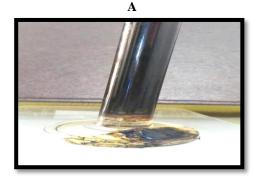**Blank**
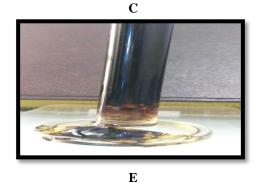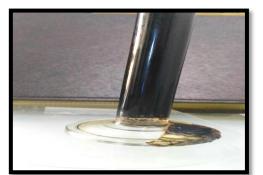

A

B

C

D

E

F

Figure 6: images (A,B,C,D,E,F) illustrate the steps of the separation process employing (OE) at different intervals times (5,10,15,20,25,30) minute respectively at 303 K.
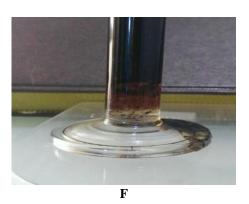
A

B

C

D

E

F

Figure (7): Images (A,B,C,D,E,F) illustrate the steps of the separation process employing an amide demulsifier (OMA) at various times (5,10,15,20,25,30) minutes at 303 K.

Conclusion

A high separation rate was achieved in a short period, demonstrating the efficacy of the demulsifiers prepared in this investigation. In the photographs, the amount of separation is exactly related to the length of time, showing that the amides used are effective demulsifiers. The synthesized amides can then be employed as demulsifiers to treat wet crude oil, which is a significant advancement over previous methods.

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