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STUDIES THE EFFECT OF HYDRAZIDE DERIVATIVES AS FLOW IMPROVERS FOR WAXY CRUDE OIL

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Abstract

Adding pour point depressants (PPD) to lower the pour point of crude oil is a powerful and economical way of increasing the cold flow properties of the oils. The impact of two ethoxylated stearyl hydrazides (E10 = 10 ethylene oxide units (e.o.) and E20 = 20 e.o.) on the pour point, and rheological properties of crude oil examples were studied. The result with their structure on the surface activity as critical micelle concentration "cmc," a maximum surface excess concentration "Γ_{max}" and minimum area per molecule, "A_{min}". The standard free energy of micellization and adsorption were calculated and discussed. Efficiencies of the two hydrazides additives were influenced by number of the ethylene oxide units, the much longer group of ethoxylate (E20) was the better result in the reduction of pour point and obvious viscosity. From the results, it is found that E20 exhibited maximum pour point depression and improve the calorific values of crude oil.

***Keywords**: Hydrazide derivatives; Surface activity; Crude oil; Flow improvers; Rheology.*

1. Introduction

One of the most actively traded commodities in the world is crude oil. The global demand for crude oil has been maintaining a stable gross annual growth rate. Crude oil with a higher wax content has a high pour point "PP" and low-temperature fluidity. In addition, the transportation and extraction of this oil became more complicated. Pour-point depressants "PPDs" are added in the industry for the wide transmission of this oil. Recently, several types of PPDs have been developed, which caused modification to the wax crystals forming a three-dimensional network, resulting in a decreased pour point of the crude oil [1-3].

Many polymeric molecules are used as flow improvers, which are chemical additives that can affect nucleation, adsorption or solubility of waxes. A copolymer of ethylene and vinyl acetate has widely used in the pipeline transportation of crude oil was studied as an excellent pour point depression efficiencies [4-5]. Another alternative method to reduce the viscosity of the oil is the utilization of flow improvers "FI" that can affect the wax properties. The modification of wax crystallization leads to depress both viscosity and PP of crude oil and give stress appreciably. Although crude oil treatment with chemical additives is not the only known methods, it remains the recommended methods comparing with pigging, heating, and biological treatments [6-8].

Pour point depressants, and movement improvers are additives that used to diminish the pour point and enhance the flow characteristics of crude oil, respectively. In doing that PPD's and movement improvers should have a lipophilic chain in addition to the lipophobic group, these requirements are achieved by surface active agents [9-11].

Because of the amphiphilic characters of surfactant molecules, they are widely used in several fields of applications. Surfactants have different kinds that differ based on the type of headgroups. Non-ionic surfactants that possess long lipophilic alkyl chain and long lipophobic ethylene oxide chain were applied as PPDs and give higher efficiency [12-14].

In this paper, the surface activities, the standard free energy of micellization and adsorption are determined of two hydrazide molecules with different ethylene oxide units (E10 and E20). These compounds are examined as pour point depressants and rheology improvers for crude oil sample from Petroleum Company. The effect of the structure of surfactant additives used as crude oil movement improver additives on the pour point and rheological properties of crude oil samples examined. The relationship between the chemical structures of these well-prepared surfactants and their influence on the calorific value of crude oil are discussed.

2. Experimentals

2.1. Crude oil used

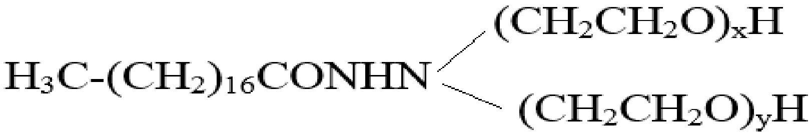
Crude oil with high wax content was obtained from Egypt (Qarun Petroleum Company). Their physicochemical properties are listed in Table 1. The n-paraffin circulation of the isolated waxes was determined by gas chromatography analysis according to American Society for Testing and Materials "ASTM" D 2887 standard.

Table 1. Physicochemical properties of the investigated crude oil

Test	Method	Result
Density@15°C, kg/L	ASTM D1298	0.865
Pour point, °C	ASTM D97	24
Flash point, °C (PMC)	ASTM D93	200
Kinematic viscosity at 40°C, cSt	ASTM D445	243.59
Kinematic viscosity at 100°C, cSt		18.94
Wax content, wt%	UOP 46/64	11.01
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. Surfactants

The prepared ethoxylated stearyl hydrazide, E10, contains 10 ethylene oxide (e.o.) units, and E20 contain 20 e.o. units (Figure 1). The compounds were prepared in previous work through two steps and are being used after chemical structure confirmation [15].



$$H_3C\text{-}(CH_2)_{16}CONHN\begin{cases}(CH_2CH_2O)_xH\\(CH_2CH_2O)_yH\end{cases}$$

Figure1. Chemical structure of E10 and E20 where x+y =10 and 20, respectively

2.3. Sample preparation

Synthetic surfactants (E10 and E20) dissolved in a certain amount of toluene. A certain volume of the toluene solution of surfactant was added gradually into a required amount of the crude oil under stirring, and the mixture utilized to form a stable and homogeneous sample. The sample was taken for measurements.

a- As pour point depressants

The prepared compounds were examined as pour point depressants using crude oil through the pour point testing in line with the ASTM-97-93, respectively. The effect of additive concentration was investigated by using different concentrations ranging from (2.5–30.0)x10^3 ppm.

b- As rheology measurements

Brookfield DV-III programmable rheometer (M/97-164-D1000) is used to determine the dynamic viscosity at different temperatures above and below the pour point of the used crude oil (15ºC, 20ºC, and 30ºC). The viscosity is measured at different shear rates in the range of 1.0-200 sec^{-1}. The measurement was carried out at 0.5% g/100 mL and 2.5% g/100mL additive concentration.

c- As the calorific values

ASTM (D240) is used to determine the calorific values for the crude oil in the absence and presence of the additives.

2.4. Surface tension measurements

The surface activity of the E10 and E20 was examined via surface tension measurements using Kruss K6 tensiometer. The ring is oriented to the interface of various ranges of concentrations (0.05 - 0.03 x 10^{-3} mol/L) and the force exerted on it is measured. After each measurement, the ring was washed with ethanol then di-ionized water. The critical micelle concentration, cmc of the investigated molecules were evaluated from the surface tension concentration curve, and the data were listed in Table 2.

Table 2. Surface activity and standard free energy of micellization and adsorption

	cmc, 10^{-3} mol/L	Γ_{max}, 10^{10} mol/cm^2	A_{min} Å^2/molecule	π_{cmc}	ΔG^0_{mic} kJ/mol	ΔG^0_{ads} kJ/mol
E10	2.479	2.479	66.976	34.2	-16.01	-17.37
E20	1.456	1.456	114.052	30.2	-14.29	-16.37

3. Results and discussion

3.1. Surface properties

3.1.1. Maximum surface excess concentration "Γ_{max}"

The concentration of surfactant molecules at the user interface per unit area is defined as the Γ_{max}, and calculated from surface tension using Gibb's equation:

$$\Gamma_{max} = \left(\frac{1}{2.303RT}\right)\left(\frac{\delta\gamma}{\delta logC}\right) \qquad (1)$$

where: γ is the surface tension; C is the concentration; R is the universal gas constant and T is the absolute temperature.

Concerning the data in Table 2, the increase in the ethylene oxide unit increase the excess surface concentration. This may explain by the coiling of the e. o. units in case of E20 which cause a decrease in the lipophobic properties. In addition, it prevents the formation of a meander type and decreases its hydrophilic character [16]

3.1.2. Minimum surface area "A_{min}"

The area occupied by each adsorbed molecule at the interface calculating from the following equation:

$$A_{min} = \frac{10^{16}}{\Gamma_{max} N} \qquad (2)$$

where N is Avogadro's number.

Concerning the data in Table 2, the increase the e.o. units shift A_{min} to higher value due to the large surface area occupied by the coiling of the long e.o. chain.

3.2. Standard free energy of micellization and adsorption

The thermodynamic parameters of adsorption and micellization of the investigated surfactants are calculated according to Gibb's adsorption equations:

$$\Delta G^0_{mic} = RTlnC \qquad (3)$$

$$\Delta G^0_{ads} = \Delta G^0_{mic} - 6.023 \times 10^{-2} \times \pi_{cmc} \times A_{min} \qquad (4)$$

The data listed in Table 2 declare that, ΔG^0_{mic} have negative values, which decrease with increasing the hydrophilic moiety indicating spontaneous micellization process [17]. ΔG^0_{ads} for both additive (E10 and E20) were less negative value comparing with ΔG^0_{mic} for each one, which implies that both additive favor adsorption rather than micellization. The chemical structure of these additives is the controlling factor influencing their thermodynamic aspects.

3.3. Pour point depressants

The test results on pour point are shown in Table 3 as evidenced by pour point reductions with regards to the pour point of the crude oil minus the pour point of crude oil with additives. Table 3 show that E10 and E20 were quite effective in lowering the pour point of crude oil. The effectiveness of the investigated compounds as a pour point depressants depended on both the concentrations and the number of e.o. units of the investigated surfactants. The performance increased with the increase in the number of the ethylene oxide units of the investigated compounds. The reason why was that the surfactants functioned by adsorption onto the crystals being developed to redirect their crystal development and by co-crystallization to create much smaller isotropic crystals and higher solubility wax in the combined crystals providing as the move improver [18]. Under the same conditions, the long ethylene oxide chain could increase the compatibility of the additives in the crude oil and could destroy the established interlocking network of the waxes.

Table 3. The effect of surfactants on pour point of crude oil

Sample, conc. g/100mL	Pour point reduction, °C E10 PP		E20 PP	
	PP	Δ PP	PP	Δ PP
0.25%	21	3	15	9
0.50%	18	6	15	9
1.00%	18	6	12	12
2.00%	12	12	6	18
2.50%	9	15	3	21

3.4. Influence of surfactants on the viscosity of crude oil

The effects of concentration of E10 and E20 on the viscosity of crude oil are shown in Table 4. The presence of additives caused a strongly reduced amount of apparent viscosity of crude oil.

Table 4. Influence of temperature on DVR of the crude oil with addition of surfactant

Temperature,ºC	DVR,% 0.5 %g/100mL E10	2.5%g/100mL E20	0.5 %g/100mL E10	2.5 %g/100mL E20
15	10.3	20.91	32.21	44.33
21	12.88	28.66	41.70	60.55
30	18.33	30.91	48.22	72.61

The obvious viscosity reduced with an increasing concentration amount of ethylene oxide unit. This could appear because the molecules getting together with the high-molecular compounds in crude oil increased with a growing concentration of the additives and the effect could prevent wax and asphaltene from developing hydrogen bonds. The degree of viscosity reduction (DVR) is created to gain access to the degree of the viscosity decrease, , and it could be determined by the following equation:

$$DVR = \frac{(\eta_0 - \eta_c)}{\eta_0} \times 100 \quad (5)$$

where: η_0 : the apparent viscosity (Pa·s) of the crude oil at a shear rate of 1.0-200 sec^{-1} and a certain temperature and η_c (Pa·s): the equivalent obvious viscosity of the crude oil after addition of the additives (E10 and E20) at shear rate of 1.0-200 sec^{-1} and the equivalent temperature [19].

The DVR of the crude oil with addition of hydrazide derivatives above the temperature range of 15- 30ºC at a shear rate of 1.0-200 sec^{-1} is detailed in Table 4. It is noted that there is a significant increase in DVR with increasing temperature. This may be related to two reasons. The first reason was that the temperature had a strong influence on the obvious viscosity of heavy components in crude oil such as wax and asphalting. The second reason was that high temperature had an effect on the chemical composition of heavy components that could lead to destroying the ordered structures of heavy components in the crude oil [19-20].The effects of e. o. unit on the DVR of crude oil are shown in Figure 2.

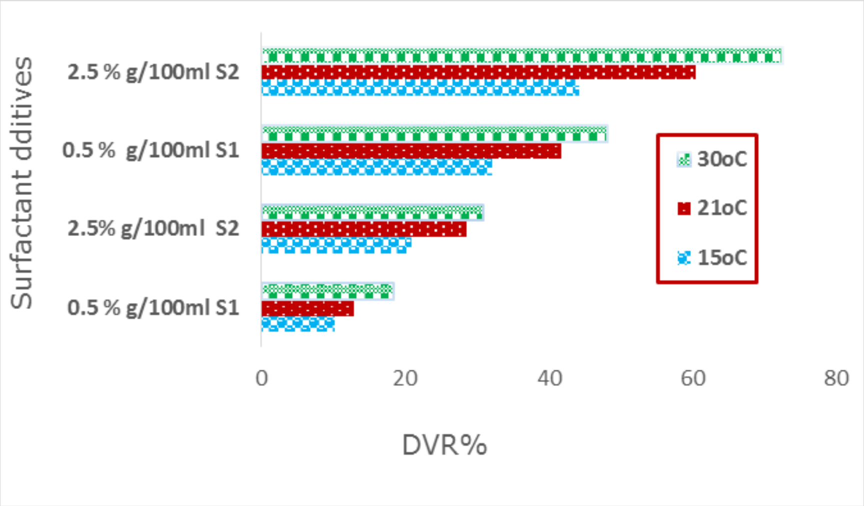


Figure 2. Variation of the temperature of DVR of the crude oil with S1(E10) and S2(E20)

It could be seen that the DVR increased with a growing hydrophilic group, which show the formation of the comb-like polymer, and the dispersion of the additives (E10 and E20) in the crude oil could be improved. Asphaltenes have hydrogen bonded phenolic OH species and nitrogen bases which can provide go up to proton transfer complexes, and the complexes are responsible for the rise in the viscosity of oil crude [21]. The heteroatom of the investigated additives "oxygen and nitrogen," may cause changes in the orientation of the aliphatic part of asphaltene and don't connect to the polar groups that can be found in asphaltene complexes to avoid the polar groups of asphaltene from developing hydrogen bonds that could destroy their ordered structures. The lipophilic chain is crystallized with the wax and the polar end groups which are responsible for disrupting the crystal composition of wax. This technique inhibits the crystals for agglomerating developing a gel-like composition to deposit on the pipeline surface. Because the efficiency of additives as move improver is influenced by their surface activities, the changes of the hydrophobic and hydrophilic groups are required [22].

Moreover, the tendency of the looked into surfactants to adsorption facilitate the well adsorption of the polar groups in the crude oil. The polar groups of the investigated surfactant are distributed into the ordered composition of the wax and asphaltene and may destroy their space network composition.

3.5. Effect calorific value of the additives on the calorific values of crude oil

The calorific values (dependent on Mohler Bomb and Boy's calorimeter) are discovered for crude in lack and occurrence of E10 and E20 and complete in Table 5. Which complete mounting brackets (Table 5) were given as gross calorific values in different commercial applications, however, the merchandise of combustion leave the place at temperature amounts will more than 25°C, which means normal water produced remains in the vapour talk about. The calorific regarding water remains as vapour is specified as net calorific value. There will vary methods could be used to calculate the calorific value of crude essential oil [23-24]. The amount of the radicals increase by incorporation of ethylene oxide group surfactants, which coupled with hydrogen as normal water and hence improved the calorific value of the analyzed crude. The incorporation of nitrogen in the applied additive escalates the calorific value for all people tested crude oil one of the set of other additives.

Table 5. Calorific values of the crude oil with and without surfactants

Additives	Crude oil
Blank	42.770
E10	42.949
E20	43.612

4. Conclusion

The surface activities of ethoxylated stearyl hydrazide E10 and E20 are affected by their structure. The value of the free energies of micellization and adsorption give an indication about their spontaneous behaviors. E10 and E20 have a good effect on reducing pour point a good effect on reducing viscosity.

The efficiency of these additives as pour point reduction increases by increasing their concentrations and by decreasing their molecular weight. The maximum pour point reduction was obtained when the crude oil was treated by the E20 additive (Δpp=21°C, at 2.5% g/100mL), and the minimum pour point reduction was obtained for the crude oil treated by the E10 additive (Δpp=15°C, at 2.5% g/100mL).

The longer the ethylene oxide units of E20 apparently blended with the paraffin chains existing in the crude oil, the better the effect on preventing their facile crystallization. The surfactant additives increase the calorific values of the tested crude oil.

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