



RESEARCH ARTICLE

POUR POINT DEPRESSION AND ASPHALTENE SOLUBILIZATION USING
NONIONIC SURFACTANTS

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ARTICLE INFO

Article History:

Received 28th July, 2012
Received in revised form
10th August, 2012
Accepted 14th August 2012
Published online 30th September 2012

Key words:

Surfactants, Surface activity,
Pour point depressants,
Crude oil, Wax,
Asphaltene, X-Ray.

ABSTRACT

Hexatriethanolamine monomyristate (HTAMM) and hexatriethanolamine monolaurate (HTAML) have been prepared by the reaction of hexatriethanol amine with myristic acid / laurate acid. The structure of the prepared compounds was confirmed by infrared spectroscopy. The prepared surfactants were investigated as pour point depressants (PPD) for crude oil (PP= 21 °C) from the evaluation, it was found that, the maximum depression of pour point was obtained by HTAMM (PP= 0 °C) while minimum depression of pour point of HTAML was PP = 6°C. HTAMM additive, show stronger interaction with wax than HTAML additive. The X- ray diffractometer patterns of asphaltene in absence and presence of investigated additives was studied. Surface tension as a function of concentration of these surfactants in aqueous solutions was measured at 35, 45 and 55°C. From these measurements, the critical micelle concentration (CMC), the maximum surface excess concentration, Γ_{max} , the minimum area per molecule at the aqueous solution / air interface were calculated.

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INTRODUCTION

If paraffin hydrocarbon liquids, including both crude oils and condensates, are cooled during transportation, the wax crystals tend to deposit on the cold pipe wall. If these deposits get too thick, they can reduce the capacity of the pipeline transportation and cause other problems. The temperature, at which the first crystal appears, called wax appearance temperature (WAT), which is considered as an important parameter (Misra *et al.*, (2004). Waxy crude oils with high molecular weight paraffinic compounds at temperatures below WAT may separate as a wax phase, causing frequent shutdowns and operational problems during transportation, production, storage and consumption (Lashkarbolooki *et al.*, 2011; Chen *et al.*, 2010; Aiyejina *et al.* 2011; Deshmukh *et al.*, 2008). In extreme cases, wax crystals may also cause oil to gel and lead to problems of restarting the pipeline, damaged zones in the formation, plugged tubing, and sludge deposits at the bottom of the tank. These deposits in the well bore can lead to restricted flow line pressure, decreased production and can cause mechanical problems (Mcclaffin, 1983). Indeed, pipeline blockage removal can be very expensive (Nyvlt and Vevrka, 1997). Many methods have been attempted for the prevention of the crystals mating together. Since, adding chemical additives, such as pour point depressants (PPDs), cold flow improvers, paraffin inhibitors or wax crystal modifiers is the most convenient and economic way, it is widely used in the industry (Chen *et al.*, 2009). Among the mechanism the aeries, adsorption, co-crystallization, nucleation and improved wax solubility are widely accepted by mechanism researchers (Zhang *et al.*, 2004). Surface activity and micellar properties of surfactants (Osman *et al.* 2003; Al-Sabagh 1998; Sugihara *et al.*, 1995; Alexandridis *et al.*, 1994; Voicu *et al.*, 1994; Chatterjee *et al.*, 2002; Burczyk *et al.*, 2002) are one of the potential importance and scientific interest. Surfactants micellize in solution after a critical micelle concentration (CMC) depends on their

molecular structure and environmental conditions (Moulik, 1996; Clint, 1991). The concept of the CMC value is very useful and perhaps the most frequently measured and discussed micellar parameter (Osman *et al.* 2003). Surface tension is one of the widely used physico-chemical property in aqueous / air interface to determine CMC value without serious difficulty (El-Gazawy *et al.*, 2005). Through surface tension versus concentration curves (SVC), several parameters are derived (Zuo *et al.*, 2004; El-Shamy *et al.*, 2011). The present work deals with the synthesis and evaluation of some type of additive; hexatriethanolamine monomyristate (HTAMM) and hexatriethanolamine monolaurate (HTAML) as pour point depressants for crude oil, also the intend to study the interaction between two synthesized additives and wax constituent in crude oil through x- ray diffraction.

Experimental

Materials

Triethanolamine, Myristic and lauric acids were purchased from Aldrich Chemicals. Isolation of the crude: Western waxy crude oil was used for evaluating the performance of the synthesized pour point depressants. Their physicochemical characteristic is given in Table 1. Asphaltene and wax were isolated from the crude by International petroleum (IP) procedure no. 143.

Esterification of hexa-triethanolamine (General procedure)

Hexatriethanolamine (HTA) was prepared according to the was mention method (El-Shamy 2008), the ester was prepared by the following method, 1mol of the prepared HTA was added to myristic acid (1mol) / lauric acid (1mol) in three necked flask in the presence of p- toluene sulfonic acid (0.005 mol, 0.086g) as a catalyst. The reaction mixture was heated at 150 °C with continuous stirring until the theoretical amount of water was collected. The product was purified by washing with a hot solution of 5 % sodium carbonate and then dissolved in petroleum ether (b.p. 40-60 °C). the organic layer was separated and the solvent was distilled off (Hafiz and Khidr,

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2007; Hafizand Abdou, 2003). The products obtained was hexatriethanolamine monomyristate (HTAMM) and hexatriethanolamine monolaurate (HTAML) after collecting 18g of water.

Surface tension measurements

The surface tensions of the tested samples were measured in aqueous solution by DeNouy Tensiometer (kruss K6 type) at different temperature ranged from 35, 45 and 55 °C. Freshly prepared aqueous solution of the product (HTAMM and HTAML) in deionized water was prepared with a concentration range 0.01-10 mmol/L. The ring was washed twice after each reading first by ethanol then distilled water. The critical micelle concentration (CMC) of the investigated surfactants were determined and listed in Table 2. The surfactant concentration above the CMC were adequately diluted so that only monomer surfactant solutions were analyzed (El-Feky, A.A. *et al.*, 2010).

Structure confirmation the prepared additives

The structure of the prepared additive was confirmed by using Forier Trasimition Infrared FTIR spectroscopic analysis Egyptian Petroleum Research Institute (EPRI) using model Genesis series (USA) infrared spectro-photometer doping KBr technique.

Evaluation tests of the prepared compound as pour point depressants

Pour point measurement (ASTM D 97)

Solution of crude oil soluble samples in toluene contains 10% active materials are prepared according to ASTM D 97 method. Different concentrations (100, 250, 500, 1000 and 2000 ppm) of PPD solutions were injected into the crude oil and tested as pour point depressants.

X-Ray Diffraction Spectroscopy

The structure of the asphaltene isolates from crude oil and asphaltene + 2000 ppm (HTAMM) and asphaltene + 2000 ppm (HTAML) were characterized using X-ray powder diffractometer, PANalytical X'Pert PRO MPD (Netherlands). Cu K α radiation with wave length= 1.5418 Å was used at a rating of 40 kV, 40 mA. The diffraction patterns were recorded at room temperature in the angular range of 4-70° (2 θ) with step size 0.02 ° (2 θ) and scan step time 0.4 (s). The crystalline phases were identified using the ICDD-PDF database.

RESULTS AND DISCUSSION

Chemical structure

The chemical structure of the prepared nonionic surfactant was confirmed by the FTIR spectra of the synthesized nonionic surfactants showed absorption band that corresponding to the (HTAMM) and (HTAML). The absorption band at 1730 cm⁻¹ indicates the formation of ester group. The absorption band at 2930 cm⁻¹ is corresponded to the stretching of the two groups CH₂, CH₃ in the fatty chains and other band appears at 1036 cm⁻¹, 1153 cm⁻¹ corresponded to C–O and C–N groups respectively illustrated Figure (1 a, b).

Surface properties

The CMC of the investigated surfactants at (35, 45 and 55 °C) were determined by plotting the surface tension (γ) versus log concentration as shown in Figure (2 a, b). The abrupt change in the slope of (γ) versus log C. The CMC values are listed in Table together with other surface parameters. By careful inspection to the values of the CMC, it can be concluded that at 35 °C the CMC increase as the hydrophobicity decrease. This increase may arise from the crowding that take place inside the micellar core leads to an increase in the surfactant – surfactant repulsion and hence alters the micelle formation (Rosen, 1978). The data listed in Table (2) shown decrease

in the CMC with temperature for all samples. This behavior may be due to increased temperature, which caused desolvation of the surfactant molecules. The surface tension data were used to calculate the surface excess concentration Γ_{\max} in mol / cm² by applying Gibbs equation (Rosen, 1978).

$$\Gamma_{\max} = -\frac{1}{2.303RT} \frac{d\gamma}{d\log C} \quad (1)$$

Where R = universal gas constant (8.314 J/mol) and T = T_C + 273.

The Γ_{\max} values in Table (1) were used to calculate the minimum area per molecule, A_{\min} in nm²/molecule at the aqueous phase interface using the relationship:

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

Where, N_A: Avogadro's number, 6.023 x 10²³.

Table 1. Physical characteristics of crude oil

Properties	Methods	Result
Specific gravity at 60/60°F	IP 160/87	0.8412
Kinematics viscosity at 40°C (cst)	IP 71/80	3.7
Pour point (pp), °C	IP 15/67(80)	21
Sulfur content (wt%)	IP 266/87	0.723
Asphaltene content, (wt%)	IP 143	0.828
Wax content, (wt%)	UOP 46/64	12.822
Total paraffins content (wt%)	ASTM D2887 (GLC)	95.180
n-paraffin (wt%)	ASTM D2887 (GLC)	89.330
Iso-paraffins (wt%)	ASTM D2887 (GLC)	05.850

The data obtained for Γ_{\max} and A_{\min} were presented in Table (2). The effect of temperature on surface area, generally increasing the temperature caused two opposite effects (Rosen, 1976) these are:

1- Decrease in the area per molecule at the interface resulting from the increase in the dehydration around the surfactant molecule upon increasing the temperature. Increase in the area per molecule due to orientation as a result of the thermal molecular motion at high temperature. For our surfactants under investigation, the dehydration effect has a priority over the orientation effect. Table 2 was shown the effectiveness (π_{cmc}), which determines the surface activity of the surfactant molecule at their CMCs. π_{cmc} may be attributed to the increase in the area occupied at the interface. It was found that for all surfactants under investigation, π_{cmc} decrease with increase with increase in temperature from 35, 45 and 55 °C.

Influence of the synthesized additives on the pour point depression

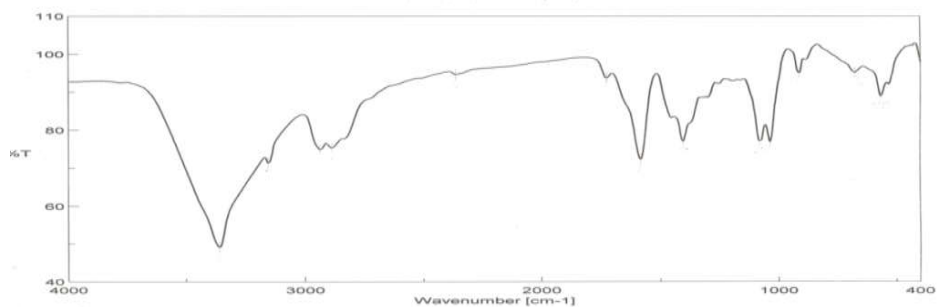
The two synthesized additives were tested as pour point depressants through pour point determinations according to ASTM- 97 procedure at concentration 100, 250, 500, 1000 and 2000ppm. Results given in Table (3) show that almost all additives achieved moderate pour point depression at concentration 1000ppm. In case of the HTAMM compound achieved the preferred pour point depression for the crude oil ($\Delta\text{PP} = 21^\circ\text{C}$) at the concentration 1000 ppm than the additive HTAML ($\Delta\text{PP} = 15^\circ\text{C}$). This is due to the increase of the number of carbon atoms which cause a decrease of the crystallization ability of pendant chain of myristate so inhibition of the wax crystal formation should be obtained accordingly, the matching average pendant chain length of additive with paraffin distribution of oil provided the greatest pour point depression.

Concentration effect on pour point depression

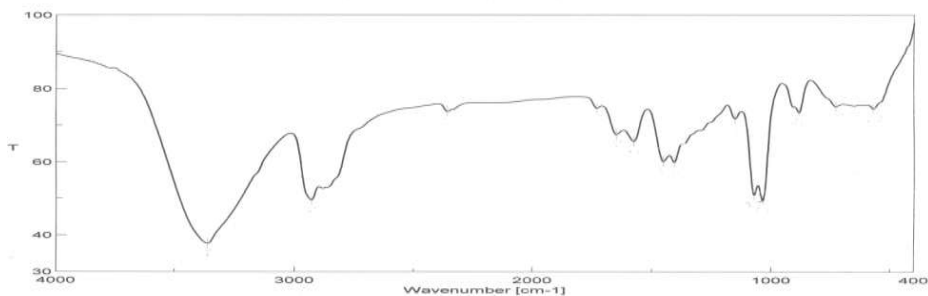
Generally it was found that, with increasing the concentration of additives from 100 to 2000 ppm, an increase of their activity was obtained and as a result, a great depression of pour point was achieved. From the demonstrated results in Table 3, it was observed that the pour point values regularly depressed as the additive concentration increases up to 2000 ppm. This means that at this concentration range, the additive may co-crystallizes with the paraffin

Table 2. The surface properties of the investigated surfactants

Surfactants	Chemical Formula	T °C	CMC (mmol/L)	π_{CMC} (mNm ⁻¹)	$\Gamma_{max} \times 10^{10}$ (mol cm ⁻²)	A_{min} (Å)
HTAMM	[C ₁₃ H ₂₇ COOCH ₂ CH ₂ NCH ₂ CH ₂ OHCH ₂ CH ₂ O] ₆	35	2.10	32.5	2.66	0.26
		45	1.75	23.0	2.58	0.64
		55	1.50	31.5	3.47	0.48
HTAML	[C ₁₁ H ₂₃ COOCH ₂ CH ₂ NCH ₂ CH ₂ OHCH ₂ CH ₂ O] ₆	35	2.80	32.0	2.64	0.74
		45	1.91	31.5	3.17	0.52
		55	1.61	30.5	3.41	0.49

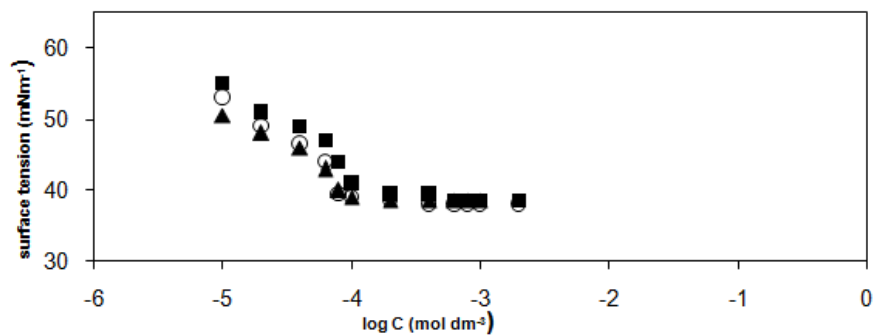


(a)

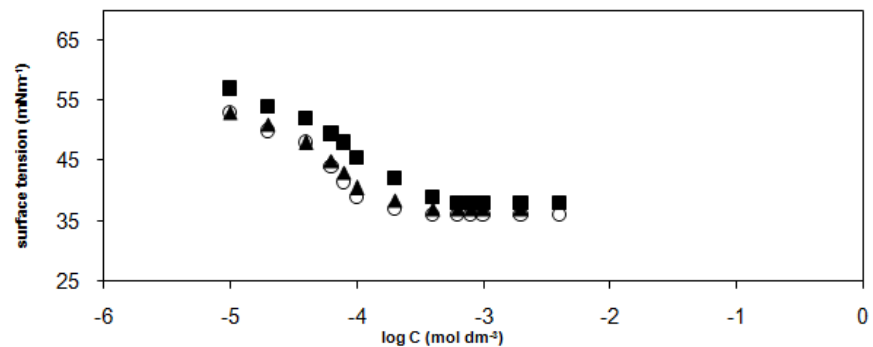


(b)

Fig. 1. FTIR spectra for (a) HTAMM and (b) HTAML



(a)



(b)

Fig. 2. Variation of surface tension with log concentration for (a) HTAMM and (b) HTAML at: (■) 35 °C; (▲) 45 °C; and (○) 55 °C.

Table 3. The effect of additives on the pour point of crude oil

Additives	Additive concentrations, ppm	PP, °C	ΔPP, °C
HTAMM	0	21	0
	100	15	6
	250	12	9
	500	6	15
	1000	0	21
	2000	0	21
HTAML	0	21	0
	100	18	3
	250	15	6
	500	9	12
	1000	6	15
	2000	6	15

and modifies their crystals. In general, at lower additives 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 (Andre, *et al.*, 2001).

X-Ray diffraction measurements

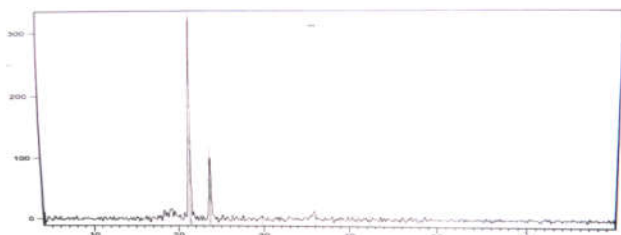
X-Ray diffraction investigation of asphaltene in absence and presence of prepared surfactants (200 ppm). The particle size of asphaltene with in presence of 2000ppm HTAMM and asphaltene with 2000ppm from HTAML were determined by using the Scherer equation (Cullity, 1967)

$$d = \frac{B\lambda}{\beta \cos\theta} \quad (3)$$

Where d is the mean particle diameter, B is Scherer constant (0.89), λ is wave length of the x- ray beam = 1.5405Å, β is full – width half maximum FWHM of diffraction lines, and θ is the diffraction angle. The computed values of particle size (Table 4) showed increasing the order of asphaltene with 2000 ppm of HTAMM = 2.19 < asphaltene with 2000 ppm of HTAML = 5.89 < Asphaltene = 8.88. The PPD additives are considered to be well in the primitive molecular orientating and nucleating process. HTAMM is considered more efficient than HTAML. Figure 3 represent the XRD spectrogram for HTAMM additives. The PPD molecules will get into the lattice part of wax crystal cells causing change in the surface properties of the wax crystals. It will also bring the n-alkane molecules to deposit on the surface of the wax crystals. Adsorption can also decrease the plane density, but the changes of the surface properties of the wax crystal are different than those with co- crystallization.

Table 4. X-Ray Diffraction results of the asphaltene in absence and presence of additive

Sample	Pos. (°2Th.)	FWHM (°2Th.)	d-spacing (Å)	Rel. Int. (%)
Asphaltene	21.3030	0.2952	4.17095	100.00
Asphaltene + HTAMM	21.3318	0.3149	4.16539	100.0
Asphaltene + HTAML	35.7519	0.6298	2.51155	2.21
Asphaltene + HTAMM	21.2772	0.2952	4.17596	100.00
Asphaltene + HTAML	19.1588	0.2362	4.63264	2.04

**Fig. 3. XRD spectra for asphaltene in presence of 200 ppm from HTAMM**

Conclusions

The conclusion of this work can be addressed in the following points:

- Synthesis hexatriethanolamine monomyristate (HTAMM) and hexatriethanolamine monolaurate (HTAML) have been prepared by the reaction of hexatriethanol amine with myristic acid / laurate acid.
- Surface properties were discussed and show that the CMC increase with increasing the hydrophobicity, while it decrease with increasing the temperature.
- Surface excess calculated and found to be increased with temperature.
- HTAMM achieved the preferred pour point depression for the crude oil ($\Delta PP_{1000ppm} = 21^\circ C$) than the additive HTAML ($\Delta PP_{1000ppm} = 15^\circ C$).
- It was found that the efficiency of the prepared compound as PPD increases with increasing the concentration of the prepared additive.
- Study X-Ray diffraction of asphaltene and asphaltene with different additives.

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