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Studies of Synthesized Nonionic Gemini Surfactant Based On Sulfonamide Moiety as Flow Enhancing Additive of Waxy Crude Oil

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Abstract

One of the most severe and long term issues in the petroleum industry is paraffin wax deposit of crude oil at low temperatures. The use of pour point depressants (PPD) has proven to be an effective method for preventing wax deposition. In this research, the synthesized nonionic gemini surfactant (NGS) is utilized as a PPD additive. The surface parameters of the NGS were assessed as the interfacial tension (IFT). The effectiveness of this additive as a PPD on the cold-flow properties of crude oil was investigated. Additionally, the commercial additive (CA) only and combined with NGS via varying ratio was properly evaluated as good PPD. The pour point (PP) measurements exhibit a significant decrease in the PP temperature, based on the particular ratio of NGS to CA and the different concentrations of additives in the crude oil sample. The additive (1mol NGS: 1mol CA) lowers pour point crude oil sample to a significant degree. At various temperatures below, high and equal to PP temperature, the shear rate-shear stress and shear rate- viscosity were estimated. The wax morphology has been observed to be substantially changed to fine, scattered crystals of a compact shape by the photomicrographic examination.

Key words: Gemini nonionic surfactant, pour point, wax modification, surface properties, and waxy crude oil.

1. Introduction

Flow guarantees are a major science and economic issue, as crude oil production in the western Egyptian desert is growing. The wax crystals (WCs) increase with a decrease in temperature, forming a crystalline net that traps liquid hydrocarbon molecules to prevent the oil flowing [1–6]. Wax deposition (WD) is in charge of the lowering in production, for the removal of deposits already produced, for raising the cost of processing and transporting crude oil products and in particular, for a variety of handling problems in areas at very low temperatures [7, 8]. When crude oil is transferred through pipelines in colder climates, the temperature of the region is lower than that of crude oil pour point, meaning that the oil is becoming less mobile and ceases flowing freely [9]. The rheological behavior of crude oil is strongly controlled by its chemical structure and temperature, as well as by its ancient thermal past. High paraffin crudes are non-Newtonian and also have is really a yield stress at and below their pour point temperature. The crude oil, although very complex chemically, is really a Newtonian fluid at a sufficiently high temperature. If the paraffin crude oil is permitted to cool, the wax will form crystals, agglomerate and entrap the oil into its structure. This phenomenon also happens if the ambient temperature of the area is below the crude oil pour point [10, 11].

Several approaches were attempted to avoid the combination of crystals. As it is the most effective and economical use for the industry, by the introduction of chemical additives, such as PPDs, cold flow (CF) enhancements, paraffin inhibitors (PIs) or wax crystal modifiers (WCMs) [12, 13].

Examples of PPD compounds are: olefin-maleic anhydride copolymer (MAC), polyethylene vinyl acetate (EVA), methyl methacrylate (MMA) and diethanolamine (DEA) [14, 15], comb polymer (maleic anhydride copolymer (MAC) and poly-acrylate/methacrylate (PA or PMA) ester polymers) [16], nonionic [17] and cationic gemini surfactants [18].

Gemini surfactants (GSs) are known as novel wax inhibitors. The surfactants can decrease the growth of WCs in diesel oils, but their abilities in waxy and heavy crude oils have only recently been explored. [16, 18, 19]. GS comprises more than one polar hydrophilic head and hydrophobic long chain tails

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that are chemically bound together with the spacer [20]. This makes (GS) more effective than other traditional surfactants. Its improved surface characteristics (to minimize surface tension) and lower critical micelle concentration (CMC) have gained increasing interest among academics and industrial practitioners.. Ahmed et al. (2018) [18] therefore proposed that the along alkyl chain performed a crucial element in affecting the depression of PP. In specifically, the surface properties relations, especially the interfacial tension (IFT) of the GS, the side chain length, and their effectiveness in the depression of PP, had been evaluated [21].

The recent work deals with utilizing nonionic gemini surfactant (NGS) as a PPD additive for waxy crude oil (without and with commercial additive by varying ratio). The rheological properties of crude oil with a PPD additive (without and with commercial additive) were also analyzed in terms of shear rate, shear stress and viscosity. Untreated and treated wax crystals with crude oil additives at 0°C below the pour point were screened by an optical polarizing microscope.

2. Experimental

2.1. Materials used

Both chemicals are of grade quality. Alexandria Petroleum Company has kindly supplied the CA. Crude oil used by Qarun Petroleum Company is Egyptian waxy crude oil.

Table 1 displays the physico - chemical properties of crude oil. The n-paraffin distribution of the isolated waxes was analyzed via examining gas chromatography in compliance with the ASTM D 2887 standard set out in **Table 1**. Waxy crude oil was used to assess the cold flow efficiency of the NGS, CA and mixed NGS with CA by differing ratios as a PPD.

Table 1: Physicochemical properties of the investigated waxy crude oil

Test	Method	Result
Density@15°C Kg/L	ASTM D1298	0.8652
Pour point °C	ASTM D97	21
Flash point °C (PMC)	ASTM D93	200
Asphaltene content, wt%	IP143	0.728
Wax Content, wt%	UOP 46/64	11.01
Water content wt%,	IP74/70	-
Total sulfur content, wt%	ASTM D4294	0.98
n-paraffins, wt%	ASTM D2887	62.27
Iso- paraffin, wt%	ASTM D2887	4.12
Total paraffins content, wt%	Urea adduct	66.39
Average carbon number (n)	calculated	28.56

2.2. Synthesis of nonionic gemini surfactant (NGS)

The synthesis of nonionic gemini surfactant, namely N,N'-(hexane-1,6-diyl)bis(4-dodecyl-N-(3-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)propyl) benzene sulfonamide) and the chemical structure confirming by spectroscopic analysis (FTIR, ^{1}HNMR and Mass spectra) was previously described **[22]**.

2.3. Interfacial tension measurement

The IFT among the crude oil & the aqueous phase of various NGS concentrations 0, 100, 250, 500, 1000, 2000 and 3000 ppm at 25 °C. was performed utilizing the Attention Theta Optical Tensiometer { Biolin Scientific Company, Finland} device which was described earlier **[23]**.

2.4. Evaluation of the prepared nonionic gemini surfactant (NGS) and commercial additive (CA) as pour point depressants (PPDs)

The various additives NGS, CA and mixed NGS with CA were evaluated as PPDs using crude oil by ASTM-97-93 pour point tests, respectively. The additive concentration influence was studied using different concentration varying from 100-3000 ppm.

2.5. Dynamic viscosity mensuration

Dynamic viscosity using (Brookfield viscometer USA), (DVII) for un-treated and processed crude oil with chosen PPDs, NGS (I), CA (II), blended [1mol NGS with 1mol CA] (III) and [2mol NGS with 1mol (CA)] (IV) at 2000 ppm and various temperatures (15, 20 and 27°C) has been studied. Furthermore, typical flow patterns which fairly define the non-Newtonian rheological flow characteristics of crude oil at temperatures around and below the PP have also been studied. The following equations will compute the shear strength, the shear stress and the viscosity.

Shear rate (D):

$D = M \times n\ (s^{-1})$

where; M = the shear rate factor and n = the actual test speed, depending on the viscometer sensor device. The actual test speed shall be determined as follows: n = speed / reduction factor (R) set.

Shear stress (τ):

$\tau = A \times S\ (Pa)$

where A = a shear stress factor, the measuring value (torque) depends on the form of measuring drive unit and sensor devic e, and S:

Apparent viscosity (η):

$\eta = (G \times S)/n\ (mPa.\ s)$

where G = an instrument factor, depending on the type of measuring drive unit and sensor system [24].

2.6. Photomicrographic analysis

The un-treated and processed wax crystals by crude oil additives at 0°C below the pour point was checked by a polarization microscope setup of Olympus BHSP with an automated 35 mm camera. The temperature of the crude oil sample measured was regulated on the microscope slide by a cooling thermostat. The magnification embraced was 100X.

3. Results and discussion

Scheme 1 indicates chemical composition of NGS.

3.1. Interfacial tension

The most critical measure of the impact of surfactant is their ability to reduce IFT among crude oil & H_2O. Fig.1 illustrates IFT values among the crude oil and the aqueous phase at different NGS concentrations. The IFT values were found to be decreased efficiently as the NGS concentration in the aqueous phase was increased. The IFT was approximately 24.4 mN /m among crude oil and water in NGS -free, and then decreased to 1 mN /m after 3000 ppm of surfactant applied. It is found that a good relationship exists between the additive's IFT and its efficiency in depressing the pour point. It will be deduced that NGS additive will alter the shape & size of the wax crystalline structure owing to the interfacial tension variation.

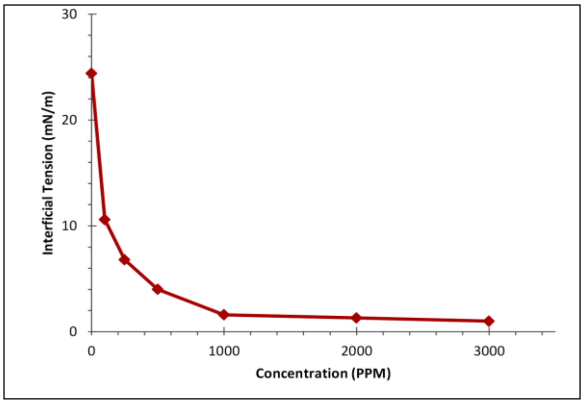


Fig. 1: IFT curve between the crude oil and aqueous phase at different surfactant concentrations.

3.2. Pour point depressing

The effect of NGS and CA on the PP of crude oil samples (I, II, III and IV) was studied. The outcomes in Table 2 and Figure 2 display the PP of crude oil samples pre and post addition of the additives at various doses (100,250,500,1000,2000 and 3000 ppm). The data indicated that the additives will minimize the temperature of the crude oil pour point from 21 to 9 °C with 2000 ppm of additive (I), from 21 to 12 °C with 2000 ppm of additive (II), from 21 to 0 °C with 2000 ppm of additive (III) and from 21 to 6 C with 2000 ppm of additive (IV). The PP of the crude oil sample under investigation is reduced as the additive concentration rises from 100 to 2000 ppm.

Analyzing the PP data given in Table 2 and Figure 2 it can be seen that the individual NGS, CA and their blend act as a good PPD. Additive II was found to be better than additive I. In the case of the blend additive III, the maximum decline in pour point was observed from 21°C (untreated crude oil) to 0°C at 2000ppm. Nevertheless, the blend additive IV give the less depressive because of to lower solubility. This means that the solubility is a significant consideration when considering boosting crude oil flow.

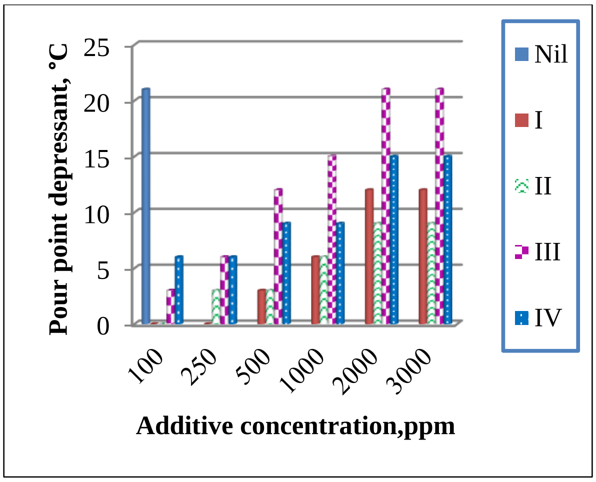


Fig. 2: Pour point of untreated and treated crude oil with different additives.

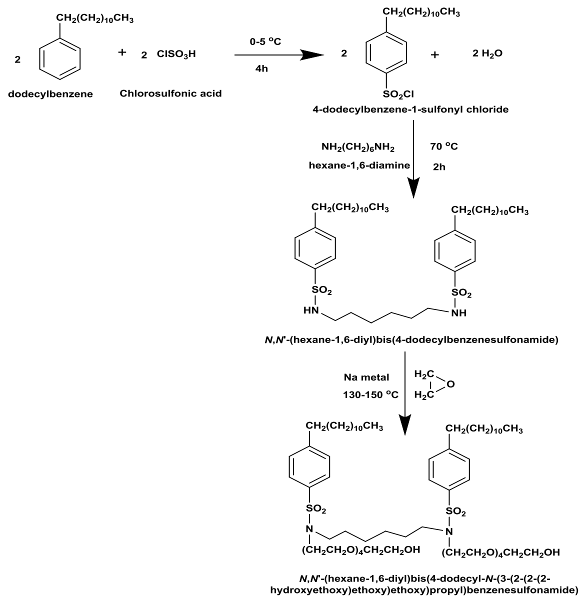
3.3. Analysis of rheological study

The WCs appear to settle on the cold pipe surface, when the oil is cooled during transport. When these deposits obtain as well dense they are able to decrease the transportation ability and lead to pigging difficulties.

Wax deposition in process equipment can result in more frequent shutdowns and operational issues WCs will also, in extreme cases, allow oil to gel and cause difficulties to restart the pipeline. A detailed understanding of the rheology of crude oil is therefore required in order to tackle these challenges, especially at low temperatures.

To a large degree, the nature, form and quantity of wax and its crystallization habits affect the flow properties. The movement properties of crude oil are heavily dependent on the shear rate, temperature, cooling rate, shearing time and crude oil composition [25].

The rheological analysis was conducted on crude oil without and with 2000 ppm I and III of additives. In Figures 3, 4 & 5 respectively, the values of dynamic viscosity against shear rate are given at 15ºC, 20ºC and 27ºC.The crude oil viscosity without the any additives is roughly constant having an increase in shear rate. This means that pure crude oil behaves at any shear rate as a Newtonian fluid. In the case of crude oil with additives, it is observed that at a low shear rate, the viscosity steadily reduces and the crude oil behaves like a non-Newtonian fluid. [26].



Scheme 1 indicates chemical composition of NGS.

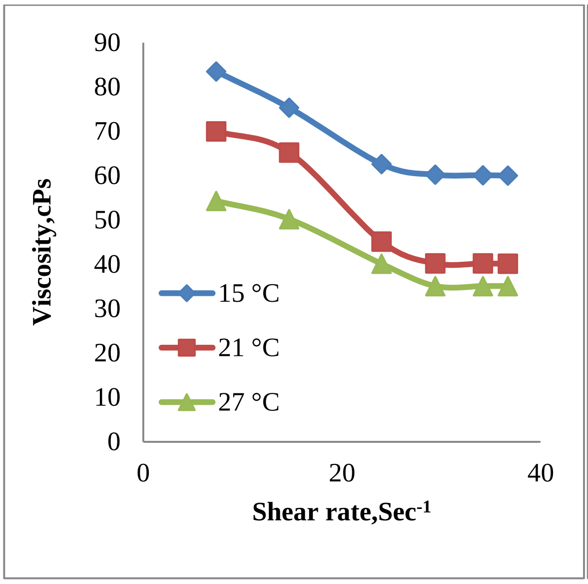


Fig. 3: Relation between shear rate and viscosity for untreated crude oil.

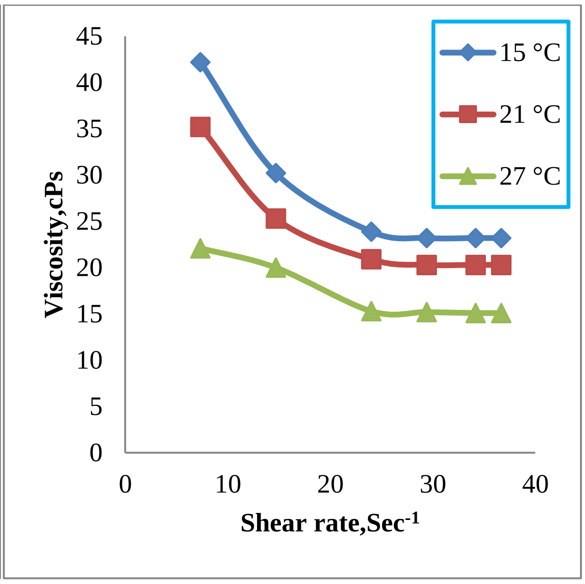


Fig. 4: Relation between shear rate and viscosity for treated crude oil with 2000ppm of additive (I)

However, the viscosity of the oil stays roughly constant at a high shear rate and it behaves like Newtonian fluids. At low temperatures, viscosity modifiers in crude oil exist as randomly aligned spherical coil and in the absence of shear, exert a high viscosity. As shear can be applied, the additives begin to rearrange themselves in direction of flow and reducing crude oil viscosity [27].

All additives are assembled in a flow direction at a high shear rate, and there is an insignificant change in viscosity. At higher temperature, viscosity-modifiers occur in an extended form in Figures 3, 4 and 5 and additives are conveniently organized in the direction of flow under shear and viscosity remains roughly constant at a high shear rate for all additive crude oil blended.

By in this manner the additives mitigate the decrease of the viscosity of crude oil under high temperature. Due to the application of shear and temperature change from 15, 20 to 27 oC, a reduction in viscosity was caused. It could be observed that shear stress increases at all temperatures with an improvement of the shears rate from the representative figures 6, 7 and 8.

Table 2: Effect of the types and concentrations of the additives on the crude oil pour point

Additives Designation	Symbol	Additives concentration, ppm	PP, ºC	Maximum change in pour point, ºC	Δ PP, ºC	Extend of solid point depression, ºC
NGS	I	0 100 250 500 1000 2000 3000	21 21 21 18 15 9 9	9	0 0 0 3 6 12 12	12
CA	II	0 250 500 1000 1500 2000 3000	21 21 18 18 15 12 12	12	0 0 3 3 6 9 9	9
1mol NGS:1mol CA	III	0 250 500 1000 1500 2000 3000	21 18 15 9 6 0 0	0	0 3 6 12 15 21 21	21
2mol NGS:1mol CA	IV	0 250 500 1000 1500 2000 3000	21 21 18 15 9 6 6	6	0 6 6 9 9 15 15	15

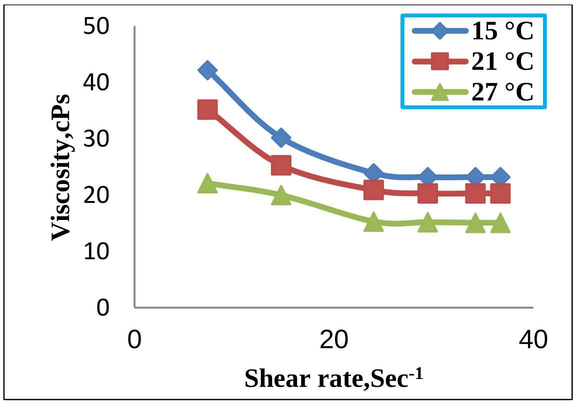


Fig. 5: Relation between shear rate and viscosity for treated crude oil with 2000ppm of additive (III).

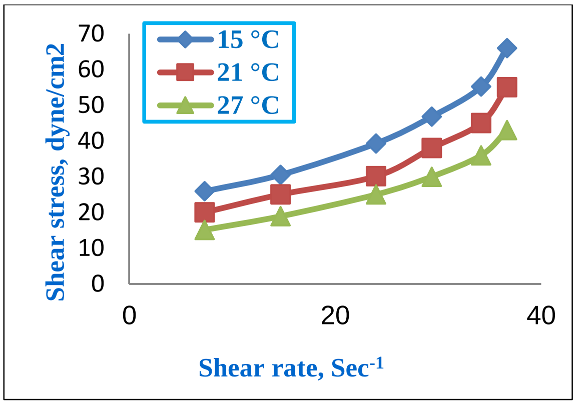


Fig. 6: Relation between shear rate and shear stress for untreated crude oil.

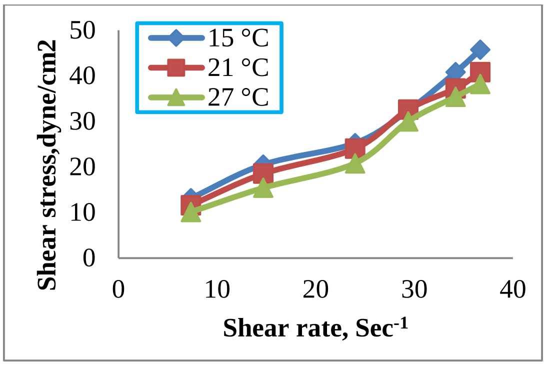


Fig.7: Relation between shear rate and shear stress for treated crude oil with 2000ppm of additive (I).

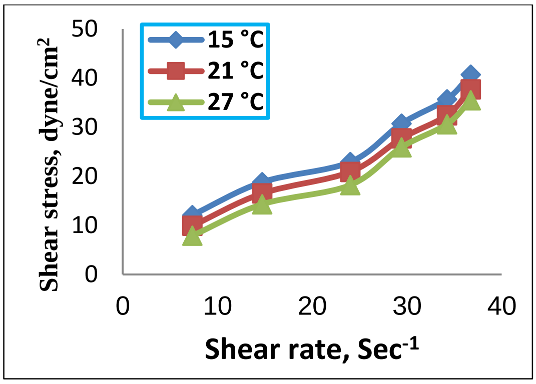


Fig. 8: Relation between shear rate and shear stress for treated crude oil with 2000ppm of additive (III).

Figures 6, 7 and **8** demonstrate the non-Newtonian pseudo-plastic properties of untreated and processed crude oil with additives in the temperature range being studied, because shear rate vs. shear stress cannot move through origin and viscosity is decreased with an increase in shear rate and after shear rate of 30 s^{-1}, and becomes almost constant. In the case of untreated crude oil, shear stress rises dramatically with a rising shear rate in such a way that the cold flow pattern follows a non-Newtonian yield pseudo-plastic rheological behavior as seen in **Figures 6, 7** and **8**. For crude oil left untreated, shear stress increases sharply with higher shear rate so that the cold flow pattern exhibits non-Newtonian produce pseudo-plastic rheological actions as proven in **Figures 6, 7** and **8**. As a consequence, the behavior of decreasing rheological parameters following the addition of prepared NGS may be attributed to their chemical structures.

The slight polarity of the benzene ring and the high polarity of oxygen and nitrogen in the NGS structure play an important role in preventing the agglomeration of WCs in crude oil. Moreover, the contact between the alkyl chain and the paraffin fraction in the oil is due to a strong fit of the length of the alkyl chain.

3.3. Paraffin crystal morphology study

For the investigation of microscopic crystal morphology the saturated hydrocarbon has been isolated from crude oil **[24]**. **Figure 9** indicates the effects of untreated/treated saturated hydrocarbon crude oil with NGS, CA and mixed NGS, CA by various ratios below 0°C. It was observed that WCs exhibit a flocculent structure in the control test as seen in **Figure 9a**, which can form a three-dimensional network, grow wax lattice and trap liquid hydrocarbon molecules until the oil cannot flow. Compared to the control sample test, WC morphology in the treated crude oil samples has substantial differences as seen in **Figures 9b** and **9c**.

Figures 9d and 9e also demonstrate that paraffin crystals in the treated crude oil samples III and IV are smaller and thinner than those in the untreated sample. Not merely does the average particle size decrease; but the particle morphology furthermore shifts to the form of fine dispersion wax, which is compatible with the interaction of crude oil additives as both a nucleation agent and a growth inhibitor. This indicates that the additive (III) is better than the other various additives as PPD. This is consistent with the PP values determined by the ASTM-97-93 method.

4. Conclusion

The conclusion of the work can be discussed in the following points:

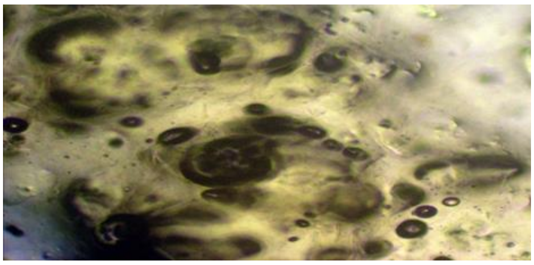
(1) The effect of NGS as a PPD and the rheological properties of untreated and processed crude oil have been studied.

(2) The IFT between crude oil and the aqueous phase has been discussed at various concentrations of NGS.

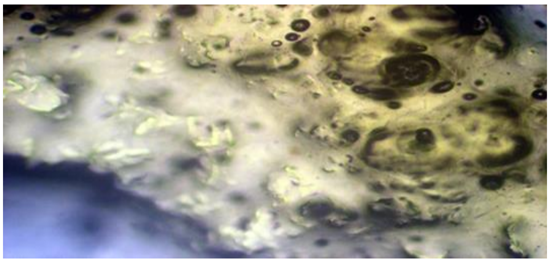
(3) Effects of NGS, CA and blended NGS with CA by varying ratios on crude oil PP were examined and it was observed that the PPD rises with an increase in the concentration of the additives used.

(4) The maximal synergistic impact in pour point depression was reached by (1mol NGS: 1mol CA), (pp2000ppm=0oC, Δpp2000ppm=21oC) of additiv (III) compared to (2mol NGS: 1mol CA), (pp2000ppm= 6oC, Δpp2000ppm =15oC) of additive (IV).

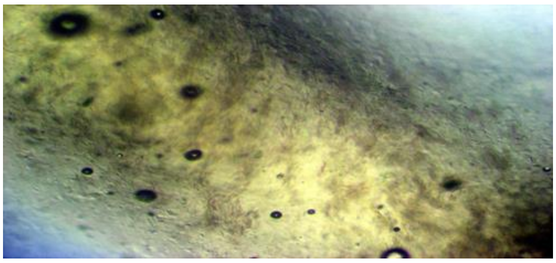
(5) Photomicrography as a simple and rapid analytical tool has been used to show the wax changes induced by PPDs in accordance with their type and compatibility of NGS and CA with crude oil through various ratios. This confirms that WCs are usually dispersed, depending on the ratio of the additive used.



a- PP = 21^{o}C

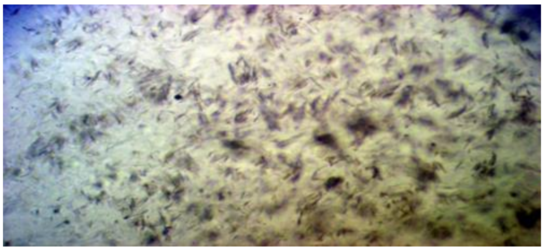


b- PP = 9^{o}C



C-PP = 12^{o}C

d- PP = 0^{o}C



e- PP = 6^{o}C

Fig. 9: Photomicrographs of a: untreated crude oil (CO), b:(CO)+2000ppm of (I), c: (CO) + 2000ppm of (II), d: (CO)+2000ppm of (III) and e: (CO)+2000ppm of (IV).

Conflicts

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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