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## Synthesis and Performance Evaluation of Newly Synthesized Waxy Crude Oil Dispersants and Inhibitors Using Styrene Based Copolymers

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## Abstract

Wax crystallization is gaining special attention and there are various techniques applied to minimize the problems caused by paraffin wax deposition to facilitate pipeline transportation and increase the production of crude oil. The application of pour point depressants is an efficient way of inhibiting wax deposition. In this work, pour point depressant additives were synthesized by the copolymerization of tetradecene (TD) with styrene (S) at ratios (1:1) and (1:2). After alkylating the synthesized copolymers by Friedel Craft they were modified by esterification and amidation. The prepared additives were characterized by Fourier transform infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, and gel permeation chromatographic analysis. Their performance as pour point depressants and paraffin inhibitors was explored. Various concentrations (500 ppm-2000 ppm) of tetradecene styrene ester and tetradecene styrene amide copolymers were injected into the collected waxy crude oil samples at 60 ℃. The obtained data showed that adding the synthesized copolymers; $ET_1S_1$, $ET_1S_2$, $AT_1S_1$, and $AT_1S_2$ into the waxy crude oil samples with a dosage of 2000 ppm enhanced the pour point depressant via decreasing the pour point temperature (PPT) value from 27 ℃ (crude oil blank) to 15 ℃, 15 ℃, 15 ℃, and 12 ℃ and achieved a paraffin inhibition of 67%, 70%, 71%, and 74%, respectively compared with the blank. The thermogravimetric study had shown good thermal stability for the esterified and amide copolymers as compared with their corresponding copolymers. So, the synthesized copolymers can be considered promising and applicable additives for depressing the pour point and inhibiting the paraffinic precipitates of the waxy crude oils.

## 1. Introduction

Improving the waxy crude oil flowability through pipelines for economical transportation has become a major challenge for the petroleum industry, which costs billions of dollars annually worldwide. Wax deposition occurs when the waxy oil temperature decreases below its wax appearance temperature (WAT) [1]. At the crystallization rate near the inner pipeline wall is faster, wax crystallizes out of oil solution with an orthorhombic structure that overlaps and combines to create three-dimensional networks [2]. With further decreases in temperature, the waxes adsorb on asphaltene and resin particles and cause severe problems in oil production, storage, and transportation [3-6]. The pretreatment with a small

dosage of polymeric additives as pour point depressants is one of the various developed strategies to overcome those problems which is usually cost-effective and time-saving [1, 7]. High pour point, yield stress, and viscosity are the main characteristics of highly waxy crude oils [8]. Pour point depressants (PPDs) addition is a promising and efficient way for wax crystallization modification via depressing the yield stress of crude oil [9-11]. Due to the higher selectivity of the PPDs additives, each additive is not effective for every crude oil. Polymeric PPDs interact with the wax crystals across four different aspects: nucleation, adsorption, solubility effects [12, 13], and co-crystallization into the paraffins structure by the interactions of van der Waals leaving the polar moiety end tail, creating a steric hindrance to the

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alignment of new input molecules of wax. Pour point depressant alkyl parts can be co-crystallized by wax, while the polar portions should be altered and interfered with the phase of wax crystallization [1, 14-17].

More attention has been paid to comb-like polymers as a type of developed polymeric PPDs to reduce the pour point of crude oils [18]. Owing to the polar groups; maleic anhydride, amine, vinyl acetate, etc., and also benzene rings presence in comb-like PPDs structure, inhibit the wax precipitation [19-21]. Accordingly, various modified ester and amide copolymers based on the waxy alkyl group can be a candidate to study their performance as pour point depressants. In the present work, comb-shaped tetradecene styrene copolymers were synthesized and characterized by various techniques including Fourier transform infrared (FTIR) spectroscopy, proton nuclear magnetic resonance ($^1$H-NMR) spectroscopy, and gel permeation chromatography (GPC). Also, their performance evaluation as wax dispersants and paraffin inhibitors for the Egyptian waxy crude oil was studied.

## 2. Experimental
### 2.1. Materials

All chemicals that were used throughout the present investigation were supplied from international companies; styrene (Fisher), toluene (Merck), tetradecene (TD), and hexadecyl amine were obtained from Acros Company. Octadecanol, p-toluene sulphonic acid monohydrate (PTSA), acetone, and methanol analytical reagents (Aldrich), and used as received. The benzoyl peroxide (BZP) initiator was received from LOBA chemicals and recrystallized from methanol. Qarun Petroleum Company fields were the source for the collected Egyptian waxy crude oil samples (NQ7 well). Table 1 summarizes the physicochemical features of the waxy crude oil as a fingerprint. Also, the distribution of n-paraffin of the isolated wax was calculated by an ASTMD 2887 gas chromatography analysis and illustrated by Fig. 1.

### 2.1. Co-polymerization of tetradecene with styrene

Different substrates of tetradecene styrene (TS) copolymers were prepared by free radical polymerization with two different molar ratios (1:1) and (1:2) of tetradecene and styrene, respectively.

**Table 1 Physical characteristics of the investigated waxy crude oil (NQ7)**

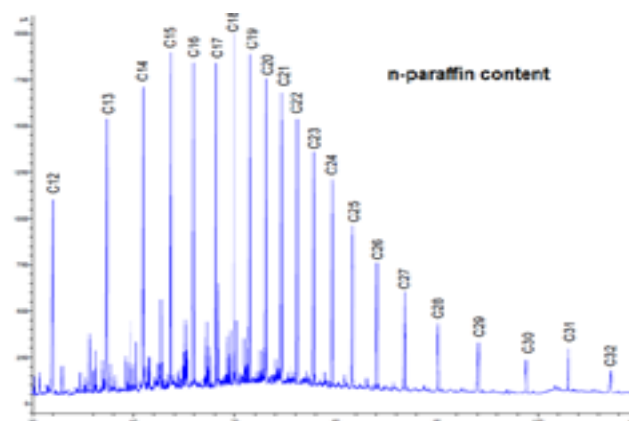| Parameter | Method | Result |
|---|---|---|
| **n-paraffins, (Wt %)** | ASTM D2887(GLC) | 55.3 |
| **API gravity at 60 °F** | ASTMD-1298 | 40.87 |
| **Density at 20 °C (g/cm$^3$)** | ASTM D1298 | 0.8201 |
| **Average carbon number (n)** | IP 372/85 (GLC) | 18.34 |
| **Kinematic viscosity at 40 °C.Cst** | ASTM D445 | 5.05 |
| **Wax content, (Wt %)** | UOP 46/64 | 12 |
| **Asphaltene content, (Wt %)** | IP 143/84 | 2 |
| **Ash content, (Wt %)** | ASTM D 482 | 0.01 |
| **Water content, (Wt %)** | IP 74/70 | 0.25 |
| **Pour point(PPt), °C** | ASTM D 97 | 27 |



**Fig. 1. Carbon number distribution of n-paraffin in waxy crude oil (NQ7).**

In detail, 19.63 g of tetradecene and 10.41 g of styrene or 19.63 g of tetradecene and 20.82 g of styrene were added in a three-necked flask with constant stirring at 60 °C for six hours in the presence of acetone as a solvent and benzoyl peroxide as an initiator (1 wt%) under nitrogen gas to perform copolymerization. Then, the copolymers were precipitated in an excess volume of methanol [19, 22], vacuum filtered and dried at 60 °C for 3 h. The prepared copolymers were designated as $T_1S_1$ and $T_1S_2$, respectively. The copolymerization reaction is illustrated as presented in scheme 1.
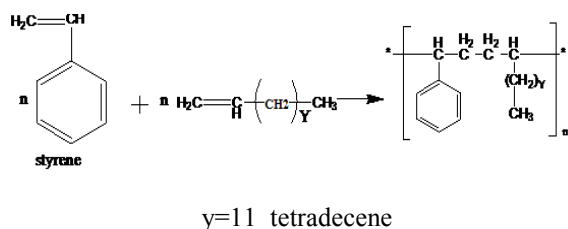
y=11 tetradecene

**Scheme 1: Copolymerization reaction of tetradecene with styrene.**

## 2.2. Fridel Craft alkylation

The synthesized copolymers (T1S1 and T1S2) were alkylated by the method described in the previous works [23, 24]. In brief, Fridel Craft alkylation reaction of the tetradecene styrene copolymers obtained from the previous step was performed with 2-chloroacetic acid for 4 h as shown in scheme 2. Then, the produced alkylated copolymers were designated as $FT_1S_1$, $FT_1S_2$.



2-chloroacetic acid
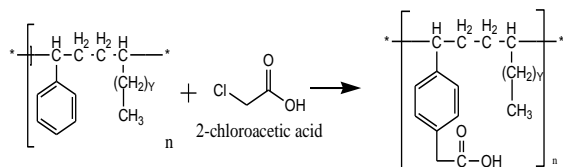
**Scheme 2: Fridel Craft alkylation reaction of tetradecene styrene copolymers with 2-chloroacetic acid.**
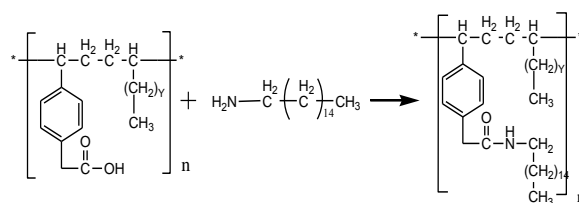
### 2.2.1. Esterification of alkylated copolymers

1 mole from each abovementioned alkylated copolymer ($FT_1S_1$, $FT_1S_2$) was esterified with 1 mole of octadecyl alcohol in the presence of *p*-toluene sulfonic acid (1 wt%) as a catalyst and hydroquinone (1 wt%) as an inhibitor. The ingredients were charged in a three-necked flat bottom flask fitted with the Dean-Stark trap until the theoretical amount of water was separated [13]. The resultant esters were collected and washed with 5% sodium hydroxide solution and distilled water and dried in air. These esterified samples were denoted as $ET_1S_1$ and $ET_1S_2$ and characterized by FTIR and $^1$H-NMR. Scheme 3 illustrated the esterification reaction of alkylated copolymers.
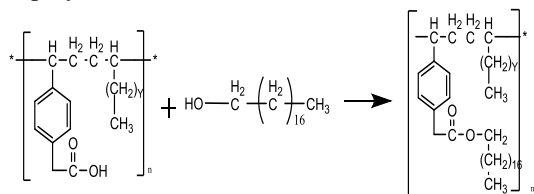


**Scheme 3: Esterification reaction of alkylated copolymers.**

### 2.2.2. Amidation of alkylated copolymers

An amidation reaction was conducted via charging 1 mole of the alkylated tetradecene styrene copolymers with 1 mole of hexadecyl amine in a three-necked flask using toluene as a solvent and the reaction was occurred at 140 $^0$C for 4 h under constant stirring. Before filtering off and washing the reaction products, they were purified by pouring in an excess of methanol. Then, the amides were dried under vacuum, denoted as $AT_1S_1$ and $AT_1S_2$ and characterized by FTIR and $^1$H -NMR. Scheme 4 illustrated the amidation reaction of alkylated copolymers with hexadecyl amine.



**Scheme 4: Amidation reaction of alkylated copolymers.**

## 2.3. Characterization

Fourier Transform Infrared Spectrometer (Nicolet IS-10 FTIR model spectrometer, ThermoFisher Scientific, Germany) over the wavenumber range of 4000–400 cm$^{-1}$ using KBr pellets was utilized to confirm the chemical structures of tetradecene styrene copolymers and their derivatives (esters and amides) [10, 23, 24]. $^1$H-NMR spectra have confirmed the structure of the synthesized polymeric additives. It was performed on Bruker High Performance Digital FT–NMR Spectrometer Avance 111 3OOMHz (Micro-analytical unit, NMR Laboratory of Pharmaceutical College, Cairo University, Egypt) using CDCL3 as a solvent and tetramethylsilane as a reference material [23, 25]. The copolymers have been investigated by gel permeation chromatography (GPC, Waters Model 515/2410, connected with a 515 HPLC pump and styragel HR THF 7.8X300 mm column, USA) at 40 $^o$C using tetrahydrofuran of 1 mL/min flowing rate as the eluent [26, 27]. Thermogravimetric (TGA) data of the copolymers were obtained from a simultaneous TGA-DSC model SDT Q-600 APPARATUS (USA) [28, 29]. In each experiment, a 0.01 g polymer sample was used at a heating rate of 10 °C.min$^{-1}$ from 25 to 600 °C under nitrogen atmosphere (25 ml.min$^{-1}$).

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### 2.4. The efficiency of the synthesized esters and amides copolymers

#### 2.4.1. As pour point depressants (PPDs)

The prepared tetradecene styrene esters and amides were incorporated in Qarun waxy crude oil sample at 60 °C at different concentrations of (500, 1000, 1500, and 2000 ppm). Then, the treated and untreated pour point of crude oil samples was measured according to ASTM D 97 [9, 13, 30]. Briefly, the pour point of a crude oil is the temperature below which the crude loses its flow properties due to wax development. ASTM D97 is used for measuring the temperature of pour point of the samples of crude oils [9, 26]. For this method, standard ASTM apparatus for pour point which includes test jar, thermometer, bath, and jacket was used for the determination of pour point. The sample was heated and the pour point was obtained at 45 $^0$C to 48 $^0$C and then cooled down and finally checked at an interval of every 3 $^0$C. When oil flow ceases on tipping the jar used for test horizontally, the particular temperature is recorded as pour point. It is used for quality estimation of the crude. Additionally, the performance of the synthesized tetradecene styrene esters and amides was compared with that of other materials reported in the literature.

#### 2.4.2. As paraffin inhibitors (PI %)

The Cold Finger experiment was performed at the Chemical Services and Development Center, EPRI, Cairo, Egypt to evaluate the synthesized copolymers' impact as PIs. This model is used as a convenient way to simulate the wax precipitation process inside the oil pipeline according to the method described in previous studies [25, 31]. After method completion, the residual deposition of wax was gradually removed from the cold finger, weighed and calculated according to equation (1):

$$PI\ \% = \frac{(\text{Weight of the blank} - \text{Weight after injection})}{(\text{Weight of the blank})} \times 100 \quad (1)$$

### 2.5. Crude oil component analysis

Wax was separated and quantified from the crude oil according to the UOP method (46/64) to determine its content [23, 26, 27]. Also, asphaltene was isolated and its content was determined by using the IP 143/84.

## 3. Results and Discussion

### 3.1. Crude oil composition

The average distribution for the molecular weight of the NQ7 was investigated through gas chromatography (i.e., IP/372/85 method) identifying the carbon number distribution of the waxy crude oil [32]. The results indicated that the n-paraffins are 55.3 wt% and the average carbon number distribution is 18.34 in the NQ7 waxy crude oil as shown in Fig. 1 and Table 1 which indicates the high wax content of this crude oil resulted in the petroleum industry serious problems.

### 3.2. Copolymers characterization
### 3.2.1. FTIR spectroscopy

Various absorption bands confirming the structure of tetradecene styrene copolymer and its corresponding alkylated copolymers, esters, and amides are presented in the collective FTIR spectrum; Fig 2. For tetradecene styrene copolymer, the stretching and bending vibrations of (=C-H, aromatic) are observed at 3052 cm$^{-1}$ and 744 cm$^{-1}$ and 823 cm$^{-1}$, respectively [29, 33, 34]. Aliphatic CH$_3$ and CH$_2$ stretching vibration bands are appeared in the range of 2910-3011 cm$^{-1}$ [25, 28], whereas their bending vibrational bands appeared at 1376 cm$^{-1}$ and 1463 cm$^{-1}$, respectively [30, 34]. The characteristic peaks of C=C (aromatic) stretching vibrations were observed at 1585 cm$^{-1}$ and 1493 cm$^{-1}$ [25, 28].
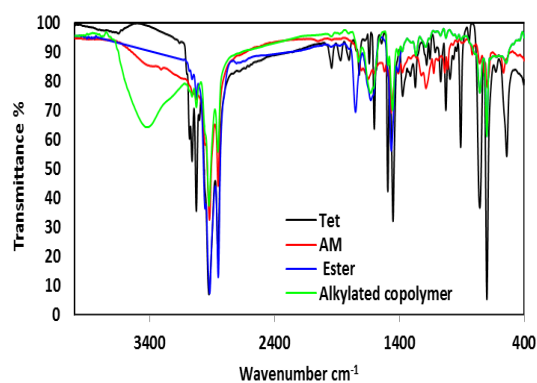


**Fig. 2. Collective FTIR spectra of tetradecene styrene copolymer, alkylated copolymer, ester, and amide.**

For the Fridel craft's alkylated tetradecene styrene (FTS) copolymer (Fig. 2), besides the stretching vibration of the (-C=O) appearance at 1720 cm$^{-1}$, the absorption band characteristic for the stretching

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(–OH) is also appeared at 3426 cm^{-1} confirming the occurrence of Fridel craft's alkylation reaction [25].

Also, the occurrence of esterification reaction for the alkylated copolymers (FTS) was revealed by the FTIR spectrum (Fig. 2). Besides disappearing the -OH stretching band of the (FTS) copolymers and the appearance of a new (C–O) ester band appears at 1173 cm^{-1} which is characteristic for the ester bond formation [25, 35].

From the FTIR spectrum of tetradecene styrene amide Fig. 2, the N-H (secondary amine) stretching vibration band appears at 3310 cm^{-1} and its bending band has appeared at 1620 cm^{-1}. Additionally, the C=O of the alkylated copolymers is shifted to a lower frequency. These findings confirmed the occurrence of the amidation reaction [25]. The C=O shift is due to the positive (+ve) inductive effect of the nitrogen atom leading to that the bond between carbon and oxygen being has single double character confirming the occurrence of amidation reaction.

### 3.2.2. ^{1}H-NMR spectra

^{1}H-NMR spectroscopy was performed to confirm the modified copolymers structures as depicted in ^{1}H-NMR patterns; Figs. (3-5). Copolymers formation is confirmed by the absence of any characteristic peaks for the olefinic double bond between 4 and 5 ppm in the ^{1}H-NMR spectrum [25, 36]. Moreover, the phenyl group of the copolymers is confirmed by the presence
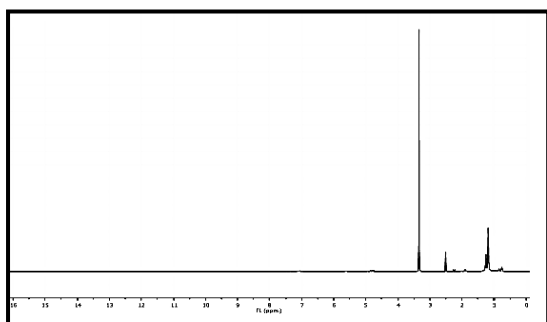


**Fig. 3. ^{1}H-NMR spectra for tetradecene styrene copolymer.**

of a signal at 7.2 ppm [37, 38]. Signals corresponding to methyl protons, long-chain methylene protons $CH_3-(CH_2)_n-CH_2$, $CH_2-C=O$ group, and the ester linkage ($CH_2O-$) group are observed at 0.9 ppm, 1. 3 ppm, 3.3 ppm, and 3.5 ppm [39, 40].
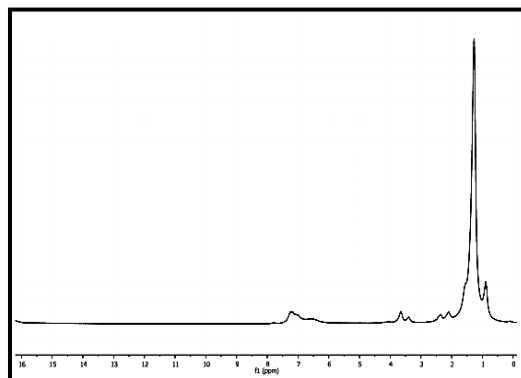


**Fig. 4. ^{1}H-NMR spectra for tetradecene styrene ester**



**Fig. 5. ^{1}H-NMR spectra for tetradecene styrene Amide.**

### 3.2.3. GPC data
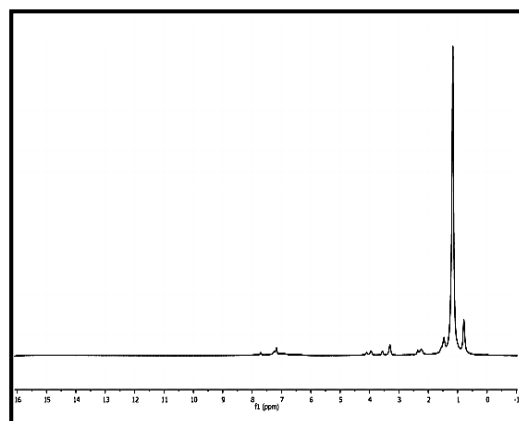
The results of the average molecular weight of the prepared copolymers which were measured by GPC are summarized in Table 2. Their average molecular weights are ranged between 100106 and 109400. The prepared tetradecene styrene amide ($AT_1S_2$) with a molecular weight of 109400 has the highest molecular weight and has the optimum effectiveness as a pour point depressant in the current study. Moreover, under the same polymerization conditions and with increasing styrene concentration, the copolymer molecular weight is increased.

| Copolymer designation | Copolymer name | Molar ratio (%) | Molecular weight (g/mol) | Polydispersity index (PDI) |
|---|---|---|---|---|
| $ET_1S_1$ | Tetrecenestyrene ester | 1:1 | 100106 | 2.546 |
| $AT_1S_1$ | Tetradecenestyrene amide | 1:1 | 105028 | 2.365 |
| $ET_1S_2$ | Tetradecene styrene ester | 1:2 | 102274 | 2.780 |
| $AT_1S_2$ | Tetradecenestyrene amide | 1:2 | 109400 | 2.665 |

**Table 2 Average molecular weights and polydispersity of the synthesized copolymer**

*3.2.4. study*

Fig. 6 represents the thermogravimetric analysis of the prepared copolymers. The degradation temperature of the copolymers is in the range of 170-465 $^0$C. Whereas the injection temperature at the wellhead starts at 60 $^o$C and the modified copolymers' degradation temperature starts at ~ 240 $^o$C, therefore the modified copolymers are stable at the injection temperature and have greater thermal stability than the corresponding origin copolymers. All the copolymers exhibit similar two-step degradation behaviour. The first degradation can be assigned to the organic modifier cleavage and correspond to the evaporation of the intra- and inter-molecular moisture [25], whereas the second degradation is corresponding to the copolymer backbone degradation.

**Fig. 6. Collective TGA of tetradecene styrene copolymer, ester ($ET_1S_2$) and amide ($AT_1S_2$)**
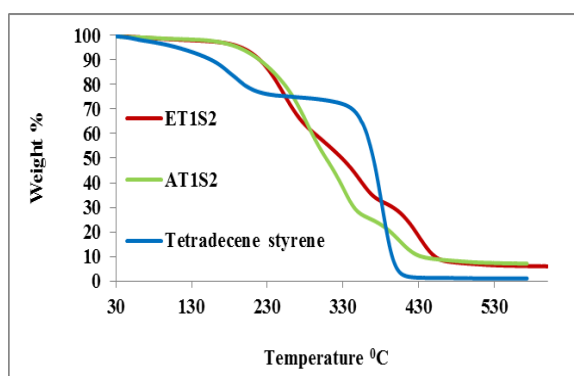


3.3 *Evaluation of the synthesized additives' efficiency*
   *3.3.2 As PPDs*

The efficiency of the synthesized tetradecene styrene esters and amides copolymers as PPDs for NQ7 Qarun waxy crude oil (blank PPT= 27 $^o$C) was studied and the resulting data were listed in Table 3. Among the various tested dosages of the prepared compounds (i.e. 500, 1000, 1500, 2000 ppm) and introduced to the waxy crude oil sample at 60 °C (injection temperature) [30], the 2000 ppm concentration of all additives exhibits the best efficiency as PPDs. This implies that the efficiency of the synthesized compounds as PPDs increases by increasing the additive concentration. Additionally, tetradecene styrene amide ($AT_1S_2$) copolymer is the optimum additive as a pour point depressant relative to other additives applied in this study. The existence of the $AT_1S_2$ electronegativity due to the polarity of this nitrogenous copolymer can support the PPD's required polarity [25-27]. Moreover, increasing the styrene percentage in this copolymer; $AT_1S_2$ resulted in increasing the benzene ring pendant of styrene leading to the enhancement of wax crystal dispersion via its adsorption on the wax crystals surface by intermolecular forces [26, 27, 41].

*3.3.3   As PIs*

The performance of tetradecene styrene esters and amides copolymers as paraffin inhibitors were evaluated by the "Cold finger test" and the obtained data are summarized in Table 4. The 9.5 g of the wax deposits isolated from the waxy oil (Blank) were reduced to 3.13 g, 2.85 g, 2.76 g, and 2.47g after injecting a dosage of 2000 ppm from ET1S1, ET1S2, AT1S1, and AT1S2 copolymers, respectively achieving paraffin inhibitions of 67%, 70%, 71%, and 74% as calculated applying equation (1). The maximum reduction of 74% for wax deposits achieved by introducing the AT1S2 copolymer to the crude oil is correlated with the abovementioned pour

point depressant results. This may be ascribed to the formation of a hydrogen bond between hydrogen and carbonyl group (C=O) which enhances the binding between paraffin and the introduced copolymers besides the occurrence of physical interactions (van der Waals forces) between paraffins [23, 26, 42]. Additionally, the alkyl groups of the prepared tetradecene styrene copolymers are co-crystallized with kinds of paraffin via replacing the paraffin molecules on the crystal lattice leading to random and more oriented wax crystals growth as a result of the extensive distribution of amidation and esterification sites [25, 27, 43].

**Table 3Effect of the prepared additives at different dosages on NQ7crude oil**

| Additive designation code | pour point depression ($^0$C), PPT | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Additive concentration, ppm | | | | | | | | |
| | Blank | 500 | | 1000 | | 1500 | | 2000 | |
| | PPD | PPD | Δ PPD | PPD | Δ PPD | PPD | Δ PPD | PPD | Δ PPD |
| Tetradecene styrene ester (ET$_1$S$_1$) | 27 | 21 | 6 | 18 | 9 | 15 | 12 | 15 | 12 |
| Tetradecene styrene ester (ET$_1$S$_2$) | | 21 | 6 | 15 | 12 | 15 | 12 | 15 | 12 |
| Tetradecene styrene amide (AT$_1$S$_1$) | | 18 | 9 | 18 | 9 | 15 | 12 | 15 | 12 |
| Tetradecene styrene amide (AT$_1$S$_2$) | | 15 | 12 | 15 | 12 | 15 | 12 | 12 | 15 |

**Table 4 Results of paraffin inhibition at the optimum dose (2000 ppm)**

| Copolymer designation | Paraffin Inhibition (PI %) |
|---|---|
| Blank of Untreated waxy crude oil | ----- |
| Tetradecene styrene amide (AT$_1$S$_2$) | 74 |
| Tetradecene styrene amide (AT$_1$S$_1$) | 71 |
| Tetradecene styrene ester (ET$_1$S$_2$) | 70 |
| Tetradecene styrene ester (ET$_1$S$_1$) | 67 |

PIs for waxy crude oil, and the obtained data are compared with the findings of other studies. As shown, the mentioned two copolymers are superior to most of the evaluated additives indicating the ability of their utilization as competitive PPDs and PIs additives. This enhancement in the AT$_1$S$_2$ additive performance over the others is due to the synergistic effect of the co-crystallization between the injected AT$_1$S$_2$ copolymer which possess high electronegativity due to the polarity of this nitrogenous copolymer and the wax crystals which inhibited the growth and precipitation rate of wax crystals in the crude oil.

*3.4. Comparing the PPD and PI results of ET$_1$S$_2$ and AT$_1$S$_2$ copolymers with other works*

As observed from Table 5, the prepared ET$_1$S$_2$ and AT$_1$S$_2$ copolymers were evaluated as PPDs and

| Additive Name | Additive dosage, (ppm) | PPD (°C) | PI% | Reference |
|---|---|---|---|---|
| Poly (alkyl linoleate-co-succinic anhydride) | 2000 | 18 | -- | [13] |
| (allyl 4-(decyloxy) benzoate) | 5000 | 18 | -- | [44] |
| (allyl 4-(dodecyloxy) benzoate) | 5000 | 15 | -- | [44] |
| ET$_1$S$_2$ | 2000 | 15 | 70 | This work |
| AT$_1$S$_2$ | 2000 | 12 | 74 | This work |

**Table 5** Comparison of the PPD and PI results of the current study additives with other additives

## 4. Conclusions

- In this article, two new copolymers were prepared by the free radical polymerization of tetradecene and styrene with two different molar ratios (1:1) and (1:2).
- The synthesized copolymers were then modified via Friedel Craft alkylation followed by modifying the alkylated copolymers by esterification and amidation reactions.
- The synthesized tetradecene styrene esters and amides were evaluated as pour point depressants and paraffin inhibitors for NQ7 Qarun waxy crude oil and their performance was compared with that of other materials reported in the literature.
- Various techniques including FTIR, 1H-NMR, TGA, and GPC were utilized to confirm the successful copolymerization of tetradecene with styrene, and the occurrence of the mentioned different modifications of the prepared copolymers.
- The chemical structure of the synthesized copolymers; T1S1, T1S2, AT1S1, AT1S2, ET1S1, and ET1S2 were confirmed by the FTIR and 1H-NMR data. The GPC results demonstrated that by increasing the ratio of styrene involved into the copolymer, the molecular weight of the produced copolymer increases.
- The TGA results demonstrated that the thermal stability of the esterified and amidated copolymers was enhanced relative to the pristine copolymers.
- All the synthesized copolymers were effective as PPDs and PIs for Qarun waxy crude oil. The PPD results indicated that the injection of 2000 ppm of AT1S2 copolymer into NQ7 Qarun waxy crude oil was the optimum dosage of this additive and exhibited the maximum pour point reduction among the series under study which reduced the pour point temperature from 27 ℃ (crude oil blank) to 12 ℃.
- Also, this optimum dosage injection achieved a PI of 74%.
- This enhancement was due to the synergistic effect of the co-crystallization between the injected copolymeric additive and the wax crystals which inhibited the growth and precipitation rate of wax crystals in the crude oil.
- So, the current study provides AT1S1, AT1S2, ET1S1, and ET1S2 copolymers with dual function as promising and efficient PPDs and PIs for the waxy crude oil.

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