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# SYNERGISTIC EFFECT BETWEEN ETHOXYLATED SURFACTANTS AND COMMERCIAL ADDITIVE ON THE DECREASE POUR POINT FOR DISTILLATE FUEL OIL

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**Abstract**

Two non-ionic ethoxylated surfactants were synthesized and confirmed by infrared spectral analysis and used individually as decrease of pour point for fuel oil then mixed with commercial flow additive. The critical micelle concentration (CMC), the surface excess concentration, $\Gamma_{max}$, the minimum area per molecule, $A_{min}$, and the effectiveness of surface tension reduction, $\pi_{CMC}$, were calculated using surface tension data. The effectiveness of these molecules as pour point depressant for fuel oil with respect to concentration and alkyl chain length of the prepared additives were discussed. Correlation between pour point depression and wax modification appeared to be merely qualitative in such heterogeneous fuel system. From these measurements, Photomicrographic analysis showed that a clear effect of the additives on the wax crystal modification which is in agreement with above results.

***Keywords:*** Nonionic surfactants; Distillate fuel oil; Pour point depressant; Surface activity; Photo micrographic analysis.

## 1. Introduction

The sedimentation of paraffin wax at low temperatures during the transportation of heavy oil difficulty distillates reduces the flow rate of these fluids. The lamellar wax sedimented forming cage-like structures which impede liquid flow and tend to plug fuel lines, screens and filters [1-3]. Wax difficulty problems in distillate fuel oil can be solved partially dewaxing processes and a linear polymer with long site chains of specific length and nature is one of the general characteristic of decrement of pour point and wax dispersion for distillate fuel oil [4-6]. Generally, pour point depressants change size of wax crystals that precipitate from the oil and diminish their tendency to interlock and set into gel [7-8]. Polymeric molecules that are constituted of hydrophobic chain are used as wax deposition inhibitors which facilitate the interaction between additive, paraffin and a polar part that is in charge of for the wax crystal, morphology modulation causing aggregation inhibition. For this reason, such wax inhibitors are known as wax crystal modifiers. For evaluation of the improved operability of the treated fuel oil, determination by cloud point and pour point tests are the most widely adopted photo analysis is used also as a screening tool confirming other laboratory tests for apprais al the flow properties of attended/unattended distillate fuel oil.

The surface active agents are assessed by their adsorption behavior, which are controlled by different factors. The effect of some of these factors was dealt with by some researchers [9-10]. Nonionic ethoxylated compounds are applied in several applications as petroleum industry, corrosion, Detergents, and others [11-13].

In this manuscript, preparation and appraisal of two nonionic surfactants have been carried out. The efficiency of these surfactants as additives to improve pour point are estimated. Effect of additive kind and mixed with other commercial additive on wax modification studied. Interpenetration of synthetic and commercial additive is a helpful trend from the economic point of view.

## 2. Experimental

### 2.1. Materials and synthesis

The fatty acids, dodecyl and octadecyl acids were purchase from Aldrich Chemicals. The fatty acids were esterified by stirring with polyethylene glycol (Merck Chemicals) according to the methods that was mention before [14]. The chemical structures of the synthesized molecules (I and II) are listed in Table 1. Commercial additive (III) was purchased from Merck.

Table 1. The HLB values and surface properties of the investigated surfactants

| Surfactants | Chemical Formula | HLB | T °C | CMC (mmol/L) | $\pi_{CMC}$ ($mNm^{-1}$) | $\Gamma_{max} X10^{10}$ ($mol\ cm^{-2}$) | $A_{min}$ ($Å^2$/molecule) |
|---|---|---|---|---|---|---|---|
| I | $C_{11}H_{23}COO(CH_2CH_2O)_{23}H$ | 16.67 | 35 | 2.00 | 38.00 | 0.83 | 2.01 |
| | | | 45 | 1.26 | 37.50 | 0.95 | 1.75 |
| | | | 55 | 1.07 | 37.00 | 1.25 | 1.32 |
| II | $C_{17}H_{33}COO(CH_2CH_2O)_{23}H$ | 15.60 | 35 | 2.51 | 34.50 | 1.15 | 1.44 |
| | | | 45 | 1.35 | 34.00 | 1.06 | 1.57 |
| | | | 55 | 1.58 | 33.00 | 1.08 | 1.54 |

### 2.2. Middle distillate fuel oil formation

Fuel oil sample sourced from Alexandria Company derived from the waxy western desert crude oil was used in appraisal of the performance of the synthesized additives. The physico-chemical preferential of the fuel oil are given in Table (2). In addition, the n-paraffin content of the used fuel oil tested to be specified by urea adduction [15]. Gas liquid chromatographic analysis (GLC) was applied to specify the average and distribution carbon number of the fuel oil.

Table 2. Physical characteristics of fuel oil

| Properties | Methods | Result |
|---|---|---|
| Specific gravity at 60/60°F | IP 160/87 | 0.8512 |
| Kinematics viscosity at 40°C (cst) | IP 71/80 | 4.7 |
| Cloud point (cp), °C | IP 219/82 | 24 |
| Pour point (pp), °C | IP 15/67(80) | 15 |
| Sulfur content (wt%) | IP 266/87 | 0.231 |
| Flash point, °C | IP 34/82 (87) | 123 |
| Total paraffins content (wt%) | Urea adduct | 21.3 |
| n-paraffin (wt%) | GLC | 20.9 |
| Iso-paraffins (wt%) | GLC | 0.40 |

### 2.3. Characterization of additives

The infrared spectra of sample (I) was recorded according to ATI Mattson Genesis series FTIR.

### 2.4. Evaluation tests

#### *2.4.1. Pour point test (ASTM D 97 -96)*

Sample of the investigated crude oil was doped individually at concentrations 200, 400, 600,1000 and 2000ppm with each of the prepared flow additives I, II, III, (I+II) at ratio (1:1) and (I+II+III) at ratio (1:1:1) successively according to IP 15/67 procedure, results are given in Table (3).

#### *2.4.2. Surface tension measurements*

The surface tensions of the synthesized surfactants were measured in aqueous solution by DeNouy Tensiometer (Kruss K6 type) at different temperature ranged from 35, 45 and 55°C for concentration range 0.04-8 mmol/L. The ring was washed by ethanol after each reading then by distilled water. The critical micelle concentration (CMC) of the synthesized molecules were evaluated from the semi logarithmic plot of surface tension versus concentration.

Table 3. The effect of additives on the pour point of fuel oil

| Additives designation | Additives | Additive concentration, ppm | PP, °C | ΔPP, °C |
|---|---|---|---|---|
| I | $C_{11}H_{23}COO(CH_2CH2O)_{23}$ H | 0 | 15 | 0 |
| | | 200 | -3 | 18 |
| | | 400 | -3 | 18 |
| | | 600 | 0 | 15 |
| | | 1000 | 0 | 15 |
| | | 2000 | 3 | 12 |
| II | $C_{17}H_{33}COO(CH_2CH2O)_{23}$ H | 0 | 15 | 0 |
| | | 200 | 3 | 12 |
| | | 400 | 3 | 12 |
| | | 600 | 6 | 9 |
| | | 1000 | 6 | 9 |
| | | 2000 | 6 | 9 |
| III | Commercial additive | 0 | 15 | 0 |
| | | 200 | 0 | 15 |
| | | 400 | 3 | 12 |
| | | 600 | 3 | 12 |
| | | 1000 | 3 | 9 |
| | | 2000 | 9 | 6 |
| PPD4 | I+II | 0 | 15 | 0 |
| | | 200 | -3 | 18 |
| | | 400 | 3 | 12 |
| | | 600 | 3 | 12 |
| | | 1000 | 6 | 9 |
| | | 2000 | 6 | 9 |
| PPD5 | I+II+III | 0 | 15 | 0 |
| | | 200 | -9 | 24 |
| | | 400 | -3 | 18 |
| | | 600 | 0 | 15 |
| | | 1000 | 0 | 15 |
| | | 2000 | 3 | 12 |

*PP = pour point, ΔPP = pour point depression*

### *2.4.3. Photo micrographic analysis*

Photomicrographs declare the independent action for wax crystallization of the attended and unattended fuel oil (FO) sample with the prepared additives at different ratios.

## 3. Results and discussion

### 3.1. Surfactant structure and characterization of the prepared additives

The chemical structure of the synthesized monoester was confirmed by the FTIR (Figure 1). Concerning the FTIR spectrum of the compounds, it is declared the following absorption bands at 2868.59 $cm^{-1}$($CH_2$str.), 1459.85 $cm^{-1}$ ($CH_2$ bend.), 1108.87 $cm^{-1}$ (C-O str.) and 1732.73 $cm^{-1}$ (C=O) [16].

### 3.2. Evaluation of fuel oil additives

### *3.2.1. As pour point depressant*

Results illustrated in Table 3 showed that the pour point diminishes with increasing the additive ratio. This is due to the oil solvation power. It is well known that the decrease the temperature, the decrease the solvation power of any solvent and vice versa. This depression in solvation power becomes clears when the ratio increases. Sufficient surface coverage is obtained additive (I) pour point depressant ΔPP = 18ºC is better in reducing the pour point than (II) ΔPP = 12ºC. The combination of (I) and (II) at ratio (1:1) leads to reduction pour

point ΔPP = 18ºC. This reduction may be attributed to entire solubility in hydrocarbon phase and due to interaction, that occurred between the two additives of the same class. I, II and commercial additive III in ratios (1:1:1) was added to the fuel oil, very nice result in reducing the pour point (PP) is observed. The pour point reducing effect of the mixture I, II and III is better than I and II and (I+II) additives ΔPP = 24ºC. These results indicated that synergistic effect occurred between the pour point depressants and commercial additive in the fuel oil.

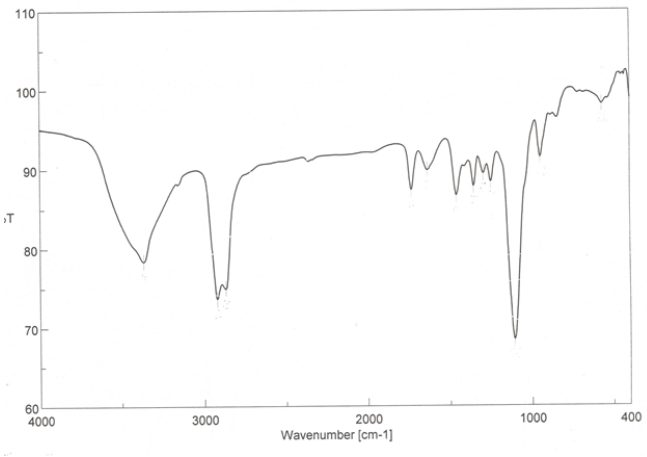


Figure 1. FTIR spectrum of an additive (I)

### *3.2.2. Surface properties*

The CMC of the investigated surfactants at 35, 45, 55ºC were calculated and listed in Table 1. By carful inspection to CMC values at 35°C, it is cleared that as the hydrophobicity decreased the CMC decreased. These linear behaviors agree with the expected trend by some investigators [17]. Also, from Table 1, it is noted that rising the temperature leads to decrease the CMC values that may be attributed to the desolvation of the surface active molecules with rising temperature [18].

The surface excess concentration $\Gamma_{max}$ in mol/cm$^2$ by applying Gibbs equation:

$$\Gamma_{max} = -\frac{1}{2.303RT}\frac{d\gamma}{dlogC} \quad (1)$$

$A_{min}$ in Å$^2$/molecule were calculated using the following relationship:

$$A_{min} = \frac{10^{14}}{N_A \Gamma_{max}} \quad (2)$$

Concerning the data listed in Table 1, slight increase in $\Gamma_{max}$ and decrease in $A_{min}$ upon raising the temperature [19]. This was expined by the priority of surfactant molecules to orientation rather than dehydration [20]. The effectiveness values ($\pi_{CMC}$), which determines their surface activity at CMCs [21] were decreased. Studies of the effectiveness of the synthesized molecules at 35ºC (Table 1) decreased with increasing the hydrophobicity. The decrease in the $\pi_{CMC}$ may be attributed to the increase in the area occupied at the interface. It was found that for all surfactants under investigation, $\pi_{CMC}$ decreased with increasing the temperature [22].

**The hydrophobic hydrophilic balance (HLB)**

For an ethoxylated non-ionic surfactant, the hydrophobic hydrophilic balance were calculated from the ethylene oxide percentage of the surfactant molecules using Griffin's equation [23].

$$HLB = \frac{mas\%EO}{5} \quad (3)$$

As the HLB increase the tendency of surfactant to partition between lypophilic and lypophobic media increase (9). The data listed in Table (1) revealed that the nonionic molecules can be considered as very good wetting and detergent according to Griffin's scale (23).

### 3.3. Kind of additive and wax inhibition

Photomicrographs assisted in Figure 2(a-d) has showed different wax morphology changes according to the kind of surfactant. Figure 4(a) showed-like crystals of approximate size of 100µm for the untreated fuel oil which on mixed with the additive (II) at 200ppm (Figure 4c) the wax crystals were impeded into the shot pointers but still of some conglomeration degree to size of 100 µm. On using the surfactants ( 2000ppm from I and 2000 ppm from I+II) higher wax inhibition degree was observed and fine disband wax crystals started to appear in (Figure 2b and 2d) respectively and creation of many number of fine disbanded crystals particularly by action of additive (2000 ppm from I+II+III) Plate 1e. Concerning the correspondent flow parameter measurement, was revealed that with the increments of additive activity in term of ΔPP, the induced wax inhibition efficiency increased according to the order: I+II+III>I+II=I >II, i.e. there is good correlation between measured flow parameters and wax.

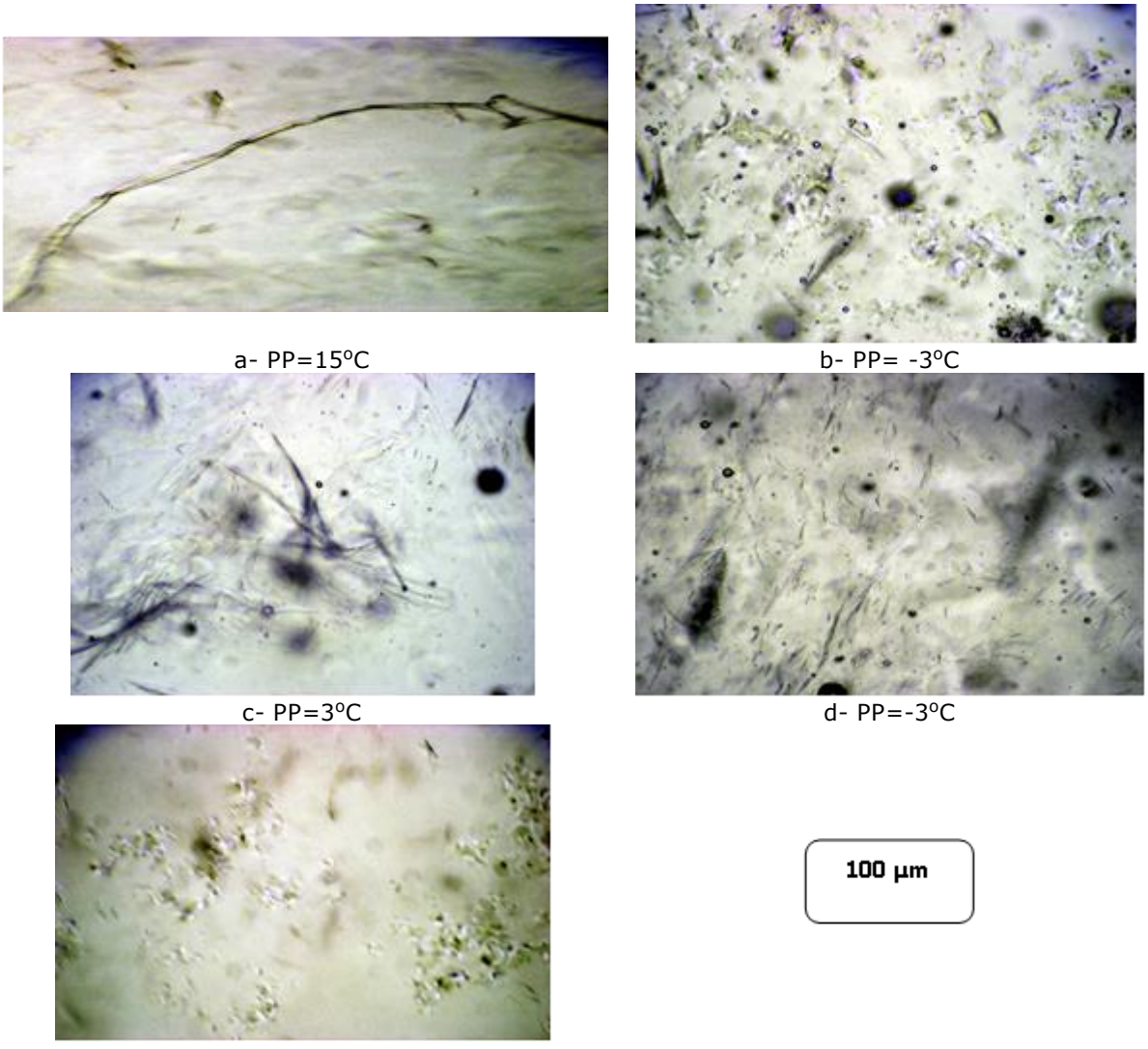


Figure 2. Photomicrographs of a: Fuel oil (FO) untreated, b: FO +200ppm (I), c: FO +200ppm (II), d: FO +200ppm (I+II) and e: FO +200ppm (I+II+III)

## 4. Conclusions

CMC and $\Gamma_{max}$ of the investigated surfactants were increased with increasing the hydrophobic chain length. $\Gamma_{max}$ increased while CMC decrease with increasing the temperature. Combination of commercial additive (III) with prepared additive (I+II) enhances the pour point depressant of the distillate fuel oil.

The effective of the prepared surfactants as pour point depressant diminishes by increasing the dosages and by grow thing the alkyl chain of the surfactants.

Compatibility of the combined additives in addition to bifunctionally in the one or more compound and commercial additive could be detected through photo micrographic analysis. A commit our self between the decrease of pour point for surfactant and grade of wax inhibitor has verified.

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