Preparation and evaluation of some surfactants as pour point depressants in oil field

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ABSTRACT

Three surfactants additives were synthesized by esterfication of polyethylene glycol with adibic, phythalic and citric acid then re-esterfication of polyethyleneglycol adipate acid (A), phythalate acid (P) and citrate (C) with triethanolamine. The prepared surfactants were evaluated as surfactants by surface tension and critical micelle concentration. It has been found that A additive is more efficient as pour point $\Delta pp_{2000ppm} = 12°C$ than P and C, $\Delta pp_{2000ppm} = 9°C$ and 6°C. Blends between the best of additive A with commercial flow improver CFI and Natural wax dispersant NWD were done and evaluated as pour point depressants (500:1000:500), $\Delta pp_{2000ppm} = -21°C$.

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INTRODUCTION

It is well known that the behavior middle distillate blends manifold increase with the light oil gradually evaporated, because recurring problems to the oil industry and user alike for the storage, transport and use of petroleum fuels at low temperatures. Essentially these difficulties arise because of the waxy components crystallization in fuel. These waxes separate out from solution as very thin rhombic plates which, when pumped, can readily met together in the form of impermeable cakes which block filters, transfer lines and pumps and lead to eventual engine failure. Use of polymer additives is one of the modern effective solutions to this problem[1,3-5,15] . To date, ethylene-vinyl acetate copolymers[11], polyolefins[10], polyacrylates[6], fumarate- olefin copolymers[13], alkyl esters of styrene maleic anhydride copolymers[2] have been widely used as flow improvers for oi l or oil products, Due to the co- crystallization of normal alkanes and long (CH_2CH_2) re-peated unit on polymer, polymer additives at the concentration of part per million (ppm) after the size and habit of waxy precipitates so that the temperature operability range is substantially increased[3,8,12].

In this present work some surfactants dicarboxylate and tricarboxylate types were synthesized and evaluated as pour point depressant for fuel oil. The surface properties of these prepared surfactants were studied. The compatibility of these additives with either commercial flow improver or natural wax dispersion were carried out and evaluated as pour point depressant for fuel oil.

EXPERIMENTAL

Materials

Adipic, phythalic, citric acid, triethanolamine, polyethylene gylcol (600). Comercial flow improvers (CFI), Natural wax dispersant (NWD).

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Fuel oil used

Middle distillate fuel oil derived from the waxy western desert crude oil with physico chemical characteristic given in TABLE 1 was used for evaluation the performance of the synthesized additives. Urea adduction[9] was used for determination of n-paraffin carbon number distribution and average carbon number for fuel oil.

TABLE 1 : Physical characteristics of distillate fuel oil

Test	Method	Value
Specific gravity 60/60°F	IP 160/87	0.8412
Kinematic viscosity mm^2 S^{-1} at 40°C Cst	IP 71/80	3.7
Cloud point (CP), °C	IP 219/82	26
Pour point (PP), °C	IP 15/67(86)	18
Total sulphur contant (wt%)	IP 266/87	0.230
Total paraffins content	Urea adduct	20.3
n-paraffins (wt%)	GLC	19.9
Iso-paraffins (wt%)	GLC	0.40
Average carbon number	calculated	21.3

Synthesis of additives

a- reaction of polyethylene glycol with different acids

Polyethylene glycol of adipic acid, phythalic acid and citric acid were prepared by esterification of these acids (0.1 mole) with polyethylene glycol (0.1 mole) in xylene as solvent. The reaction was heated at 140°C in the presence of (0.001mole) of p-toluene sulphonic acid as catalyst with continuous stirring, until theoretical amount of water was collected. The solvent was distilled off and the product washed with dry petroleum (60-80°C) several times for further purification[14].

b- Re-estrification of polyethyleneglycol adipate, phythalate and citrate with triethanolamine.

These compounds were prepared as the above reaction.

Characterization of the synthesized products

These compounds were confirmed by FTIR spectra. Infrared spectra were measured by using AVATAR 230 FTIR spectrometer to measure intensity of absorption bands for the prepared surfactants.

Evaluation test

Cloud point measurements:

Solution of oil soluble samples A, P and C in xylene

contain 10% active material are prepared, according to IP 219/82 method. Different concentration of cloud point depressant (300, 700, 1000, 1500 and 2000 ppm) solutions were injected into fuel oil were tested.

Pour point measurement (ASTM, D97)

Solution of oil soluble samples A, P and C in xylene contain 10% active material are prepared, according to ASTM, D97 method. Different concentration of pour point depressant (300, 700, 1000, 1500 and 2000 ppm) solutions were injected into fuel oil and tested as pour point depressants results are given in Figure 1.

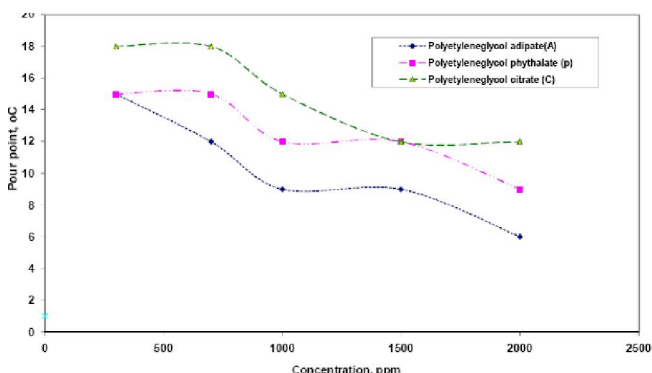Compatibility of synthesized additive with commer-

Figure 1: Effect of the prepared additives on pour point of the distillate fuel oil

cial flow improver (CFI) and natural wax dispersant (NWD).

The commercial flow improver and natural wax dispersant were dissolved in the appropriate solvent at a concentration lower than the critical concentration of the prepared additive in the same solvent then solutions of the evaluated additives were mixed at the prescribed combination ratio up to total concentration of 2000ppm, shacked manually for five minutes then the mixed solution was injected into the tested fuel oil sample at 90°C, left to cool at 40°C then flow tests, CP and PP were evaluated according to ASTM/IP procedure without reheating results in are given TABLE 2.

Surface tension measurements

Surface tensions measurements were obtained using DeNouy Tensiometer (kruss K6 type) Gmburg. Germany) at 25°C results in TABLE 3. Freshly prepared aqueous solution of the product (A, P and C) in deionized water was prepared with a different concentration at ambient temperature. The ring was washed twice after each reading first by ethanol then distilled[7].

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TABLE 2 : Activity and compatibility of the synthesized additives with natural wax dispersant (NWD) and commercial flow improvers (CFI) in terms of pour and cloud point depression.

Additives combination ratio, ppm	CP	ΔCP	PP	ΔPP
Untreated fuel oil	26	--	18	--
Natural wax dispersant (NWD): polyethyleneglycol adipate (A)				
2000 : 0	22	4	3	15
1000 : 1000	22	4	0	18
500 : 1500	23	3	3	15
250 : 1750	23	3	6	12
0 : 2000	23	3	6	12
Natural wax dispersant (NWD): polyethyleneglycol phthalate (P)				
2000 : 0	22	4	3	15
1000 : 1000	23	3	3	15
500 : 1500	24	2	6	12
250 : 1750	24	2	9	9
0 : 2000	24	2	9	9
Natural wax dispersant (NWD): polyethyleneglycol citrate (C)				
2000 : 0	22	4	3	15
1000 : 1000	24	2	6	12
500 : 1500	25	1	9	9
250 : 1750	25	1	9	9
0 : 2000	25	1	6	12
Commercial flow improver (CFI):Natural wax dispersant(NWD) : polyethyleneglycol adipate (A)				
2000 : 0 : 0	24	2	12	6
0 : 2000: 0	22	4	6	12
0 : 0 :2000	23	3	6	12
500 : 500 : 1000	23	4	3	15
500 : 1000 : 500	21	5	- 3	21
1000 : 500 : 500	23	3	0	18

Critical micelle concentration (CMC) was determined from the semi logarithmic plots of surface tension versus surfactant concentration, the point as the curve breakdown is CMC.

RESULT AND DISCUSSION

Chemical structure and characterization of the synthesized products

In this present work, polyethylene glycol (600) and triethanolamine were used in the preparation of three sets of surfactants additives. These additives were confirmed by means of infrared spectral analysis. The IR a showed a characteristic broad bands of (OH) stretching at 3400 cm^{-1}. The appearance of the strong band at 1735 cm^{-1} stretching vibration of ester, this indicates the formation of the ester group. The disappearance of beak at 1440 – 1365 cm^{-1} in the products (A, P) which represents (COOH) stretching means that these products are completely etherified and the appearance of a very weak band at 1440 – 1365 cm^{-1} at compound (C) that means that there is one carboxylic group free. The appearance of the peak at 2750- 3000 cm^{-1} is due to CH$_3$ and CH$_2$ stretching and they appeared also at 1400 – 1600 cm^{-1}.

Surface properties

Surface tension (γ) and critical micelle concentration (CMC), variation in the surface values vs. Log concentration values for solutions of the prepared surfactants at 25ºC CMC were determined from intersection points in the log concentration. The CMC values were found to component A < P < C are represented in TABLE 4. The decrease in CMC values can be attributed to a decrease in the hydration of the surfactant molecules i.e, the hydrophobic of the surfactant molecule increased as the number of (OH) decrease.

Effectiveness (πcmc) above the CMC γ did not change with concentration, so γ values at the CMC were used to calculate surface pressure (effectiveness) values.

$$\pi = \gamma o - \gamma \qquad\qquad (1)$$

TABLE 3 : Critical micelle concentration (CMC) and surface parameters of the prepared compounds at 25ºC.

Compound	CMC(mM/m)	Π_{cmc}(mM/m)	τ_{max}(mol/L)	A_{min}(nm)	ΔG^o_{mic}KJ/mol	ΔG^o_{ads}KJ/mol
Polyethyleneglycol adipate(A)	1.5×10^{-2}	57	1.073×10^{-10}	1.547	- 32.1835	- 32.1975
Polyethyleneglycol phythalate (P)	2×10^{-2}	54	1.790×10^{-10}	1.256	- 24.23	- 24.297
Polyethyleneglycol citrate (C)	2.5×10^{-2}	52	1.7466×10^{-10}	0.95059	- 18.258	- 18.2882

(π_{cmc}) effectiveness; (τ_{max}) maximum surface excess; (A_{min}) minimum surface area ; (ΔG^o_{mic}) standard free energies of micellization; (ΔG^o_{ad}) standard free energies of adsorption.

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Where γ_o is the surface tension measured for pure water at the appropriate temperature and γ is the surface tension at the CMC. The most efficient surfactant was the one that lowered the surface tension the most at the CMC. Compound (A) was the most efficient in achieving the maximum reduction of the surface tension at CMC as shown in TABLE 3. Maximum surface excess τ_{max} can be calculated according to the Gibbs equation

$$\tau_{max} = 1/RT \ (d\gamma/d \ Lnc) \qquad (2)$$

Where τ_{max} the surface excess, d isγ is the surface pressure, and c is the concentration of surfactant the substance so that lowers the surface energy is thus present in excess at or near the surface. The values of τ_{max} as shown in TABLE 4 as the surface tension decreased with increasing surfactant activity τ_{max} was positive.

Minimum surface area (A_{min}) the average area occupied by the surfactant molecule at the air/water interface of the surfactant solution is called the minimum surface area and can be calculated from the following equation:

$$A_{min} = 1016[NA * \tau Amin \ max] \qquad (3)$$

Where (N) is the Avogadro number. A_{min} values decreased with an increase in the alkyl chain length. This indicates that the molecules were more tightly packed at the air/ water interface for the more hydrophobic group surfactants.

Standard free energy of micellization (ΔG^o_{mic}) and standard free energy of adsorption (ΔG^o_{ads}), ΔG^o_{mic} can be calculated from the following equation

$$\Delta G^o_{mic} = RT \ Ln \ CMC \qquad (4)$$

ΔG^o_{mic} for the synthesized surfactants were always negative values, indicating that micellization was spontaneous process. At a constant temperature, ΔG^o_{mic} increased with an increase in the number of carbon atoms throughout the surfactant molecules i.e it became less negative. Conversely ΔG^o_{ads} can be calculated by the relation

$$\Delta G^o_{ads} = \Delta G^o_{mic} - 6.023 \ x \ 10^{-1} \ \pi_{cmc} \ A_{min} \qquad (5)$$

TABLE 4 shows some increase in ΔG^o_{ads}, supporting the idea of micellization over adsorption on the solution surface to over come the repulsion forces occurring at the water/ hydrophobic interface ΔG^o_{ads} and ΔG^o_{mic} were always negative in the value due to the spontaneity of these two processes.

Effect of the synthesized products on the cloud point (CP) of the fuel oil

Results showed that the prepared additives have no effect on the cloud point with 300, 700 ppm concentration except for repeatability limit of $\Delta CP = 2^oC$ in (A) only but in (p) and C no effect $\Delta CP = 0^o$ and0^o C. An increase in the concentration of the its effective up to 2000ppm for fuel oil. (A) compound has achieved the optimum values of the cloud point depression $\Delta CP = 3^oC$ at concentration 2000 ppm. This may be due to the high interaction between alkyl chain lengths of hydrocarbon moiety of these additives with paraffin wax in fuel oil.

Effect of the synthesized products on the pour point (pp) of the fuel oil

The three prepared additives were tested as pour point depressants through pour point determination according to ASTM D-97 procedure at concentration 300, 700, 1000, 1500, 2000 ppm, and results in Figure 1 show that all additives achieved moderate pour point depression at concentration 1000ppm. The activity of these additive as pour point depressant has the following the order A > P > C. Compound (A) additive is more effective in depressing the pour point $\Delta pp_{2000ppm} = 12^oC$ than (P) additive $\Delta pp_{2000ppm} = 9^oC$ and (C) additive $\Delta pp_{2000ppm} = 6^oC$ illustrated in Figure 1.

Effect of concentration of the synthesized products on their performance as pour point depressant

The synthesized additives were tested at 300, 700, 1000, 1500, 2000. From the demonstrated result in Figure 1, it was observed that the pour point values regularly depressed as the additive concentration increased up to 2000 ppm. This means that at this concentration range, the additive may Co-crystallize with paraffin and modifies their crystals. In general, at lower additive concentrations, side way growth of the crystal faces may be slightly restricted and accordingly, the crystal grows relatively slower. However crystallization may still be able to form. At higher concentrations of the additives, the side way growth becomes so much more difficult for the wax crystal.

The influence of compatibility of the additives with commercial flow improver (CFI) and natural wax dispersants (NWD) on the flow properties of the fuel oil

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The compatibility of any additive with CFI may exhibit synergistic or antagonistic effect on the cold flow properties of fuel oil. The total additive concentration was 2000ppm. Results given in TABLE 2 show the influence of compatibility of the additive A, P and C additive with CFI at different ratio on the flow properties of the fuel oil. It is obvious that combination of (A) additive with CFI at the ratios (1000ppm: 1000ppm) and (500ppm: 1500ppm) enhanced the flow ability to an optimum value of $\Delta pp_{2000ppm}$ = 15 and 15°C respectively. Results given in TABLE 2 and show the influence of compatibility of the additives A, P and C with NWD on the flow properties of the fuel oil. It is obvious that combination of the (A) additive with NWD at the ratio (1000ppm: 1000ppm) enhanced the flow ability improvement to an optimum value of $\Delta pp_{2000ppm}$ = 18°C. Also, It is obvious that combination of the (CFI: NWD: A) at the ratio (500ppm:100ppm:500ppm) enhanced the flow ability improved to an optimum value $\Delta pp_{2000ppm}$ = 21°C.

By analysis of the surface active properties TABLE 4 and the data presented of pour point in Figure 1, at was found a relation between negative values of ΔG^{o}_{ads} of the used polymers and their performance to be -24.297and - 18.2882 KJ/mol for P and C additives. The maximum reduction of pour point was achieved with (A) additive $\Delta pp_{2000ppm}$ = 18°C, its ΔG^{o}_{ads} values was - 32.1975 KJ/mol. This means that, there is a strong relation between the surface active properties of pour point depressants (surfactants) even in oil/liquid adsorption and their performance to depress the pour point.

CONCLUSIONS

- Three sets of surfactants additives (A, P and C) were synthesized by esterification of polyethylene glycol with adibic acid, phythalic acid and citric acid then re- esterfication of polyethylene glycol adipate, phythalate and citrate with triethanolamine.
- The prepared additive gives good surface properties.
- The prepared additive gives good results as pour point depressant for fuel oil.
- The activity of prepared additive as pour point depression for fuel oil as follows A> P>C.
- The eventual performance of pour point depres-

sion depends on the physico- chemical characteristics of the additive.

- The prepared additives exhibited good compatibility with both commercial flow improvers (CFI) and natural wax dispersant (NWD).

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