

Dispersion of Waxy Gas Oil by Some Nonionic Surfactants

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ABSTRACT

Straight chain fatty alcohols having the following number of carbon atoms C_{12} , C_{14} , C_{18} and C_{21} each alcohol was ethoxylated to the same of ethylene oxide content, characterized through average molecular weight and elemental analysis. The surface properties of these compounds were studied through surface tension measurements. The synthesized additives were tested as flow improvers for improving the cold flow properties of two waxy gas oils through pour point test. The results show the right efficiency of these compounds in improving the flowability. Comparative evaluation of the synthesized products with available commercial additive (com) showed their efficiency and suitability to use in gas oils. Wax modification was assisted through photoanalysis. Correlation between wax modification and flow improvement in term of pour point depression appeared to be merely qualitative in such heterogeneous gas oil systems.

Key words:-

Ethylene oxide, nonionic surfactants, pour point depressant, flow improver, waxy gas oils.

INTRODUCTION

In the manufacture of synthetic nonionic surfactants⁽¹⁻⁴⁾, ethylene oxide condensation is one of the principal processes employed to introduce hydrophilic functional groups into an organic molecule. The ultimate objective of the process is the production of surface active agents having the desired hydrophile lipophile balance (HLB). The term, nonionic surfactants refers chiefly to polyoxyethylene and polyoxypropylene derivatives. They are usually prepared by the addition of ethylene oxide or propylene oxide to compounds containing one or more active hydrogen atoms such as fatty alcohols⁽⁵⁾.

Paraffin wax deposition from gas oil at low temperature is one of the serious and long-standing problems in the petroleum industry. At low temperatures, the crystals of wax easily form impermeable cakes, which can block filters and eventually lead to engine failure. Many methods have been attempted for the prevention of the crystals mating together⁽⁶⁻⁸⁾, Adding pour point depressants (PPDs) is one of the most important methods for improving the low temperature flow properties of gas oils. Certain PPDs are known to have a significant effect on both the rate of wax deposition and resulting crystallization⁽⁹⁻¹²⁾.

Many postulated mechanism have been put forward to explain this phenomenon and to instruct the PPD product design. Among the mechanism theories, adsorption, Co-crystallization, nucleation; and improved wax solubility are widely accepted by mechanism researchers^(13,14).

The wax deposition inhibitors are compounds constituted⁽¹⁵⁾ such as by a hydrocarbon chain which provides the interaction between additive and paraffin, and a polar segment that is responsible for the wax crystals morphology modification necessary to inhibiting the aggregation

stage. For this reason, such inhibitors are known as waxy crystals modifiers⁽¹⁶⁻¹⁷⁾.

The present paper describes the synthesis and evaluation of the prepared nonionic surfactants and commercial additive, as flow improvers for two gas oils. The effect of additive type and concentration on wax crystal modification are studied.

Experimental

Material:

Fatty alcohols (1-dodecanol, 1-tetradecanol, 1-octadecanol and long-chain alcohol blends (C₂₁) were supplied by CONDEA chemical company, ethylene oxide, potassium hydroxide, nitrogen gas commercial flow improver (2437) which it was kindly supplied from Alexandria Petroleum company.

Gas oil composition

Two paraffinic gas oils designated Gas I and Gas II derived from the waxy western desert crude oils with the physicochemical characteristics given in table 1 were used for evaluating the performance of the synthesized additives. The n-paraffin content of gas oils composition is determined by urea adduction⁽¹⁸⁾. In addition, a sample of the tested Gas I and Gas II and their respective n-paraffin content are subjected to gas liquid chromatographic analysis (GLC) for determination of n-paraffin carbon number distribution and average carbon number as presented in Tables (2,3) and illustrated in Figures (2,3).

Ethoxylation of fatty alcohols

Straight long chain fatty alcohols dodecyl alcohols, tetradecyl alcohol, octadecyl alcohol and long chain alcohols blends C₂₁. The following procedure described in⁽⁵⁾ was followed: A mixture of the hydrophobe (0.05 mole) and potassium hydroxide (0.002 mole) was

stirred and heated to 170-180°C in nitrogen atmosphere. The nitrogen flow was stopped and ethylene oxide was passed into the reaction mixture and the experiment was repeated for different intervals of time (1-5hrs) and the results were presented in Figure (4). Each hydrophobe was ethoxylated with the same ethylene oxide moles. The found values of the reacted ethylene oxide moles were determined as given and calculation values were derived for the difference in the weight of the hydrophobe and that of ethoxylate products. Such as:

R₁₂-O-[CH₂-CH₂]-OH (C₁₂E.O),

R₁₄-O-[CH₂-CH₂]-OH (C₁₄E.O),

R₁₈- O-[CH₂-CH₂]-OH (C₁₈ E.O) and

R₂₁- O-[CH₂-CH₂]-OH (C₂₁ E.O.)

The four synthesized additives were characterized through elemental analysis and average molecular weights illustrated in Table (4).

Evaluation tests

Determination of the surface properties of the prepared surfactants:

The cloud points ⁽¹⁹⁾, surface and interfacial tensions, foaming ⁽²⁰⁾ and emulsification power of the prepared surfactant were examined by standard methods. Results are given in table (5)

Determination of pour points

Pour points were determined according to ASTM-97 procedure comparison between low temperature properties of the two tested gas oil samples before and after treatment with synthesized and commercial pour point depressants with different doses were carried out. The obtained results are shown in Tables (6,7) which represent the effect of pour point depressants on the two tested samples (Gas I) and (Gas II) respectively.

Photomicrography analysis

Photomicrographs showing wax crystallization behavior of untreated and treated gas oil samples with the synthesized and commercial additive. An

Olympus polarizing microscope model BHSP fitted with automatic camera with 35mm format was used for photomicrograph analysis. The light source was a helium lamp. The temperature of the tested gas oil samples was controlled on microscope slide by an attached cooling thermostat at 0°C. All photos were taken at 100X magnification.

Discussion of the results

The aim of the present work is to find certain possible utilization of some new surfactants which were prepared in order to study the influence of nonionic surfactant on the pour point and wax modification for waxy gas oils. During the displaying of the results the interaction between the gas oils and the additives is discussed.

The rate of ethoxylation is represented in Figure (4) and gave the following results:

- 1) The rate of ethoxylation of fatty alcohols was high due to the presence of free OH group.
- 2) Effect of the alkyl chain of each hydrophobe on the rate of the ethoxylation in the order of $R_{12} > R_{14} > R_{18} > R_{21}$ due to the fact that long chain causes coiling of the molecule.

The effect of chemical structure of the prepared nonionic surfactants on their surface active properties may be explained as follows:

1- Cloud point increases in the order:

$$R_{12} > R_{14} > R_{18} > R_{21}$$

2- Surface and interfacial tensions increase in this order

$$R_{12} > R_{14} > R_{18} > R_{21}$$

So decrease in their surface activity.

3- Foaming power

$$R_{12} > R_{14} > R_{18} > R_{21}$$

4- Emulsification power

$$R_{21} > R_{18} > R_{12} > R_{14}$$

5- Biodegradability of the prepared nonionic compounds as shown in Table (8). The change will be in the order:

$$R_{12} > R_{14} > R_{18} > R_{21}$$

Effect of additives on pour point of gas oils

The synthesized products (C₁₂E.O), (C₁₄ E.O), (C₁₈ E.O) and (C₂₁E.O), are evaluated as pour point depressants (PPD) by testing them in gas oil samples GI and GII at different concentration 250,500,750,1000, 2000ppm. These gas oil samples represent the regular winter and summer grades. Their specifications are listed in Table (1). The effect of additive dosage on the cold flow properties of paraffinic gas oils are presented in Table (6,7). With decreasing concentration of additive an increase in performance is observed, this means that the additive Co-crystallizes with paraffin modifying crystals, but additive in excess concentration can act as a crystallization nucleation agent. The effectiveness increase in the order C₁₂E.O < C₁₄ E.O. < C₁₈E.O < C₂₁E.O.

This clearly showed that the average carbon number of the alkyl group plays an important role on the efficiency of a flow improved and wax dispersant.

The effect of synthesized additives on sample (Gas I) is much better than on sample (Gas II). This may be due to the presence of high n-paraffin components in sample Gas II (paraffin = 24.353 wt%) than that content exist in sample gas I (paraffin content 18.496 wt%). Product C₂₁E.O as well as commercial additive and good response as pour point

depressants and flow improvers for test Gas I sample but less Gas II sample.

Photomicrographs analysis

Photomicrographs analysis are illustrated in plate (1-3) show variant wax morphology changes according to types and concentrations of additive photoanalysis confirms with pour point test that evaluate the cold flow properties of untreated/ treated waxy gas oil through wax crystallization behaviors

Plate (1a) of untreated GI shows along rad-like crystals. On treatment GI with flow additives have been various performance under the effect of concentration of each of the additives C₁₂E.O. and C₂₁E.O. The wax modification of the (GI) was evaluated at (250), (2000)ppm by photoanalysis, results shown in (Plate 1) explain that the wax crystal size becomes gradually smaller until it becomes very fine.

Decreasing the concentration of the additives increasing the pour point depressant in the following order G₁+250ppm C₂₁E.O > G₁+250ppm C₁₂ E.O. photomicrographs illustrated in (plate 1) show various was morphology change according to the type and concentration of the additive. The effect of the concentration of the additive was explained through photographic analysis or wax modification of 250 and 2000ppm.

Results are illustrated in plate (2a) from which it is apparent that the untreated highly paraffinic Gas II (plat 2a) displays elongated thick rod-like crystals.

Successively plate (2b-2e) show that with decreasing of additive concentration, the wax crystal size significantly decrease from very large crystal to a great number of very small dots dispersed in the oil phase of the gas oil system. Decreasing the concentration of the additives increase pour point depressants in the following order: G II + 250 ppm of C₂₁E.O

> G II + 250 ppm C₁₂E.O. when GI was treated with commercial, a significant reduction crystal size has been observed.

Plate (3a) by treatment with the commercial additives for their crystal size reduction with the formation of very fine dispersant crystal additive (plate 3b) when the gas oil sample (GII) was treated with the commercial additive (plate 3c, 3d) a slight wax modification has been observed.

Results are illustrated in plate (1,2 and 3) show that with decrease of additive concentration, the wax crystallization is significantly decreased to abundant number of very small dots dispersed in the oil gas system

Conclusion

From this study we can conclude that :

- The performance of nonionic surfactants R-O-[CH₂-CH₂]-OH where R= C₁₂, C₁₄, C₁₈, C₂₁ as pour point depressant and wax modification for gas oil strongly depends on long chain of alkyl group and the additive lost its efficiency when concentration was increased to 1000 and 2000ppm.
- For the gas oil (Gas I) the best performance as pour point depressant was obtained with 250ppm C₂₁E.O.
- When the additive concentration is decreased the wax crystal size significantly decreased to abundant number of waxy small dots dispersed in Gas I and Gas II.
- A correlation between the depression of flowability and degree of wax modification has been verified.
- Comparative evaluation for synthesized products with commercial available additives showed their efficiency and suitability to use in gas oil samples.

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Table (1) Characteristic of waxy western Desert Gas Oils

Test	Test method	Gas I	Gas II
Specific gravity 60/60°F	IP 16/87	0.8512	0.8077
Kinematic viscosity at 40°C, cst	IP 71/80	3.30	5.00
Flash point, °C	IP 34/85 (87)	120	140
Cloud point, °C	IP 219/82	19	35
Pour point, (PP) °C	IP 15/67 (86)	9	26
Total paraffine content (wt.%)	Urea adduct	18.496	24.353
n-paraffin (wt.%)	GLC	17.49	23.352
Iso-paraffinic (wt.%)	GLC	1.006	1.001
Total sulphur content (wt.%)	IP 266/87	0.190	0.382
Distillation, °C	ASTM D-86		
IBP		191	240
10%		206	248
20%		218	255
30%		255	273
40%		265	286
50%		280	298
60 %		295	310
70%		306	340
80%		329	360
90%		360	398
FBP%		372	405

**Table (2) Carbon Number Distribution of n-Paraffin Fraction
Separated from the Gas Oil Gas I**

Carbon No.	Wt%	Mol. wt	No. of moles x10⁻⁴
C ₁₁ H ₂₄ (n-)	0.005	156	6.871
C ₁₂ H ₂₆ (n-)	0.015	170	16.54
C ₁₃ H ₂₈ (n-)	0.036	184	35.11
C ₁₄ H ₃₀ (n-)	0.040	198	36.18
C ₁₅ H ₃₂ (n-)	0.064	212	53.98
C ₁₆ H ₃₄ (n-)	0.083	226	66.07
C ₁₇ H ₃₆ (n-)	0.083	240	62.00
C ₁₈ H ₃₈ (n-)	0.086	254	60.80
C ₁₉ H ₄₀ (n-)	0.095	268	63.80
C ₂₀ H ₄₂ (n-)	0.102	282	65.23
C ₂₁ H ₄₄ (n-)	0.104	296	63.29
C ₂₂ H ₄₆ (n-)	0.076	310	44.29
C ₂₃ H ₄₈ (n-)	0.032	324	18.07
C ₂₄ H ₅₀ (n-)	0.013	338	7.188
C ₂₅ H ₅₂ (n-)	0.008	352	4.501
C ₂₆ H ₅₄ (n-)	0.009	366	4.760
C ₂₇ H ₅₆ (n-)	0.010	380	4.978
C ₂₈ H ₅₈ (n-)	0.012	394	5.782
C ₂₉ H ₆₀ (n-)	0.014	408	7.529
C ₃₀ H ₆₂ (n-)	0.018	422	7.628
C ₃₁ H ₆₄ (n-)	0.019	436	7.908
C ₃₂ H ₆₆ (n-)	0.015	450	6.336
C ₃₃ H ₆₈ (n-)	0.012	464	4.783
C ₃₄ H ₇₀ (n-)	0.007	492	2.789
C ₃₅ H ₇₂ (n-)	0.005	506	1.903
Total	17.490		657.49

Total wt.% of paraffins determined by urea adduction = 18.496

Wt% of n-paraffins = 17.490

Wt% of Iso-paraffins = 1.006

Average molecular weight = 265.89 = C_n

H_{2n+2}

Average carbon number (n) = = 18.85 ≈ 19

**Table (3) Carbon Number Distribution of n-Paraffin Fraction
separated from the Gas oil (Gas II)**

Carbon No.	Wt%	Mol. wt	No. of moles x10⁻⁴
C ₁₁ H ₂₄ (n-)	0.023	156	2.15
C ₁₂ H ₂₆ (n-)	0.225	170	13.235
C ₁₃ H ₂₈ (n-)	0.370	184	20.14
C ₁₄ H ₃₀ (n-)	0.325	198	29.42
C ₁₅ H ₃₂ (n-)	1.468	212	69.245
C ₁₆ H ₃₄ (n-)	1.480	226	65.486
C ₁₇ H ₃₆ (n-)	1.703	240	70.97
C ₁₈ H ₃₈ (n-)	1.699	254	75.848
C ₁₉ H ₄₀ (n-)	2.212	268	82.52
C ₂₀ H ₄₂ (n-)	2.412	282	85.517
C ₂₁ H ₄₄ (n-)	3.457	296	87.304
C ₂₂ H ₄₆ (n-)	1.628	310	52.517
C ₂₃ H ₄₈ (n-)	1.468	324	45.304
C ₂₄ H ₅₀ (n-)	0.998	338	29.55
C ₂₅ H ₅₂ (n-)	0.929	352	26.42
C ₂₆ H ₅₄ (n-)	0.744	366	20.35
C ₂₇ H ₅₆ (n-)	0.699	380	18.42
C ₂₈ H ₅₈ (n-)	0.591	394	15.00
C ₂₉ H ₆₀ (n-)	0.370	408	9.07
C ₃₀ H ₆₂ (n-)	0.252	422	5.48
C ₃₁ H ₆₄ (n-)	0.180	436	4.14
C ₃₂ H ₆₆ (n-)	0.119	450	2.65
Total	23.352		831.236

Total wt.% of paraffins determined by urea adduction = 24.353
Wt% of n-paraffins = 23.352
Wt% of Iso-paraffins = 1.001
Average molecular weight = 280.931 =
C_n H_{2n+2}
Average carbon number (n) = 19.92 ≈ 20

Table (4) Physico Chemical Characteristics of Synthesized Additives

Additive type	M.wt	Elementary analysis					
		C		H		O	
		Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
C ₁₂ E.O.	624	60.56	61.34	10.44	10.54	29.06	28.11
C ₁₄ E.O.	655	62.01	62.39	11.01	10.70	26.98	26.91
C ₁₈ E.O.	710	63.72	64.14	10.76	10.97	25.52	24.71
C ₂₁ E.O.	754	65.11	65.42	10.99	11.17	33.90	23.40

Table (5) Surface Properties of the Prepared of Alcohol Ethoxylates

Type of ethoxylates	Cloud point, °C 1%	Surface tension dynes/cm 0.1%	Interfacial tension dynes/cm ⁻¹ 0.1%	Foam high volum/ ml 0.1%	Emulsification power
C ₁₂	76	34.7	7.9	40	86
C ₁₄	80	36.5	9.2	55	95
C ₁₈	89	40.2	10	39	96
C ₂₁	> 100	44.5	11.6	Unstable foam	89

Table (6) Effect of the Prepared Product on the Flowability of Waxy Gas Oil (Gas I)

Additive designation	Gas I					
	Additive concentration, (ppm)					
	Nil	250	500	750	1000	2000
	Pour Point, °C					
C ₁₂ E.O.	9	- 3	- 3	0	3	3
C ₁₄ E.O.	9	- 12	- 6	- 3	0	0
C ₁₈ E.O.	9	- 12	- 12	- 6	0	0
C ₂₁ E.O.	9	- 18	- 18	- 12	- 6	- 3
Com.	9	- 15	- 12	- 12	- 6	0

Table (7) Effect of the Prepared Product on the Flowability of Waxy Gas Oil (Gas II)

Additive designation	Gas II					
	Additive concentration, (ppm)					
	Nil	250	500	750	1000	2000
	Pour point (°C)					
C ₁₂ E.O.	26	14	14	20	20	23
C ₁₄ E.O.	26	11	14	14	20	20
C ₁₈ E.O.	26	11	11	11	14	20
C ₂₁ E.O.	26	8	8	11	11	14
Com.	26	14	14	14	20	20

Table (8) Biodegradability of the prepared nonionic compounds

Type of Ethoxylate	Biodegradability %							
	1 st day	2 nd day	3 rd day	4 th day	5 th day	6 th day	7 th day	8 th day
C ₁₂	42	53	58	62	67	74	77	81
C ₁₄	37	48	55	59	66	71	77	80
C ₁₈	36	42	45	49	60	65	69	73
C ₂₁	32	37	42	47	60	61	69	71

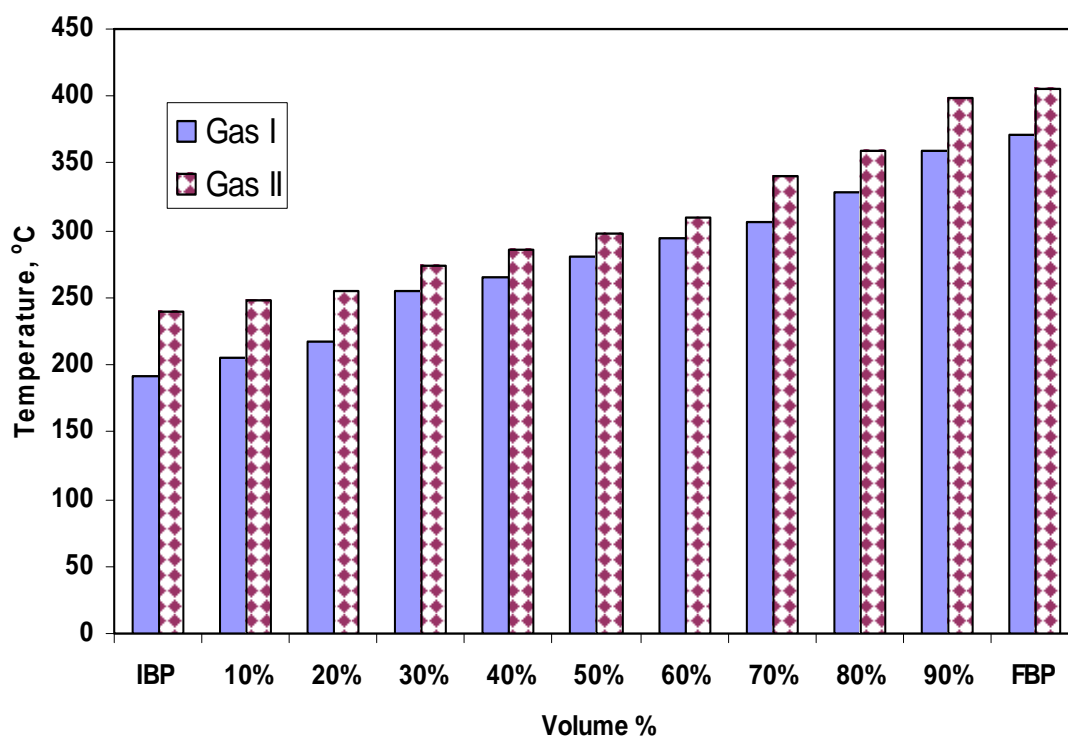


Figure (1): Comparative distillation for gas oil samples Gas I and Gas II

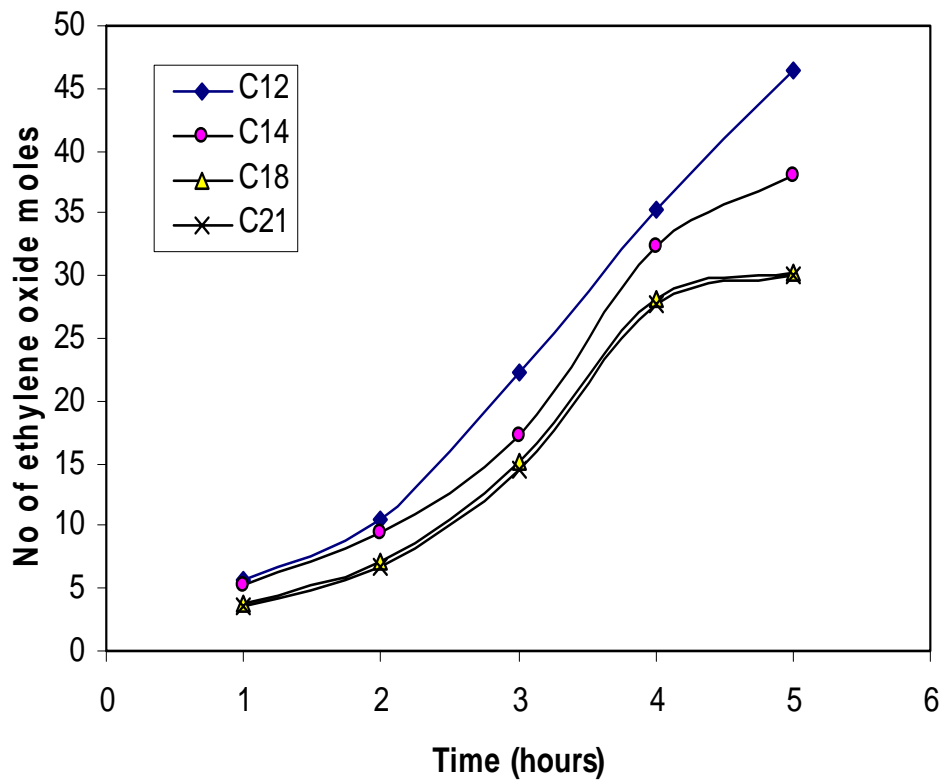


Figure (4) Condensation of the hydrophobes with ethylene oxide