RESEARCH ARTICLE

APPLICATION OF SOME NONIONIC SURFACTANTS AS CORROSION INHIBITORS FOR CARBON STEEL AND POUR POINT DEPRESSANT OF MIDDLE DISTILLATE FUEL OIL

Khidr, T. T., Doheim, M. M., *El-Shamy, O. A. A. and Abdelraheem, O. H.

Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

ABSTRACT

A series of ethoxylated nonionic surfactants, $C_n E_{14}$ (n = 12,14 and 18), surfactants were prepared by reacting polyethylene glycol (molecular weight 600) and different fatty acids: Lauric acid, Myristic acid and Oleic acid. The chemical structures of these prepared surfactants were confirmed by High Performance Liquid Chromatography (HPLC) and Proton Nuclear Magnetic Resonance (NMR) Analysis. The surface tension of the synthesized surfactants was measured at ambient temperature and the Critical Micelle Concentration (CMC) values were obtained. In addition the effectiveness of adsorption at Liquid/Air interface Γ_{max} and minimum surface area A_{min} were calculated. The effect of these nonionic surfactants on the corrosion behavior of carbon steel in acidic medium 0.5M HCl was investigated. The pontentiodynamic polarization measurements showed that surfactants achieved a substantial decrease in the corrosion. The present study investigates the effect ethoxylated nonionic surfactant on depression of pour point waxy distillate fuels. Comparison of morphologies and structures of waxy crystals or aggregates in fuel oil beneficiated with and without a pour point depressant was done by micro photographic studies which show the modification in wax morphology due to additive.

INTRODUCTION

Recently, many surfactants are widely used as corrosion inhibitors for carbon steel in petroleum field [1]. Acidic solutions are widely used in different fields of application, especially acidic pickling, acidic descaling, oil-well acidizing and petrochemical processes. Most of acidic media cause detriment for metallic materials which leads to considerable economic losses [2], to overcome this problem, corrosion inhibitors are generally used. Many researchers reported that inhibiting effect of these inhibitors mainly depends on some of their physicochemical characteristics [3]. Hydrocarbon fuel oils, for example, petroleum distillate fuels contain n-paraffin waxes that tend to be separated from the oil in low temperature. The waxes generally crystallize as an interlocking net work of fine sheets, thereby entrapping the remaining fuel in cage like structures and causing the cold flow problems such as blockage of fuel lines and filters in engine fuel system. Studies have shown that the network waxes amounting to as little as 1-2wt% of the sample are still capable of causing low temperature fluidity and operability problems in distillate fuels. The pour point is the lowest temperature at which oil will flow freely under its own weight under specific test conditions [4-7]. Several methods have been available to improve the low- temperature properties of fuel oil[8]. Pretreatment with pour point depressant (PPD) is an attractive solution for transportation of fuel oil via pipelines. One function of such pour point depressants has been to change the nature of the crystals that precipitate from the oil, thereby reducing the tendency of wax crystals to interlock and set into a gel[9]. Since adding chemical additives (such as pour point depressants, cold flow improvers or wax crystal modifiers) is the most convenient and economic way [10]. Different types of polymeric materials are reported to work with different mechanisms. Holder and Winkler[11] proposed that these materials act to poison and hinder the growth of wax crystals resulting in the formation of dendrites and ultimately needle shaped crystals, These modified cannot interlock with each other,

remaining dispersed in the system and thus lowering the pour point, Ethylene vinyl acetate copolymers are reported to perform a similar function [12]. Such polymeric additives contain crystalline as well as amorphous segments. The crystalline segments particularly made from polymethylene chains and the polar functional groups such as -COO-, -CONH$_2$, ether, etc. make the amorphous segments. The polymethylene chains may be present as the backbone or pendant chains or even as both depending upon the type of additive. In general, inhibition of wax crystallization has been considered to occur in the presence of PPD by nucleation, co-crystallization or adsorption. It is generally believed that the PPD function by disrupting or preventing the formation of three-dimensional wax networks, leaving the amount of crystalline wax unaffected [13,8].The structure and composition of wax dispersants is similar to conventional flow improvers in some features but different in others. They often possess highly polar functional groups. This polarity may reach as surfactant character which is considered as the basic prerequisite for the dispersant potential [14]. For evaluation of improved operability of treated waxy distillate fuel determination of flow properties (cloud point, pour point and cold filter plugging point tests. Photo micrographic analysis is the most widely adopted [15]. The aim of this study is to prepare and evaluate some nonionic surfactants as corrosion inhibitors for carbon steel in acidic medium and as pour point depressants for distillate fuel oil. The efficiencies of these prepared compounds were correlated with the chemical structures.

Experimental

Materials

Lauric acid, Myristic, Oleic acid, and Polyethylene glycol 600 are all of chemical grade and purchase from Aldrich. Middle distillate fuel oil derived from the waxy western desert crude oil with physicochemical characteristics given in Table (1) was used for evaluation of the performance of the synthesized additives. The n-paraffin content of the fuel oil tested was determined by urea adduction[16]. The fuel oil was subjected to gas liquid chromatographic

Corresponding author: El-Shamy, O. A. A
Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

analysis to determine the average carbon number and carbon number distribution.

Table 1. Physical characteristics of fuel oil

Properties	Methods	Fuel oil
Specific gravity at 60/60°F	IP 160/87	0.8412
Kinematics viscosity at 40°C (cst)	IP 71/80	3.7
Cloud point (cp), °C	IP 219/82	24
Pour point (pp), °C	IP 15/67(80)	18
Sulfur content (wt%)	IP 266/87	0.231
Flash point, °C	IP 34/82 (87)	123
Total paraffins content (wt%)	Urea adduct	20.3
n-paraffin (wt%)	GLC	19.9
Iso-paraffins (wt%)	GLC	0.40

Synthesis of the ethoxylated surfactants

A series of ethoxylated nonionic surfactant, C_nE_{14}, (n = 12, 14 and 18) were synthesized by mixing fatty acids, Lauric acid, Myristic acid and Oleic acid respectively with polyethylene glycol of molecular weight equal to 600 according to the previously mentioned procedure[17].

Critical Micelle Concentration (CMC)

Surface tensions of the surfactant aqueous acidic solutions (0.5M HCl) were measured at ambient temperature according to the Wilhelmy plate method as a function of concentration that ranged from (4×10^{-5} to 1×10^{-2} mole dm^{-3}) using kruss K8 tensiometer. The changes of the equilibrium surface tension with the logarithmic surfactant concentration at ambient temperature are given in Figure 1 for $C_{12}E_{14}$, $C_{14}E_{14}$ and $C_{18}E_{14}$. The surface tension of the tested surfactant solutions changes regularly with the concentration and follows the trend that was previously reported[18]. The curves can be characterized by two linear regions Figure 1 meeting each other at a definite concentration known as the critical micelle concentration (CMC), where the formation of a cluster, i.e., micelle, starts in the bulk solution; the values of CMC were determined and are presented in Table 2.

The values of Γ_{max} (mol cm^{-2}) evaluated by equation (1) for the tested surfactants are given in Tables 2 for the investigated nonionic surfactants.

Minimum Surface Area per Molecule at L/A Interface (A_{min})

The minimum area per molecule at the L/A interface at surface saturation reflects the surface activity of surfactants and provides information on the degree of packing and the orientation of the adsorbed surfactant molecule[20]. From the surface excess concentration [equation (1)], the area per molecule at the interface, A_{min} (Å^2), is calculated from the relationship equation (2),

$$A_{min} = 10^{16} / (\Gamma_{max} N_A) \tag{2}$$

Where N_A is Avogadro's number (6.032 x 10^{23} molecules/mol) and Γ_{max} is in mol cm^{-2}. A_{min} at L/A interface was calculated for each of the investigated surfactants and the values obtained are tabulated in Table 2.

Evaluation tests

Corrosion inhibition

Polarization measurements were performed in 0.5M HCl solution with and without different concentrations of the three nonionic surfactants. Specimens of L5 X52 carbon steel petroleum pipelines were used as metallic substrate, they were obtained from Petroleum Pipeline Company, Cairo, Egypt. The chemical composition of the steel contains 0.28%C, 1.25%Mn, 0.04%P, 0.05%S, and 98.38% Fe. Potentiodynamic polarization studies were made using a corrosion measurement system (Voltab 80) with software (Voltamaster 4), with scan rate of 1 mV.sec^{-1}. Conventional three electrodes cell was used with a platinum counter electrode and saturated calomel electrode (SCE) as reference electrode. The steel working electrode was embedded in Alardite resin, leaving a free flat surface area of 1 cm^2 to

Table 2. The CMC of the investigated surfactants

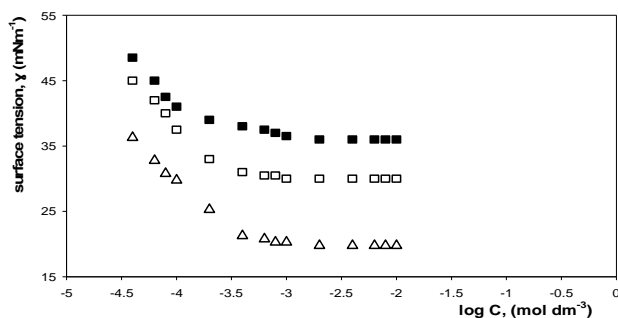| Surfactants	Chemical Formula	CMC x 10^{-4} (mol dm^{-3})	Γ_{max} X10^{-10} (mol cm^{-2})	A_{min} (Å)
$C_{12}E_{14}$	$C_{11}H_{23}COO(CH_2CH_2O)_{14}H$	2.38	3.82	43.40
$C_{14}E_{14}$	$C_{13}H_{27}COO(CH_2CH_2O)_{14}H$	2.30	3.36	49.34
$C_{18}E_{14}$	$C_{17}H_{33}COO(CH_2CH_2O)_{14}H$	2.51	3.94	42.10

Figure (1): Variation of surface tension with log concentration for: a (□) $C_{12}E_{14}$; b (■) $C_{18}E_{14}$; and c (△)$C_{14}E_{14}$.

Effectiveness of Adsorption at the Liquid / Air Interface Γ_{max}

The surface excess concentration at surface saturation Γ_{max} is a useful measure of the "effectiveness" of adsorption. The effectiveness of adsorption of the surfactant at the Liquid/Air (L/A) interface is estimated from the slope of the straight line taken from the plot of surface tension vs. logarithmic concentration in the concentration region just below the CMC[19],

$$\Gamma_{max} = \frac{1}{RT} \frac{d\gamma}{dlnC} \tag{1}$$

contact the solution. Prior to measurements, the working electrodes were abraded in sequence using wet emery papers of grade number range 320-1200, washed several times with distilled water then degreased with acetone and finally dried at room temperature.

Flow properties

The soluble ethoxylated non ionic surfactant additives, C_nE_{14}, (n = 12, 14 and 18) were evaluated as pour point depressants using pour point test according to ASTM D-97. Different concentrations ranging between 0 and 2000ppm were used to study their effect on pour point. In addition, they were tested for improving the filterability of the distillate fuel oil through cloud point test (CP) according to IP 309 procedures.

Photomicrography [8,21]

The photomicrographs showing wax crystallization behavior of the untreated and treated gas oil sample with a series of ethoxylated non ionic surfactant C_nH_{14} (n = 12,14 and 18) additives. An Olympus polarizing microscope model BHSP fitted with an automatic camera with a 35mm format was used for photo micrographic analysis. The light source was a Helium lamp. The temperature of the tested gas oil sample was controlled on the microscope slide by an attached cooling thermostat at 0 °C. All photos were taken at 100X magnification.

RESULTS AND DISCUSSION

High Performance Liquid Chromatography (HPLC)

The HPLC chromatograms of the surfactant samples showed a main peak that corresponds to ethoxylated esters and noise due to fatty acids starting material.

Proton Nuclear Magnetic Resonance NMR Analysis

The examination of the NMR spectra of the three samples under investigation showed the following positions of the chemical shifts[22-24]. The protons signal of the CH_3 group at the extremity of the saturate chain (fatty acid part) appeared at 0.73 ppm, the $(CH_2)_n$ of the saturate chain centered at 1.11 ppm while the CH_2 adjacent to the carbonyl group appeared at 2.17 ppm and the CH_2 in β of the carbonyl group appeared at 1.46 ppm. On the other hand signals of the protons of the ethoxylated chain appeared as follow: the protons of the repeated ethylene oxide chain $(CH_2\text{-}CH_2\text{-}O)_n$ are centered at 3.5 ppm, the CH_2 adjacent to the ester group at 3.84 and the CH_2 in α of the OH at the end of the chain appeared at 4.14 ppm. The presences of all the signals of the esters produced confirm correctly to the structure of the produced ethoxylated esters. The comparative calculated study of the integration values of the NMR spectra are summarized in Table 3 and Figure 2. The investigation of the tabulated data revealed that the number of the ethylene oxide units in the three samples is nearly exactly with the same as the empirical values.

Table 3. NMR calculation for the investigated surfactants

Surfactants	Fatty acid part (tail)	Ethylene part (head)	Tail /Head
$C_{12}E_{14}$	31.69	53.26	0.595
$C_{14}E_{14}$	36.15	51.62	0.700
$C_{18}E_{14}$	40.06	43.92	0.911
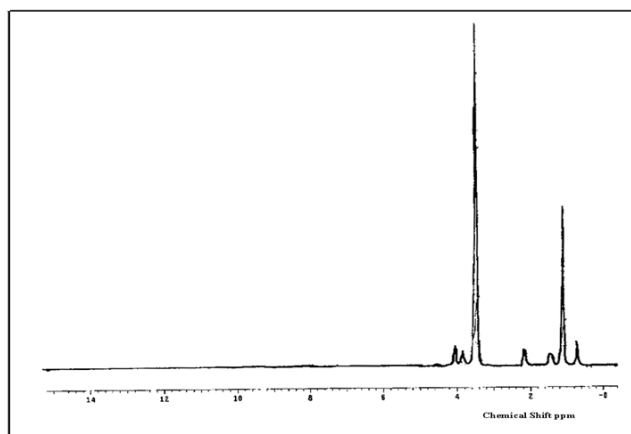
Figure 2. NMR spectrum of sample a $C_{12}E_{14}$

Effectiveness of Adsorption at the Liquid / Air Interface Γ_{max}

Table 2 shows that the effectiveness of adsorption for the tested nonionic surfactants decreases as the hydrophobic chain increase from 12 carbon atoms to 14 carbon atoms. Logically, Γ_{max} must increase with the increase in the hydrocarbon chain length, but the reverse is observed increase hydrophobic chain length could suffer some coiling that makes it behave as being shorter than that of $C_{12}E_{14}$ [25,17]. This coiling is accompanied with an increase in the value of A_{min} as shown in Table 2. The double bonds present in the hydrophobic chain of $C_{18}E_{14}$ facilitates the interaction between the neighboring hydrophobic saturated chains. Moreover, the introduction of a double bond in the hydrocarbon chain increases its effective chain area [26] as well as its hydrophilic character [17, 27], thus leading to an increase in the value of Γ_{max}.

Polarization measurements

Polarization curves exhibiting Tafel behavior for carbon steel electrode in 0.5M HCl solutions in the absence and presence of the inhibitors at different concentrations are given in Figures 3,4and 5 respectively. The electrochemical parameters, corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes (βa , βc) and polarization resistance (R_p)were calculated from Tafel plots and shown in Table 4.

Table 4. Electrochemical polarization parameters for the corrosion of carbon steel in 0.5M HCl containing various concentrationf inhibitors at 25°C.

| Inhibitor	Conc. (ppm)	E_{corr}, m.V	I_{corr}, mA.cm^{-2}	β_{a}, mV.dec^{-1}	β_{c}, mV.dec^{-1}	Rp, Ω.cm^2	IE %
Blank	0.00	-521.2	3.2725	238.2	-231.4	13.96	0.00
$C_{12}E_{14}$	100	-491.6	0.5519	148.0	-163.8	63.97	83.135
	200	-486.5	0.3108	123.7	-123.9	73.08	90.503
	300	-485.0	0.1885	114.5	-113.3	104.93	94.24
	600	-481.4	0.1238	117.7	-102.6	156.09	96.217
	1000	-488.6	0.0796	135.9	-98.2	251.15	97.568
$C_{14}E_{14}$	100	-518.5	0.5118	146.9	-165.7	71.12	84.361
	200	-520.5	0.4378	132.9	-157.8	78.19	86.622
	300	-517.9	0.4157	132.7	132.7	80.79	87.297
	600	-516.7	0.3238	121.2	-142.9	87.21	90.105
	1000	-520.2	0.0769	97.2	-105.7	241.76	97.65
$C_{18}E_{14}$	100	-500.6	0.7348	154.4	-144.1	42.14	77.546
	200	-494.7	0.3568	127.3	-126.2	69.25	89.097
	300	-492.5	0.3218	127.4	-123.3	74.83	90.166
	600	-495.5	0.1522	126.1	-109.8	138.72	95.349
	1000	-491.2	0.1411	135.2	-112.0	164.00	95.688
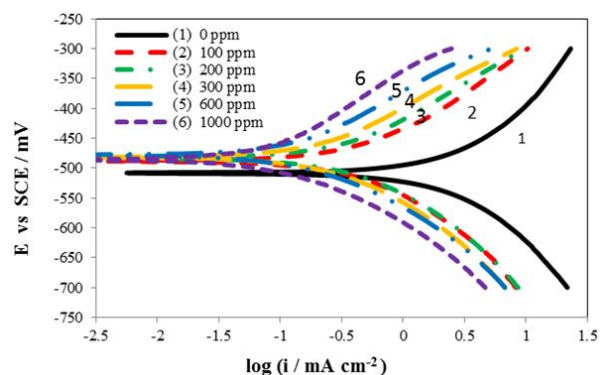
Figure 3. Potentiodynamic polarization curves of carbon steel in the presence of different concentrations of $C_{12}E_{14}$
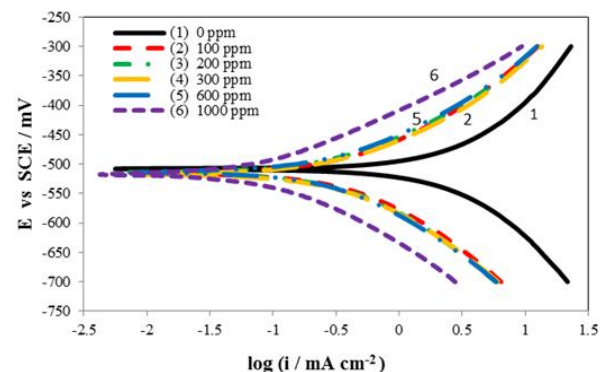

Figure 4. Potentiodynamic polarization curves of carbon steel in the presence of different concentrations of $C_{14}E_{14}$

Both anodic and cathodic currents were drastically inhibited in the presence of the surfactants, revealed that compounds act as a mixed-type inhibitors [28]. The current density also decreased with increasing concentrations of the inhibitors and the inhibition effecency (IE%) calculated according to the following equation [29]:

$$IE\% = (1 - I_{corr}/I^{\circ}_{corr}) \times 100 \qquad (3)$$

where I°_{corr} and I_{corr} are corrosion current densities in the absence and presence of inhibitors, respectively. It is noted that the effeciency increasses by increasing the concentration of the surfactants and tends to atain maximum value when the concentration reaching value close to its CMC. In presence of $C_{12}E_{14}$ and $C_{18}E_{14}$ the corrosion potential (E_{corr}) shifted towards noble direction with increasing concentration, while corrosion potential remained almost constant in the presence of $C_{14}E_{14}$. Furthermore, it was also found that the used inhibitors, generally, induced a slight change in both cathodic and anodic (βa) and cathodic (βc) Tafel lines slopes with inhibitor concentrations, revealing that the mechanism of corrosion reaction did not change and the inhibition of the surfactants involved a simple adsorption [30]. All results confirm the inhibitive effect of the nonionic surfactants on the acidic dissolution of carbon steel as a result of the adsorption of surfactants molecules on steel surface creating a barrier layer of surfactant protecting the metallic surface.
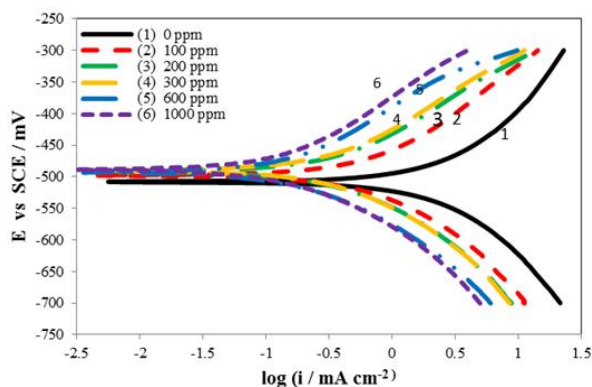

Figure 5. Potentiodynamic polarization curves of carbon steel in the presence of different concentrations of $C_{18}E_{14}$

Evaluation of the prepared additives as flow properties of fuel oil

The depression in pour point is mainly due to wax crystal modification. PPD Molecules are adsorbed on various crystal faces, thereby decreasing the interlocking forces between two nuclei of wax molecules and deforming the regular crystal growth. It is recognized that transition from plate like to spherulitic crystal structure accompanies the lowering of pour point [11, 31- 32]. The wax crystal habitat depends on crude source (where distillate fuel oil derived from the waxy western desert crude oil) and rate of cooling. Table 5 reveals that maximum depression in pour point is obtained with optimum concentration of the additive, pour point depressants of the $C_{14}E_{14}$ is more successful to reduce pour point of fuel oil up to -3 $^{\circ}$C from 18 $^{\circ}$C, so there is a clear depression of 21 $^{\circ}$C at 2000 ppm in pour point, also

this additive is more successful to reduce cloud point of fuel oil up to 20 from 24 $^{\circ}$C, so there is a clear depression of 4 $^{\circ}$C at 2000 ppm in cloud point.

Effect of pendant-chain length of additives on the flow properties of fuel oil

The interaction between wax control additives and paraffin in the fuel oil is crucial, and the additives work best when they are matched to the paraffin distribution in the fuel oil. It was shown from Table 5 and Figure 6 that the pour point depressant increased from C_{12} to C_{14} then decreased again by increasing the chain length from C_{14} and C_{18}. The reason is that the pendant alkyl chain is preferred of moderate alkyl chain length $C_{14}E_{14}$ to enhance steric hindrance. Long alkyl chain lengths $C_{18}E_{14}$ making the additive bulky and less soluble making the polymer effective.
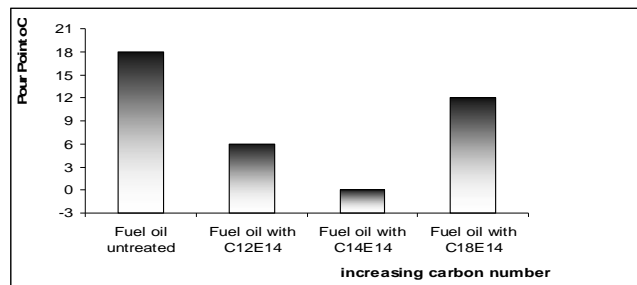

Figure 6. Effect of pendant chain length on the pour point of fuel oil without and with additives at 2000ppm

Effect of additive concentration on pour point depressant of fuel oil

With increasing the concentration of additives, an increase of their activity was obtained. As a result, a great depression of pour point was achieved [33]. From the demonstrated results in Table 4, it was observed that the pour point and cloud point regularly depressed as the additive concentration increased up to 2000 ppm for distillate fuel oil, the pour point of the untreated fuel oil was 18 $^{\circ}$C. With addition of pour point depressants, the best additive $C_{14}E_{14}$ PP$_{2000\ ppm}$ = -3 $^{\circ}$C while additives $C_{12}E_{14}$ and $C_{18}E_{14}$ PP$_{2000\ ppm}$ = 6 and 12°C respectively. This means that at this concentration range, the additive may co-crystallized with the 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 concentration of the additives, the side way growth becomes so much more difficult for the wax crystals [33].

**Table 5. Effect of side chain length and concentration of the additive on the flow properties for fuel oil**

Additives designation	Additive concentration, ppm	CP, $^{\circ}$C	$\Box$ CP, $^{\circ}$C	PP, $^{\circ}$C	$\Box$PP, $^{\circ}$C
$C_{12}E_{14}$	0	24	0	18	0
	300	24	0	15	3
	600	24	0	12	6
	1000	24	0	9	9
	1500	23	I	9	9
	2000	22	2	6	12
$C_{14}E_{14}$	0	24	0	18	0
	300	23	1	12	6
	600	23	1	9	6
	1000	22	2	9	9
	1500	21	3	3	15
	2000	20	4	-3	21
$C_{18}E_{14}$	0	24	0	18	0
	300	24	0	18	0
	600	24	0	18	0
	1000	24	0	15	3
	1500	24	0	12	6
	2000	24	0	12	6

PP = pour point , ΔPP = pour point depression, CP = cloud point, Δ CP = cloud point depression

Effect of additive type on wax crystal modification

Photo analysis is confirms other standard flow tests that evaluate the cold flow properties of untreated/ treated waxy distillate fuel oil through wax crystallization behavior. Photo micrographs illustrated in Figure 7 (a,b,c,d) show variant wax morphology changes according to the type additive. Figure (7a) of untreated waxy distillate fuel shows a feather like growth. On treatment with $C_{12}E_{14}$ at 2000 ppm, the wax crystals are converted from the feather like structure to small particle crystallites illustrated in Figure (7b). On using $C_{14}E_{14}$ at 2000 ppm, the feather like type structures have completely disappears giving small dot size crystals as observed in Figure (7c). Additive $C_{18}E_{14}$ showed a low efficiency to modify the shape of the crystals as in Figure (7d). Correlation between wax modification and flow improvement in terms of cloud and pour point depression appeared to be merely qualitative in such heterogeneous fuel system.
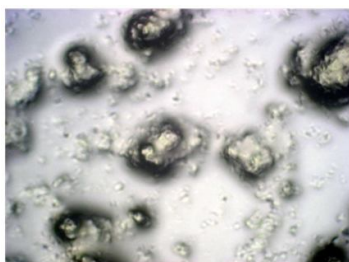
100µm
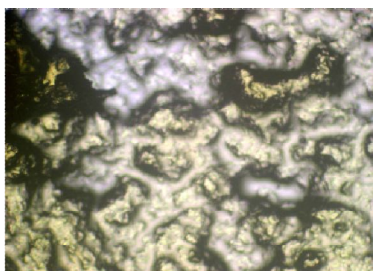
a- Fuel oil untreated, PP = 18ºC, CP = 24ºC
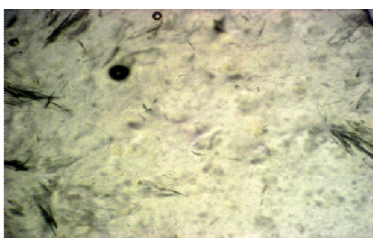
b- Furl oil + 2000 ppm $C_{12}E_{14}$, PP = 6ºC, CP = 22ºC

c- Fuel oil + 2000 ppm, $C_{14}E_{14}$, PP = -3ºC, CP = 20 ºC

d- Fuel oil +2000ppm, $C_{18}E_{14}$, PP = 12 ºC CP = 24 ºC

Conclusions

- A series of ethoxylated nonionic surfactant were synthesized
- The prepared nonionic surfactants showed good corrosion inhibition of pipeline carbon steel L5 X52 in acidic medium 0.5M HCl.
- Polarization measurements demonstrate that the investigated surfactants act as mixed type inhibitors.
- The efficiency of pour point depressants increase with increasing its concentration of the additive.
- The prepared additive $C_{14}E_{14}$ which posses lower CMC value showed higher pour point depressant characteristics in comparison with $C_{12}E_{14}$ and $C_{18}E_{14}$.
- A correlation between the depression of flow parameters (PP, CP) and degree of wax modification has been verified.

REFERENCES

[1] A.M. Al-Sabagh, M. M. Osman, A. M. Omar, and I.M. El-Gamal "Organic Corrosion Inhibitors for Steel Pipelines in Oilfields" Anti-Corrosion Methods and Materials, 43 (6), 11-16 (1996).

[2] Keera S.T. and Deyab M.A., Impedance spectroscopy a technique for studying corrosion inhibition of carbon steel in formation water. Egypt. J. Petrol.2008; 17:53-64.

[3] Hegazy, M.A.; Ahmed, S.M. and Aiad, M., Some Cationic Surfactants Based on P-N, N, Diethylaminoaniline As Corrosion Inhibitors For Low Carbon Steel Alloy Egypt. J. Petrol. 2008; 17: 93-102.

[4] Carcia, M. D.; Carbognani, L.; Orea, M. and Urbina, A., The influence of alkane class-types on crude oil wax crystallization and inhibitors efficiency Journal of petroleum Science and Engineering 2000; 25:99-105.

[5] Han, S.; Wang, P.; Wang, Y.; Song, Y. and Ren, T., The Sustainability of clean coal technology IGCC with/without CCS. Process Safety and Environmental protection 2010; 88: 41 -46.

[6] Bharambe D.P., Designing maleic anhydride-α-olifin copolymeric combs as wax crystal growth nucleators; Fuel Processing Technology, 91, 997–1004, (2010).

[7] Chen, W.; Zhao, Z. and Yin, C., The interaction of waxes with pour point depressants. Fuel 2010; 89: 1127- 1132.

[8] Al-Sabagh, A.M.; Kafrawy, A.F.; Khidr, T.T.; El- Ghazawy, R.A. and Mishrif, M.R., Synthesis and Evaluation of Some Novel Polymeric Surfactants Based on Aromatic Amines Used as Wax Dispersant for Waxy Gas Oil. Journal of Dispersion Science and Technology 2007; 28: 976- 983.

[9] Maria, E.; Chevalier, Y.; Edoux, F.; Germanuad, L. and Flores, P., Control of n-alkanes crystallization by ethylene–vinyl acetate copolymers, Journal of Colloid and Interface Science 2005; 290: 406-418.

[10] El-Shamy O.A.; Khidr T.T. and Doheim, M.M., Effect of Ethoxlate Chain Length on the Pour Point Depressant of Middle Distillate Fuel Oil. Journal of Dispersion Science and Technology 2011; 32: 654-658.

[11] Holder, G.A. and Winker, J., Cloud and pour point phenomena exhibited by solutions of binary n-paraffin mixtures. J. Inst. Pet. 1965; 51: 228-234.

[12] Ashbaugh, H. S.; Guo, X.; Schwahn, D.; Prudhome, R. K.; Richter, D. and Fetters, L. J. Energy Fuels, Synthesis of poly (maleic acid alkyl amide-co-olefine-co-styrene. 2005;19: 138-144.

[13] Deshmukh, S. and Bharambe, D.P. 2008. Synthesis of polymeric pour point depressants for Nada crude oil (Gujarat, India) and its impact on oil rheology Fuel. Processing and Technology 89:227-233.

[14] El-Gamal, I. M.; Khidr, T. T. and Ghuiba, F.M. 1998. Nitrogen - Based Copolymers as Wax Dispersants for Paraffi nic Gas Oils. Fuel 77:375-385.

[15] El-Gamal, I. M.; Atta, A.M. and Al-Sabagh, A. M. 1997. Polymeric Structures as Cold Flow Improvers for Wax Residual Fuel Oil. Fuel 15: 1471-1478.

[16] Marquat, J. R.; Dellow, G. B. and Freitas, E. R. 1968. Determination of normal paraffins in petroleum heavy distillates byurea adduction and gas chromatography. Anal. Chem. 40: 1633- 1637.

[17] El-Shamy O.A. 2008. Study of Some Physicochemical Properties for Surfactant-Polymer Systems and Their Application as Remedial Agents for Water, PhD thesis, Faculty of Science, Ain Shams University.

[18] El-Feky, A.A.; Shalaby ,M.N. and El-Shamy , O.A.A. 2009. Polymers as Hydrophobic Adsorbent Surface for Some Surfactants. J. Disp. Sci. and Technol. 30:445-450.

[19] Inoue, T.; Nakashima, K. and Szuki, M. J.Oleo. Sci. 2002; 51:753 – 760.

[20] Zhang, Z. and Yin, H., J. Zheijiang University Sci. 2005; 6:219-221.

[21] Shishkin, Y. L.; Yazynina, I.V. and Ovchar E.V., Study of crystallization and melting of solid waxes by photometric and thermal methods. Chemistry and Technology of Fuels and Oils 2008; 4: 65-70.

[22] Edwin D. Becker. High Resolution NMR (3) Theory and Chemical Applications ISBN: 978-0-12-084, Elsevier-Inc. 2000.

[23] Ivan S. O.; Tito J.B.; Roberto S. S.; Jair C.F. and Eduardo R.D. 2007. NMR Quantum Information Processing, ISBN: 978-0-444-52782-0 Elsevier B.V.

[24] Metin, B. 2005. "Basic 1H- and 13C-NMR Spectroscopy" ISBN: 978-0- 444-51811- 8 Elsevier B. V.

[25] El Feky, A. A. Shalaby, M. N. El-Shamy, O. A. A. and Selim, S. A. 2010. Adsorption of Some Surfactants onto Polyvinyl Alcohol as Hydrophobic Polymer Surface J. Disp. Sci. and Technol. 31:1091-1099.

[26] Clint, J. H. 1992. Surfactant Aggregation, Chapman and Hall, New York.

[27] Burezyk, B.; Wilk, K. A.; Sokoowoki, A. and Syper, L. 2001. Influence of surface hydrophobic groups on the adsorption of proteins onto non porous polymeric, particls with immobilized metal ions. J. Colloid Interf. Sci. 240: 552.

[28] Khaled K.F. and Hackerman N. 2004. Ortho-substituted anilines to inhibit copper corrosion in aerated 0.5 M hydrochloric acid. Electrochim. Acta 49: 485–495.

[29] Roberge P. R. 2000. "Handbook of Corrosion Engineering", McGraw-Hill, USA.

[30] Ramji, K.; Cairns D. R. and Rajeswari S. 2008. Synergistic inhibition effect of 2-mercaptobenzothiazole and Tween-80 on the corrosion of brass in NaCl solution. Appl. Surf. Sci. 254, 4483–4493.

[31] Chanda, D.; Sarmah, A.; Borthaku, R. A.; Rao, K.V.; Subrahmanyam, B. and Das, H. C. 1998. Combined effect of asphaltenes and flow improvers on the rheological behaviour of Indian waxy crude oil. Fuel 77, 1163 –1167.

[32] Adewusi V. A. 1998. An improved inhibition of paraffin deposition from waxy crudes. Pet. Sci. and Technol. 16 (9 & 10), 953 - 970

[33] Machado, A.L.; Lucas E.F. and Gonzalez, G. 2001. Poly(ethylene-co-vinyl acetate) (EVA) as wax inhibitor of a Brazilian crude oil: oil viscosity, pour point and phase behavior of organic solutions. Pet. Sci. Eng. 32(2-4) 159-165.

****