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Synthesis and Characterization of New Petroleum Demulsifies from Poly Acryl Amide with Poly Vinyl Alcohol and Studying Photolysis

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Abstract

One of the most important problems associated with oil production is the formation of stable (water-in-oil) emulsions, and these emulsions greatly affect the process of treating the oil and ridding it of water.The creation of these emulsions throughout the oil production process is an expensive state, and the low water level of crude oil emulsions enhances performance while lowering the risk of equipment and pipeline deterioration. One technique to lower the water content is to break down crude oil emulsions chemically by demulsification. The water droplets quickly collide because the emulsifier renders the thin film separating the water droplets and the crude oil emulsion fragile. The current research includes the synthesis and characterization of novel demulsifiers for acrylamide based on Schiff bases and polyvinyl alcohol, which are both beneficial to the environment and highly effective in comparison to imported emulsifiers from other countries. Due to the application of highly hazardous industrial emulsifiers, new ecologically friendly demulsifiers were developed in this study that help reduce river water pollution. Employing nuclear magnetic resonance and infrared spectroscopy, the produced compounds were investigated. All of the polymer's spectrum signals corresponded well with the compounds' chemical structures. The photodegradation of the emulsions used was also studied and it was found that they are characterized by high disintegration and have the ability to reduce surface tensions. The thermal stability of the prepared compounds was also measured.

Keywords: Acrylamide, Demulsifies, Petroleum, Photolysis, Poly vinyl alcohol.

Introduction

A family of specific compounds known as demulsifiers or emulsion breakers are utilized to separate emulsions, like oil in water. They are widely used in the extraction of crude oil, which is typically produced in combination with significant volumes of briny water [1]. Demulsifiers are mostly polymeric substances with high molecular weights which assist in lowering water droplet surface tension and emulsifying agent reaction balance; however, overuse of this material may result in more stable emulsions [2]. Furthermore, because of its capacity to pass through the oil phase to the droplet border, this material may be used to separate water from oil. In general, the demulisifier aids in the droplet membrane's separation and neutralization of the emulsifying agents, which speeds up assembly. Disintegrating the droplet membrane results in a large increase in the size of the water droplets when the emulsifying component is unstable [3].

Emulsification Mechanisms

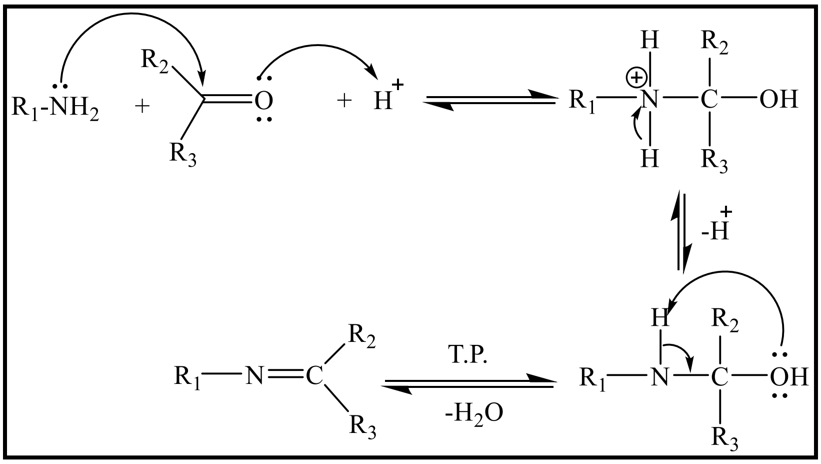
Emulsification takes place by the reduction of interfacial tension between two phases. Emulsification happens when interfacial tension is broken down into two phases. On the contrary, the repulsion theory proposes that the emulsifying agent develops films covering one of the stages, causing droplets to repellent against one another. When an emulsifier, such as phospholipid, protein, or nanoparticle, is combined with two incompatible liquids, such as water and oil, an emulsion is typically created. But still, the form of used emulsifier could influence the type of created emulsion [4,5]. Demulsifier biochemistry is dependent on a variety of variables, such as epoxy resins, polyamines, polyethylene imines, di-epoxides, phenol-formaldehyde resins that are catalyzed by acids or bases, and polyamines [6,7].

Emulsions of water polar or oil nonpolar solutes can be broken down via demulsifying chemicals. These compounds occur in transformers, metal, and oxidation and rust elimination fluids as functional liquids. When researchers assessed the likelihood of the (W/O) emulsion in crude oil becoming fragile when employing a water-soluble demulisifier instead of an oil-soluble demulisifier, they observed that utilising a water-soluble surfactant could negatively affect the emulsion. In contrast, the W/O emulsion could get broken down by adding polymers with varying molecular weights, structures, and HLB to the water phase. Desalting and drying crude oil is a common application for demulsifying agents, characterized by low molecular weight compounds with high hydrophilic functionalities [8]. The processes of demulsification comprise chemical, biological, and physical processes. Chemical approaches use demulsifiers, which are classified according to their chemical structure and utilization, to accelerate the dissolution of films while reducing emulsion stability [9], separated into three groups: polymeric surfactant, nanoparticles, and ionic liquids. When two unmixable phases (α and β) such as oil and water are contacted, interfacial regions are formed which are not single-molecule thickness but rather have a thickness δ and that region has different properties than α and β phases and undergoes certain changes which cause significant changes in the internal energy [10]. For instance, if a probe is moved from α interior to β, some deviations in structure, composition, and density, and its deviation gets larger when the probe gets closer to the β phase until arriving eventually at the homogeneous β phase. The thickness of transitional layers depends on the interface nature. The two different phases are having thermodynamic properties with high uniformity up to the interface regions, as the interface tension γ by assuming mathematical planes Zσ in the regions of interface. Furthermore, the region of interface and the mathematical plane of Gibbs are given in Gibbs dividing line Z which uniforms the thermodynamic properties [10, 11].

Persistent emulsions like water in oil (W/O) are considered not recommended in refinery processes and may cause steel corrosion and pump failure, which is why they are avoided in the petroleum industry. These emulsions are highly stable due to the creation of stable coatings at water or oil droplets created by crude oil components like asphaltene and resins or oilfield chemicals used in the various crude oil production activities. Emulsions of crude oil can be mechanically demulsified, thermally, electrically, or chemically to remove water. Since chemical demulsification is more effective and rapid at demulsifying crude oil emulsion compared with other methods, researchers consider it tempting to use [12, 13].

In 1957, due to their durability and strength, Poly Schiff bases were studied extensively [14–16] and frequent application in pH sensors [17] and light-emitting diodes [18], poly(Schiff base)s have been the subject of substantial research. Thus, poly(azomethine)s, or poly(Schiff base)s, have been recognized for more than 50 years. Furthermore, it has been reported that these materials possess unique optical, electrical, and catalytic characteristics that are absent from traditional metal complexes[19]. Being a water-soluble synthetic polymer, poly(acrylamide) (PAAm) is experiencing extensive commercial use, such as a coating in the construction and textile sectors. The proportion of amine to carboxyl groups affects these uses. Small structural alterations may alter PAAm's characteristics, including permeability and mechanical strength. Understanding the unique characteristics of polymers could represent a key strategy to employing them in untested area [20]. A review of literature demonstrated that reports of conventional synthetic techniques were submitted for poly(Schiff base)s [21]. We have described a novel method for synthesizing polymers with NH_2 groups that heavily relies on Schiff base synthesis [22]. In this study, a spectral approach was used to identify the

Schiff base groups in the polymer. The newly developed synthesis of poly(acrylamide)s including Schiff bases and their characterization are presented in this study as shown in scheme 1.



Scheme1. Mechanism of Schiff base

Photolysis

Photolysis (also called photo dissociation and photodecomposition) is the decomposition of chemical bonds by natural or artificial light, which includes both direct and indirect photolysis. In the direct photolysis process, organic substances absorb UV light or the result of a transfer of light; whereas photosensitizers such as oxygen and hydroxyl or peroxide radicals break down light in the indirect photolysis process or radiant energy to the chemical bonds [23]. If the organic molecules are light-sensitive, optical dispersion will be the primary mode of elimination. The photolysis process is prevalent in surface water and serves as an extra stage of elimination in surface water or wastewater treatment [24].

Furthermore, the photolysis of dissolved organic matter is crucial in the global carbon cycle because it is involved in the binding and releasing nutrients like P and N [25,26].

Three phases constitute the photochemical mechanism of photolysis in this process:

1.The adsorption of light which excites electrons in the molecule,

$R + h\nu \rightarrow R^*$...... (1-1) $R^* \rightarrow P$ 2-1

R= reactant molecule, R*= excited reactant molecule, P= degraded product.

2.The principal photochemical reactions that modify or de-excite the molecular excitation.

3.The subsequent (dark) heat reactions that change the intermediates created in step 2 of the preceding process [24].

Generally, the types of compounds that have been degraded contain alkanet, halo alkanet, aliphatic alcohols, carboxylic acids, alkenes, aromatics, halo aromatics, polymers, surfactants, herbicides, pesticides, and dyes [27]. Furthermore, before photolysis can take place, the photochemically excited state must be deactivated, which can be accomplished through a radiative process (fluorescence) in which energy (usually in the form of light) is emitted during the transition to the ground electronic state and some residual vibrational excitation is rapidly lost through collision processes [28,29]. Based on ZnO have gained a lot of attention, and there is a major reliance on this substance in our modern industry and daily life [30] Zinc oxide (ZnO), another possible photocatalyst, is an n-type semiconductor possessing a thermodynamically stable hexagonal wurtzite structure. It is nontoxic and low-cost, with unique electrical, catalytic, optoelectronic, and luminous features [31]. Zinc oxide (ZnO) is a semiconducting, piezoelectric, and optical waveguide material utilised in solar cells, transparent electrodes, sensors, and surface acoustic devices [32, 33]. The effective functioning of devices based on ZnO structures depends on controlling the physical properties of ZnO by considering several variables including doping and temperature escalation. The use of both (n and p) conduction types in light-emitting devices is fundamental [34]. A portion of the study involved the synthesis and characterization of brand-new acrylamide demulsifies based on polyvinyl alcohol and Schiff bases, which are both environmentally friendly and far more efficient than emulsifiers that are imported from other nations. In this study, new environmentally friendly demulsifies that assist minimize pollution in river water were created as a result of the use of extremely dangerous industrial emulsifiers.

Materials and Methods

All the substances were obtained from Aldrich and Merck. Melting points were measured in uncorrected open capillary tubes. Shimadzu 8400s FT-IR spectrophotometer and Shimadzo (Ir prestige-21) FTIR spectrophotometer FT-IR spectra acquired using KBr e discs. ^{1}HNMR spectra were obtained using a DMSO solvent, Bruker ultra-shield 300 MHz, and are given in parts per million. Thermal analyses TGA/DTA were performed using TGA/DTA Q600- US and were achieved at Iran University of Tehran.

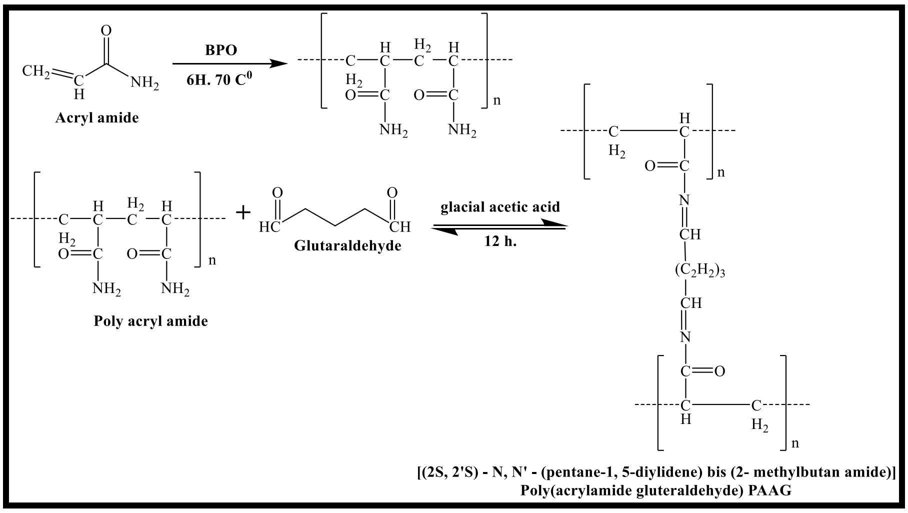
Synthetic Procedures

Synthesis of (H) Polymerization of AAM

An amount of 10 g of acrylamide was incorporated with 0.5 g of di-benzoyl peroxide as an activator in a round-bottom flask at a temperature of 70℃. The PAA homopolymer was isolated from the mixture by subjecting it to continuous stirring in a water bath at an elevated temperature for a duration of 6 hrs [14,15]. The reaction mixture was cooled to be at room temperature, and the resulting product was rinsed with diethyl ether and then dried in an oven at 50℃ for 1 hour. A percentage of 55% concentration of the viscous white polymer was achieved.

Synthesis of (H1) [(2S, 2'S) – N, N' - (Pentane-1, 5-diylidene) bis (2- methylbutan amide)]

The process of polymerization is shown in Scheme 2. A Schiff base [H1] was synthesised in the second stage by dissolving 1.0 g (0.0143 mol) of polyacrylamide in 5 mL of absolute ethanol (99.95%). Three drops of glacial acetic acid were then added, and the mixture was stirred consistently at ambient temperature (25ºC). After adding 5 mL of 100% ethanol, 2 mL of glutaraldehyde (0.0286 mol) is added to the mixture. The mixture is subsequently heated with continuous stirring at 78°C for 12 hrs in a water bath [35, 36].



Scheme 2. Synthesis of compound (H1) [(2S, 2'S) – N, N' - (pentane-1, 5-diylidene) bis (2- methylbutan amide)

The final product was then air-dried overnight at ambient temperature previous to being rinsed with diethyl ether then recrystallization by ethanol show in Fig. 1.

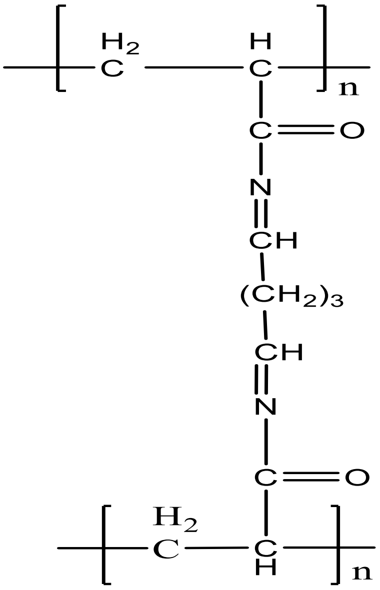


Figure 1. Compound (H1)

Synthesis of (Acrylamide -g-PVA-phthalate) (H2)

Two grams of polyvinyl alcohol that had been dissolved in EtOH +H_2O (50:50 vol) is mixed with 1gm of phthalic anhydride[37], and the mixture was heated for about 6hrs at 80C^0. The resulting clear white precipitate (H2) was washed with ethanol absolute and 1gm of (H2) was dissolved in 10 mL of DMF and mixed with (2 g) of H. for 8 hrs. at 90 °C, the mixture was reflexed in a circular flask bottom. The resulting clear white precipitate (H2) was washed with 10 mL of diethyl ether show in Fig. 2.

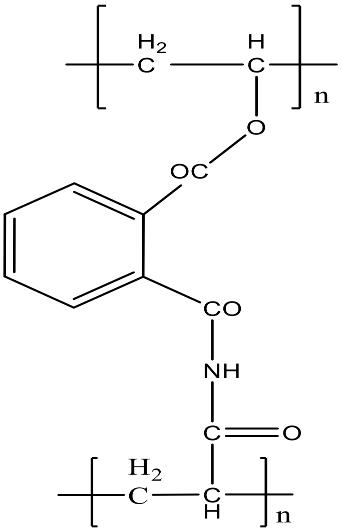


Figure 2. Compound (H2)

Preparation of W\O Emulsion [38]

In order to produce the W/O emulsion, 70 % vol Basra crude oil and 30% volume water with 1g of NaCl were blended at room temperature. This produced water with characteristics comparable to those of oil well water. After that, the W/O emulsion was vigorously stirred for 2 hrs. at a rapid rate. Ultimately, the emulsion underwent a 30-minute homogenization process to guarantee the creation of a one-phase emulsion. At 25°C, the produced emulsion demonstrated excellent stability.

Demulsification Performance Test (EC2134A)

The performance test for demulsification was conducted in compliance with EC2134A, which is a commercial demulisifier summarized in Table 1. Dimethyl sulfoxide, an organic solvent, is used to dissolve the polymer before it is constructed into a demulisifier solution at a concentration of 0.1 g/100 mL. The 0.1 g/100 mL demulisifier solution was used as a stock solution for the preparation of the following concentrations 10, 20, 30, 40, 50, 60, 70, 80 ppm. The first step involved adding demulisifier to the 70/30% weight of W/O emulsion. Next, the cylinder was manually agitated 200 times in less than two minutes, and it was left undisturbed for 30 minutes. Afterwards, the cylinder was placed back into the hot water bath that had been set up previously. The demulsifying effectiveness was determined by taking a certain quantity of water out of the emulsion sample.

Table 1. Physical properties of the commercial demulsifier (EC2134A).

Appearance	Liquid
Colour	Dark amber
Odour	Hydrocarbon-like
Flash point	66^{O}C
Melting point	-45^{0}C,ASTM D- 97
Relative density	0.962 (25 ^{0}C)
Viscosity,dynamic	11 mpa.s(40^{0}C)
Water solubility	insoluble

Calculating the Volume of Isolated Water

An amount of 10 mL of the oil sample was taken in a volumetric flask, 20 mL of petroleum ether was added to it, the volumetric flask was connected to the Dean Stark Apparatus, and the mixture was heated at a temperature of 70 °C. After that, the amount of condensed water at the bottom of the clappers was calculated according to Tables 2-4.

Table 2. The amount of water in crude oil.

Original crude oil without additives	Amount of water drawn
10 mL of crude oil dded to 20 mL of petroleum ether	4.5mL

Table 3. The amount of water remaining in emulsion (W/O) by using compound (H1).

Crude oil with additives	Amount of water drawn
10 ppm	2.5 mL
20ppm	2.7 mL
30ppm	2.9 mL
40ppm	3 mL
50ppm	3.2 mL
60ppm	zero mL
70ppm	zero mL
80ppm	3.4 mL

Table 4. The amount of water remaining in emulsion (W/O) by using (H2).

Crude oil with additives	Amount of water drawn
10 ppm	2 mL
20ppm	2.2 mL
30ppm	2.5 mL
40ppm	1.5 mL
50ppm	zero mL
60ppm	zero mL
70ppm	2.6 mL
80ppm	2.8 mL

Photolysis Method

Ultraviolet light source medium pressure mercury lamp (150 W) (MPML) equipped with a focusing lens to ensure a parallel beam of light. The lamp was fixed with a photoreaction cell in this operation. The preceding source produces UV light with a wavelength range of 260-450 nm and a maximum intensity of 365 nm. A thermostat-controlled Pyrex cylindrical photolytic cell with a 75 mL capacity was utilized for the photolysis tests. During the photolysis studies, a magnetic stirrer was utilized to maintain the catalyst aqueous solution homogeneous. A circulating thermostat was used to regulate the reaction temperature.

Solutions Preparation:

The absorption readings were measured at a wavelength of 265 and 254 nm, respectively, using a prepared solution containing 10 ppm of (H1). The reaction temperature was 25˚C.

First Treatment:

Without the use of any additives, the polymers (H2) were irradiated and measurements of absorbance are measured at various stages of the process.

Second Treatment:

1- Zinc oxide powder (0.04 g) was added to a known concentration polymer solution (H2) in the photocell. The interaction mixture is then irradiated by the UV lamp while the subject was parallel to the photovoltaic window, and absorption spectra were recorded between 265, 254 nm.

2- At various irradiation time intervals, five milliliter samples were collected.

3-Centrifuge was used to remove the zinc oxide from the samples. UV was used to identify photo degradation products.

In the first method, the emulsifier was added to the crude oil without using a catalyst, and it was observed that the disintegration rate was low, while it was observed that when using zinc oxide as a catalyst, the disintegration rate was high.

Results and Discussion

This study included prepared different demulsifies and studying their capacity and photo degradation of some of them. Schiff base [37] resulted from the reaction of Acrylamide and of glutarlaldyde Scheme 2.

The newly derivatives of acrylamide [39] with glutaraldehyde for preparing them in acidic media, FT-IR spectra of derivative Fig. 3 compound H1, interpreted the presence of a band at 3329 cm^{-1} stretching vibrations of (O-H), and (3209) cm^{-1} that refers to the (N-H). Two bands appeared at 2900-2800 cm^{-1} and 3133 cm^{-1} which correspond to ($C-H_{Alph}$) as well as ($C-H_{Ar}$) respectively. Bands at 1643 cm^{-1} refer to the ($C=N_{imine}$)[40].

Fig. 4 exhibits moderate intensity bands that appear in the infrared spectra in a range of 3421 cm^{-1}, corresponding to the expanding vibrations of hydroxyl groups. The appearance of two bands of 2927-2850 cm^{-1}, which correspond to $C-H_{Alph}$ (1705) cm^{-1}, which belongs to the $C=O_{ester}$, (1635) cm^{-1}

refers to the $C=O_{amid}$, while C=C extending vibration of benzene rings in these compounds appeared as a strong bands at (1562) cm^{-1}.

Figs. 5 and 6 display the synthesized H1's ^{1}H-NMR spectra, which provide the following proton signals: δ(4.24-4.93) ppm (m, CH_2,CH), δ(5.02-5.11) ppm (s, 2H, O-H) and δ(8.44) ppm (s, 1H, HC= N)[41].

The thermos gravimetric analysis was used to assess the thermal stability of several selected chemicals (TGA). The procedure measures loss of weight as an outcome of temperature effect at stable rate of heating or as a function of time at constant temperature. In this study, the thermogravimetric technique was utilized to evaluate the thermal stability of the generated compounds by measuring the weight of the specimen difference at a preset rate of heating. The weight change was monitored as a function of temperature, providing useful information about the thermal stability of the produced compounds. Thermo gravimetric analysis compound -H1- in Fig. 6 revealed four stages of weight loss:

1.With a weight loss of 8.200%, the first stage, which took place at 140.23 °C, is assumed to have been caused by the compound's water evaporation as moisture or the glass transition.

2. The second phase, which took place at 180°C, is related to the breakdown of acrylamide bonds with glutaraldehyde melting which causes a 13.91% of weight loss.

3. The third phase exhibited a loss of 25.07 percent at 320 °C, leading to the crystallizing of acrylamide-forming bonds.

4.The fourth and final phase had the most weight loss of 23.00 %, showing that carbon dioxide was still being released and acrylamide was continuously degrading.

Fig. 7 illustrates the H3 ^{1}H-NMR spectra, which exhibit the subsequent signals of protons: δ(1.5-2.52) ppm (m, 9 protons, CH_2,CH), δ(3.3-3.5) ppm (s, 2 protons, CH_2-OH), δ(3.8-4.3) ppm (t, 2 protons, $COOCH_2$ ester), δ(7.47) ppm (m, 4 protons, aromatic protons across various environments), and δ(8.14) ppm (s, 1 proton, CONH amide).

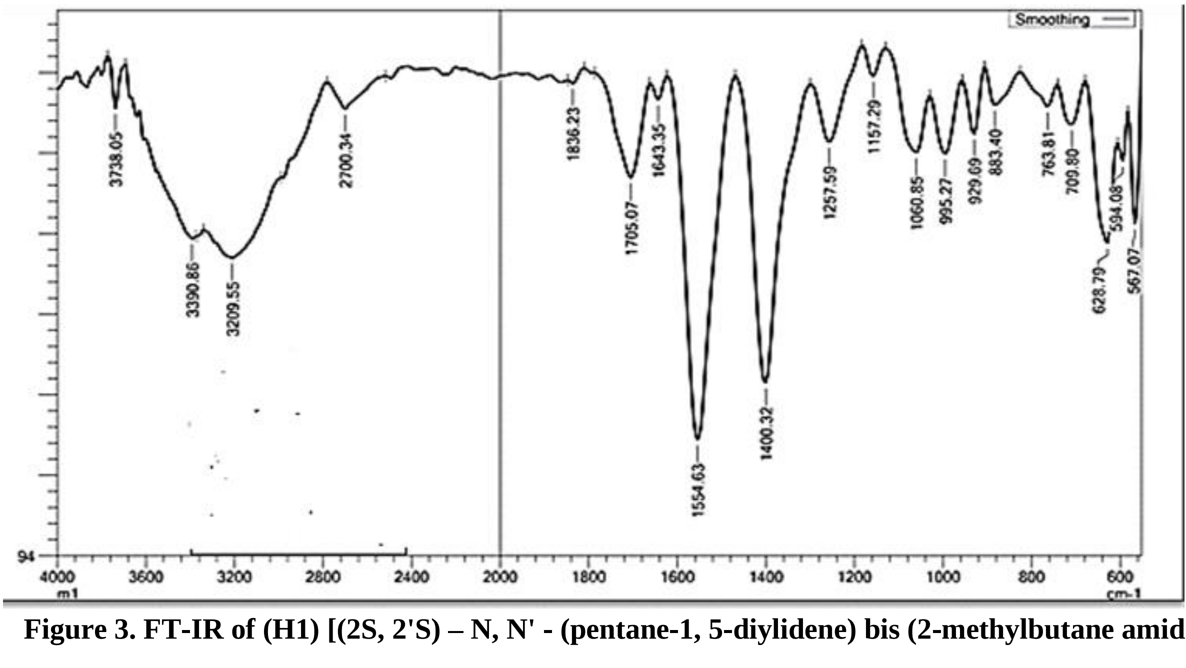


Figure 3. FT-IR of (H1) [(2S, 2'S) – N, N' - (pentane-1, 5-diylidene) bis (2-methylbutane amide)

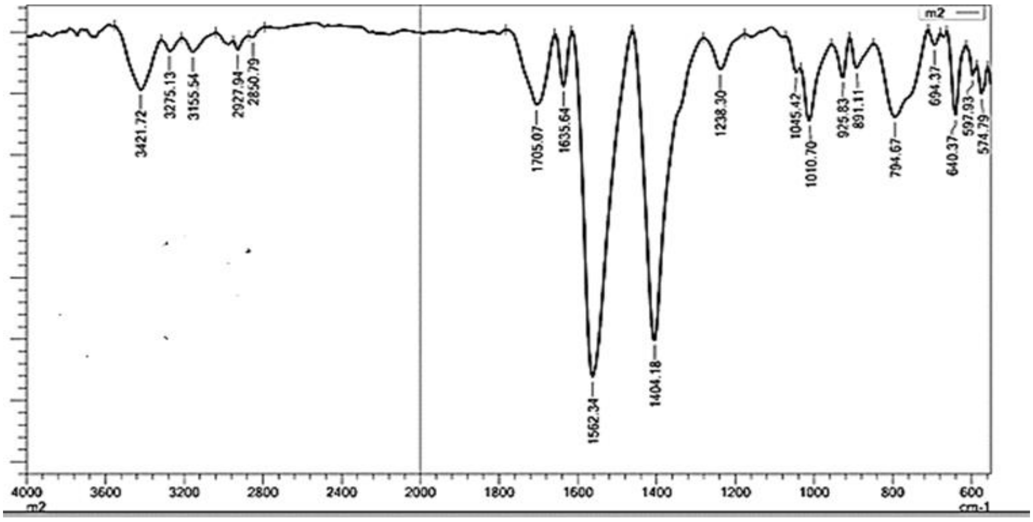


Figure 4. FTIR of (H2) compound.

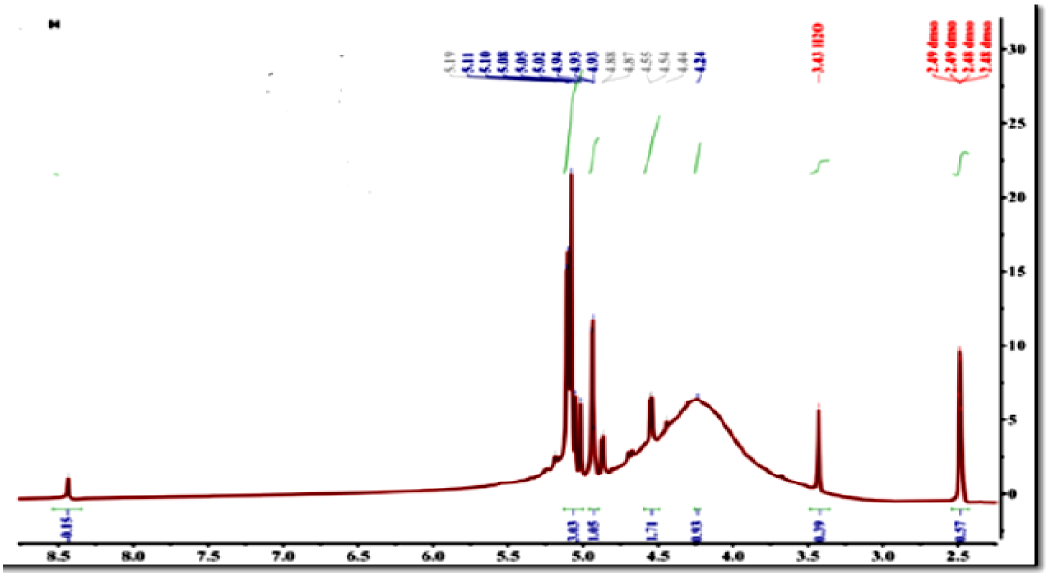


Figure 5. ^{1}H-NMR of (H1)

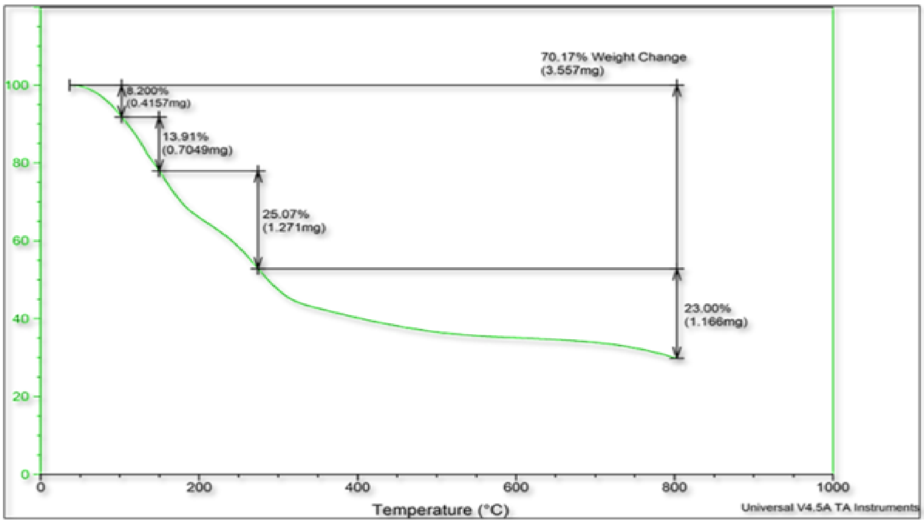


Figure 6. Thermal analysis of compound(H1)

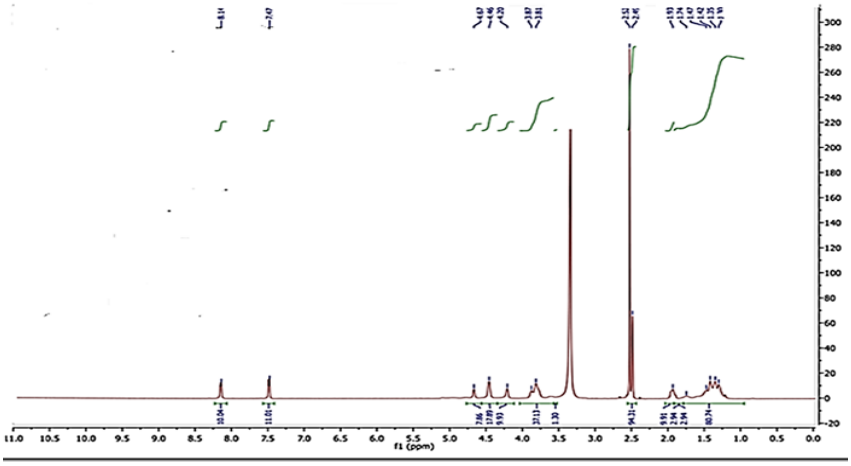


Figure 7. ^{1}H-NMR of compound (H2)

The thermal gravimetric measurement of this chemical, as shown in Fig. 8, displayed four distinct stages of weight loss:

1. The first step, which took place at 150 °C, is attributed to the evaporation of water from the compound as moisture or glass transition, resulting in a 5% weight loss.
2. The second step, occurred at a temperature of 220.98°C, is believed to be the result of the melting of the co-polymer and the breakdown of polyvinyl alcohol bonds with phthalic anhydride, resulting in a weight loss of 6.219%. The third stage exhibited a 26.87 % loss at 380.10 °C, which is related to the compound's crystallization.
3. At 808.38°C, the fourth and final stage exhibited a highest weight loss of 24 %, suggesting that carbon dioxide emissions and polyvinyl alcohol decomposition are continuing. The remaining weight % is composed of carbon waste as shown Tables 5 and 6.

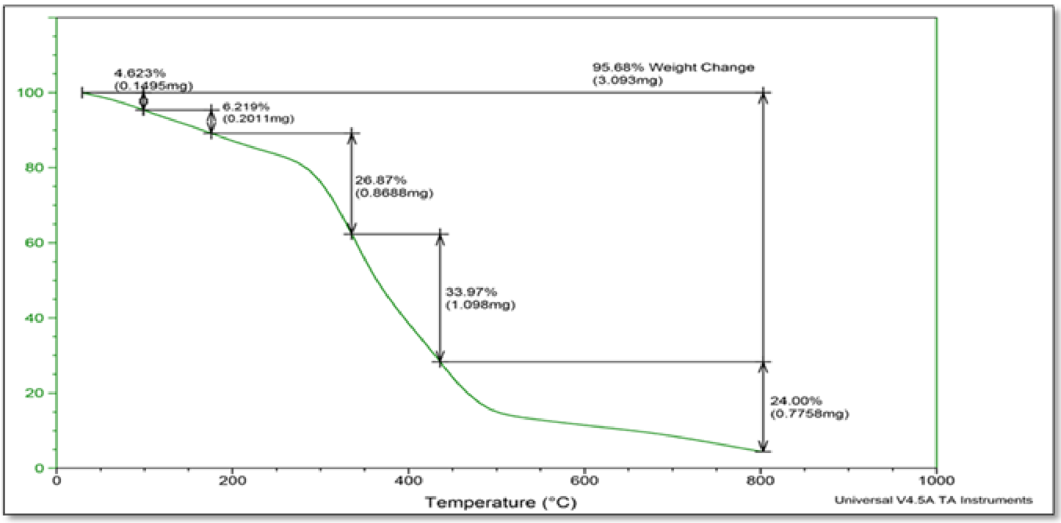


Figure 8. Thermal analysis of compound (H2).

Table 5. Water amount extracted from the H1 demulsifier.

Demulsifier (H1)	**Temp.**	**10 ppm.**	**20 ppm.**	**30 ppm.**	**40 ppm.**	**50 ppm.**	**60 ppm.**	**70 ppm.**	**80 ppm.**
Room Temperature	(20)°C	35 mL.	36 mL.	37 mL.	38 mL.	39 mL.	40 mL.	41 mL.	42 mL.
Hot water bath	(80)°C	43 mL.	45 mL.	46 mL.	47 mL.	48 mL.	50 mL.	51 mL.	52 mL.
Commercial demulsifier	(80)°C	21 mL.	23 mL.	24 mL.	25 mL.	26 mL.	28 mL.	29 mL.	30 mL.

Table 6. Quantity of water removed from the H2 demulisifier.

Demulsifier(H2)	Tem.	10 ppm.	20 ppm.	30 ppm.	40 ppm.	50 ppm.	60 ppm.	70 ppm.	80 ppm.
Room Temperature	(20)°C	32 mL.	33 mL.	35 mL.	37 mL.	41 mL.	43 mL.	44 mL.	47 mL.
Hot water bath	(80)°C	35 mL.	37 mL.	40 mL.	42 mL.	43 mL.	45 mL.	48 mL.	49 mL.
Commercial demulisifier	(80)°C	20 mL.	22 mL.	24 mL.	26 mL.	27 mL.	28 mL.	29 mL.	30 mL.

Separation Efficiency

Figs. 9, 10 and 11 illustrates the impact of chemicals and EC2134A on the time-dependent efficiency of water separation. For Re-SOLC ®EC2134A, water separation increases throughout the duration of the following 60 minutes, and then levels drop when separation of low rates occurs. But after 100 minutes, the 80% EC2134A separation was shown to be the most effective division among ready-made emulsifiers. This indicates that the rate of separation increases rapidly over the first 30 minutes before spotting a major decrease. The best separation for 100 minutes was 85 percent. Nonetheless, the time limit was set at 60 minutes, after which demulsifiers could not improve separation. The threshold value was related to the concentration of demulisifier.

Furthermore, because polymeric chains contain active chemical groups such as OH, C=O, and COOH, they are active demulsifiers. Then, the commercial demulisifier EC2134A was detected after 60 minutes, it needs high temperatures more than 70°C to increase the separation efficiency. (EC2134A) gave a small separation rate compared with the prepared emulsifiers, as its efficiency increased when the temperature raised to 80°C, and this occurs with most commercial.

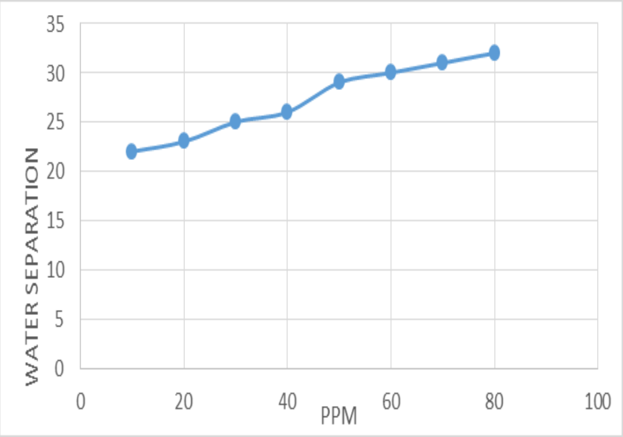


Figure 9. The influence of various concentration of (H1) on the separation of water. The water phase was vol 15% and the temperature was 20 ^{0}C.

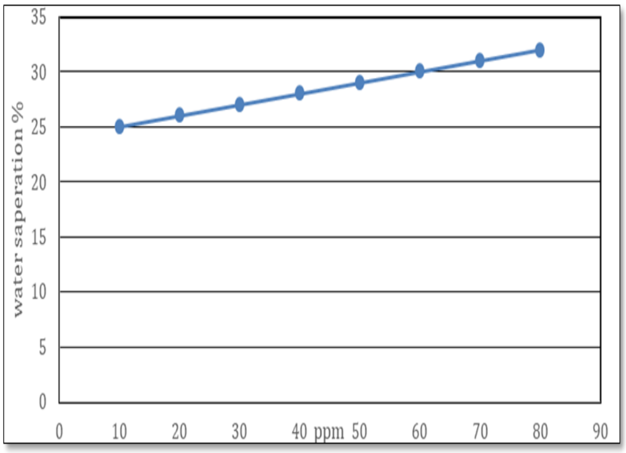


Figure 10. The influence of various concentration of (H2) on the separation of water. The water phase was 15% and the temperature was 80 ºC.

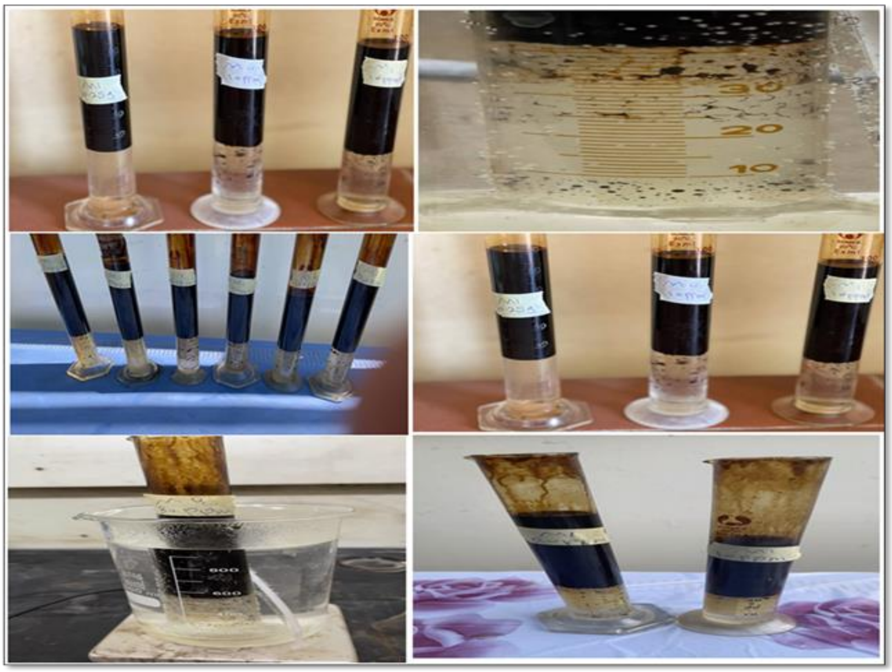


Figure 11. Images of water separation.

Influence of the Demulsifier Concentration

Through water separation tables from crude oil, the best separation table was the compound H2 Table 4-8 , which is a superimposed polymer of H2 due to the presence of the active polar active groups that draw water such as OH, C=N,C=O ,COOH, (N-H) amide and (C=O) ester in the prepared compound. The more polarizing the compound is due to the hydrogen bonds with water and thus the withdrawal of good water. These prepared compounds have good water solubility and carry water-loving limbs, and therefore their polarization is high and the end is a good effectiveness water withdrawal from crude oil.

One of the most important factors affecting demulisifier adsorption at the surface is the dose of the demulisifier. The demulisifier dosages used were manufactured and commercialized (10–80 ppm). Because the demulsification process was much accelerated by the rise in demulisifier concentrations, a significant amount of water was removed from the emulsion. The effectiveness of demulsifying prepared compounds at different dosages [39].

Demulsification effectiveness only increase with increasing levels in the crude oil/water emulsion (90/10% vol), maintaining constant in other emulsion components with different concentrations. For 50/50 and 70/30 vol crude oil/water emulsions, it achieved 100% demulsification effectiveness; nevertheless, it required longer time to reach balance than synthetic demulsifiers. The effectiveness of demulsification is 96 %. More natural emulsifiers are substituted as emulsifier concentration increases. The demulsification efficiency is thus boosted [36].

Effect of Temperature on Demulsifying Performance of Polymer

As the demulsification temperature is increasing from 60 °C to 80 °C, the demulsification efficiency shows a clear increase curve. The results show that at 60 °C the demulsifying efficiency is just 40%. In addition, it is found that demulsification effectiveness is around 80% when the temperature increases to 70 °C. Then a rise in temperature would result in a decrease in the mechanical strength and viscosity of the oil/water interface. On the other hand, a rise in temperature would increase water droplet kinetic and increase tensions between the densities of the water and oil phases (Brownian motion).

It has been shown that the stated effect may help to effectively coalesce and collect water drops and separate crude oil emulsions. This is because the heat reduces the interfacial viscosity of the inner phase due to the increased rate of destruction of the interfacial membrane [37].

Photodegradation of Polymers (H1, H2)

This research included a study for the photodegradation of some demulisifier preparation (H1 and H2) by using UV- light with catalyst ZnO and without ZnO and the estimation of removal of degradation was done according to the following equation:

$$\text{Degradation } \% = (A_0 - A_t)/A_0 \times 100$$

Where A0 is the absorption at zero irradiation time and, at absorption at irradiation time.

The effect of UV-light in photodegradation of H1and H4 an experiment was conducted out in a photolytic cylindrical by using 75mL of 10 ppm of both natural polymer H1 and synthetic polymer H3 for 180 minutes of irradiation time with using 0.04 g of ZnO as catalyst, the experiment was repeated without using zinc oxide, and the results were included in Tables 6 and Figs. 12,13.

Table 7. UV light's influence on H1's polymer photodegradation at 25 °C with and without ZnO.

Time(min)	Abs. without ZnO	Degradation %	Abs. with ZnO	Degradation %
0	0.143	0	0.143	0
15	0.102	28.6	0.097	32.1
30	0.092	35.5	0.066	53.8
60	0.083	41.9	0.052	63.6
90	0.078	45.5	0.037	74.1
120	0.058	59.4	0.024	83.2
180	0.038	73.4	0.016	88.8

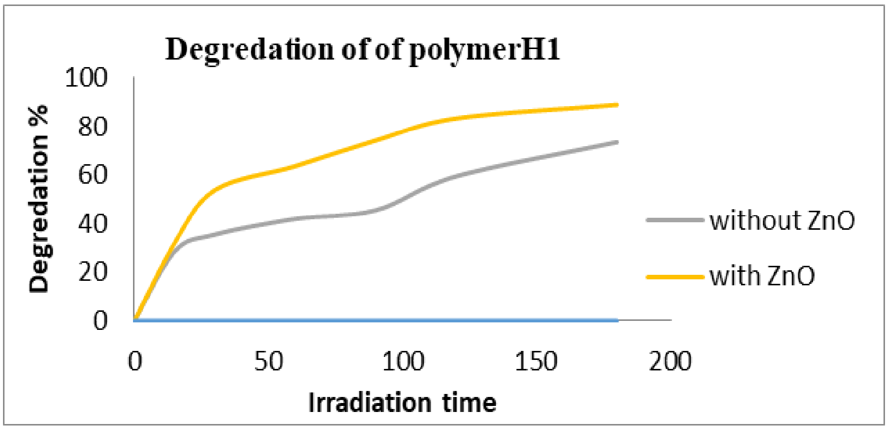


Figure 12. Radiation's influence on H1's polymer photodegradation at 25 °C with and without ZnO.

Table 8. UV light's influence on the photodegradation of H1 polymer at 25 °C with and without ZnO.

Time(min)	Abs. without ZnO	Degradation %	Abs. with ZnO	Degradation %
0	0.157	0	0.157	0
15	0.129	23.5	0.103	34.3
30	0.117	25.4	0.099	36.9
60	0.107	31.8	0.097	38.2
90	0.102	35	0.091	42.0
120	0.094	40.1	0.087	44.5
180	0.089	43.3	0.075	52.2

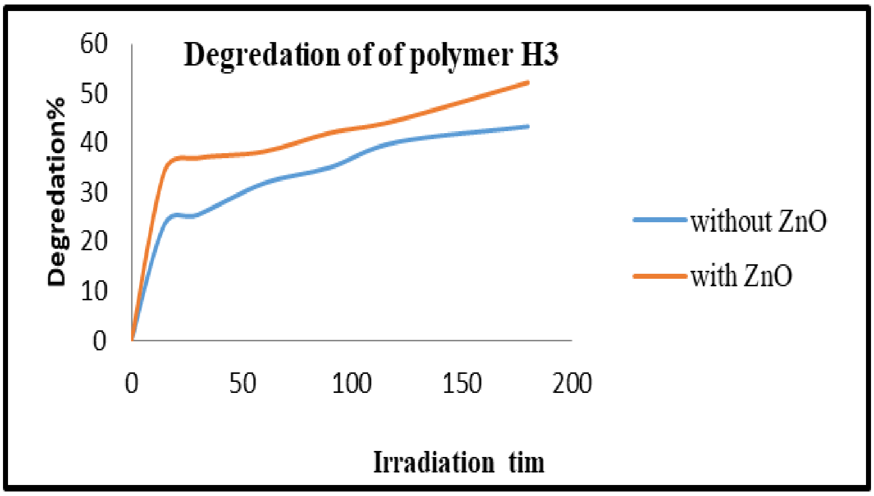


Figure 13. The effect photo degradation of polymer H2 with and without ZnO at 25 °C.

Photodegradation accelerates when ZnO is used as a catalyst for both H1 and H3On the other hand, UV contributes significantly to photodegradation in ZnO. When the light reaching the semiconductor exceeds or equals the band gap energy, as a consequence of the ZnO catalyst absorbing it, a positive hole (h+) is simultaneously generated in the valence band and an electron (e) is promoted from the valence band to the conduction band. This process of radical formation (•OH and $\bullet O_2\bullet$) can be described mechanically as follows:

$ZnO + hv\ (UV) \rightarrow ZnO\ (eCB^- + hVB^+)$
$ZnO\ (h\ VB^+) + H_2O \rightarrow ZnO + H^+ + \bullet OH$
$ZnO\ (h\ VB^+) + OH^- \rightarrow ZnO + \bullet OH$
$ZnO\ (eCB^-) + O_2 \rightarrow ZnO + \bullet O_2^{-}$
$\bullet O_2^{-} + H^+ \rightarrow HO_2 \bullet$

The fact that photocatalyzed degradation of organic materials in solution is recognized to be launched by the development of electron-hole pairs on the catalyst surface upon photoexcitation further supports the findings of these tests, which also show that UV light and the photocatalyst ZnO have a bigger impact on the efficient breakdown of H1 than H2.

Conclusion

This research has the potential to facilitate the development of novel synthetic polymers with exceptional qualities, which have garnered significant interest within the area of Emulsification. The modulation of artificial polymers has resulted in the acquisition of new or enhanced properties. The study on Modified Polymers focuses on developing various demulsifiers systems. Based on the current empirical study, multiple conclusions are to be sketched. To begin with, enhancing the separation time of the tested c leads to an improve in water separation. Additionally, the level of demulsifier concentration may significantly impact the prevention of water separation. Finally, enhancing the dose of demulsifiers will enhance the efficacy of water separation. Consequently, the addition of the polymer into the W\O emulsion triggers a process in which water droplets combine and merge. This demulsifier exhibits more deterioration than the commercial demulsifier.

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Authors’ Declaration

- Conflicts of Interest: None.

- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at University of Baghdad.

Authors' Contribution Statement

All the authors took part in the study by preparing experiments to synthesize the compounds, identifying the products, carrying out applications, and working together to write the final manuscript.

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تحضير وتشخيص مستحلبات نفطية جديدة مشتقة من البولي اكريل امايد مع بولي فنيل الكحول ودراسة تفككها الضوئي

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الخلاصة

من أهم المشاكل المصاحبة لإنتاج الزيت تكوين مستحلبات ثابتة من نوع (ماء في زيت) ، وهذه المستحلبات تؤثر بشكل كبير على عملية معالجة الزيت وتخليصه من الماء. يعتبر تكوين هذه المستحلبات أثناء إنتاج النفط مشكلة مكلفة ، كما أن المحتوى المائي المنخفض لمستحلبات النفط الخام يزيد الإنتاجية ويقلل من احتمالية تآكل خطوط الأنابيب والمعدات المستخدمة. يعد كسر الاستحلاب الكيميائي لمستحلبات الزيت الخام إحدى الطرق المستخدمة لتقليل محتوى الماء. يؤدي وجود المستحلب إلى عدم استقرار طبقة رقيقة بين مستحلب الزيت الخام وقطرات الماء ، مما يؤدي إلى اندماج قطرات الماء بسرعة. تضمن هذا البحث إعداد وتوصيف مزيلات الاستحلاب الجديدة من قواعد شف للاكريل امايد وكذلك من بولي فنيل الكحول التي تعتبر مركبات صديقة للبيئة صديقة للبيئة وفي نفس الوقت تتمتع بكفاءة عالية مقارنة بالمستحلبات المستوردة الأجنبية.. في هذا العمل ، تم إعداد مزيلات مستحلبات جديدة صديقة للبيئة وتساهم في خفض تلوث مياه الأنهار نتيجة استخدام المستحلبات الصناعية ذات السمية العالية. فحصت المركبات المحضرة باستخدام التحليل الطيفي بالأشعة تحت الحمراء والمطيافية بالرنين المغناطيسي النووي ، وكانت جميع الإشارات الطيفية للبوليمرات متوافقة بشكل جيد مع التركيب الكيميائي للبوليمرات. كذلك تم دراسة التحلل الضوئي للمستحلبات المستخدمة وقد وجد انها تمتاز بتفكك عالي ولها القدرة على خفض التوترات السطحية كذلك تم قياس الاستقرارية الحرارية للمركبات المحضرة .

الكلمات المفتاحية: اكريل امايد، مزيل الاستحلاب، النفط،، التحلل الضوئي، كحول بولي فاينيل.