



## DEVELOPMENT OF MULTIFUNCTIONAL FORMULATIONS FOR INHIBITION OF WAXES AND ASPHALTENES DEPOSITION

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### ABSTRACT

The development of formulations that solve at least two problems simultaneously (called multifunction or combo formulations) is very useful. In this study, different formulations were prepared in an attempt to find one that could act at the same time to inhibit deposition of waxes and asphaltenes. Formulations were prepared containing EVA 33 and one of the additives for asphaltenes dispersion (dodecylbenzenesulfonic acid, cardanol and two commercial products called INH1 and INH2), at various concentrations. The results showed that none of the asphaltenes stabilizers exhibited any influence on the performance of EVA33. Nevertheless, the EVA33 affected slightly the performance of the asphaltenes stabilizers. The formulations containing cardanol and EVA 33 performed better at inhibiting deposition of both asphaltenes and waxes than the other formulations did.

### KEYWORDS

multifunctional formulations; organic deposition; precipitation onset; pour point; wax appearance temperature

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## 1. INTRODUCTION

Crude oil is a complex mixture of hydrocarbons, which are divided into different groups, such as waxes, aromatics, naphthenes, resins and asphaltenes. Among these substances, waxes and asphaltenes stand out as the main causes of organic deposition (Embrey & Larke, 2010; Lucas et al., 2009; Mansur et al., 2012; Vieira et al., 2010). Problems related to crystallization and deposition of heavy organic fractions during the production, transportation, and storage of crude oil can cause huge losses to the petroleum industry. These heavy organic fractions, such as waxes, resins and asphaltenes, can be found in petroleum in different quantities, forms and states. All of them can cause problems from the extraction to the refining stages (Araújo et al., 2008; Junior et al., 2007; Kane et al., 2003; Oliveira et al., 2007; Piroozan et al., 2010).

The deposition of the waxes present in crude oil results from the crystallization process which, in turn, is a consequence from the ordering of the paraffin chains favored by cooling. The crystallization process can be divided into three stages. The first is the nucleation, where the crystalline nuclei initially start to appear. In the next stage, the crystals grow, provided that the temperature of the system remains below the nucleation temperature. In the last stage, the crystals unite to form a three-dimensional wax network that impedes the oil flow (Hutter et al., 2004; Terry et al., 2003; Zhang et al., 2005). At this point, called the pour point (PP), the oil is highly viscous. The pour point is defined as the lowest temperature at which the oil will flow freely under the action of its own weight (Chen et al., 2010; Visintin et al., 2008). Various authors have mentioned the efficiency of polymers to inhibit deposition of waxes. These polymers have structures based on ethylene, acrylic and methacrylic esters with long alkyl groups, and phosphoric esters, among others (Aiyejina et al., 2011; Castro & Vazquez, 2008; Gentili et al., 2005; Mansur et al., 2006; Marie et al., 2005; Silva et al., 2004; Soni et al., 2010, Vieira et al., 2012).

Asphaltenes are the petroleum components with the highest polarity and molar mass. They have great structural complexity due to their polycondensed aromatic rings, containing alkyl radicals of different sizes and functional groups

formed by oxygen, nitrogen and sulfur, as well as heavy metals such as vanadium, nickel and iron (Honse et al., 2012; Mullis, 2007). Asphaltenes are defined as the petroleum fraction that are insoluble in n-alkanes (n-pentane, n-heptane etc.) and soluble in aromatic solvents (benzene and toluene) (Fan et al., 2010). They are found in crude oil as a stable colloidal suspension (Chouparova et al., 2004). However, during oil production, the suspension can become destabilized due to variations in pressure and temperature, changes in the oil's chemical composition, and field operations such as acid stimulation (Smith et al., 2008; Vargas et al., 2009; Juyal et al., 2010). Asphaltenes are deposited due to the aggregation of these molecules. Various studies have mentioned the use of amphiphilic molecules as asphaltene dispersants, which contains acids groups and long alkyl chains, such as p-alkylphenols (Chang & Fogler, 1994; Moreira et al., 1998). A recent study carried out by this group showed that polymers containing specific polar groups in their structure, such as sulfonic groups, act to stabilize asphaltene molecules (Lima et al., 2010).

The present study examined the performance of different formulations in an attempt to obtain a combo formulation that can, at the same time, inhibit the deposition of waxes and asphaltenes. Due to the similar solubility of waxes and asphaltenes deposition inhibitors, the development of a multifunctional formulation that mitigates both of these deposition problems is very attractive to the petroleum industry. For this purpose, various concentrations of dodecylbenzenesulfonic acid (DBSA), cardanol, and two commercial products (INH1 and INH2) were evaluated as asphaltene dispersants. In turn, commercial ethylene-co-vinyl acetate copolymer containing a 33 wt.% of vinyl acetate (EVA33), at various concentrations, was analyzed as a wax deposition inhibitor. Various formulations were prepared containing EVA33 and one of the additives with action on asphaltene, at various concentrations. The development of multifunctional formulations that mitigate different problems during petroleum production has been gaining importance due to cost reductions and greater operational efficiency (Gonzales et al., 2012; Hernandez-Altamirano et al., 2012; Jackson, 2007; Mc Naughtan et al., 2004). Another important advantage of such formulations is the reduction of the problem of chemical

incompatibility of additives, a common occurrence in operations that use different products that have been evaluated individually (Collins et al., 2001).

## 2. MATERIALS AND METHODS

### 2.1 Materials

The crude oil was supplied by the Petrobras Research Center (CENPES), Rio de Janeiro, Brazil, with relative density, at 25°C, of 0.88806 g/cm<sup>3</sup> and API° of 26.47. The commercial ethylene-co-vinyl acetate copolymer (EVA33) was supplied by Braskem S.A., Triunfo, Brazil. The cardanol was supplied by Satya Cashew Chemical, India. The dodecylbenzenesulfonic acid (DBSA) was supplied by Sigma Aldrich, São Paulo, Brazil. The commercial asphaltene dispersant samples, INH1 and INH2, were provided by CENPES. Finally, the toluene (commercial grade) and n-heptane (P.A. 99.5%) were supplied by Vetec Química Fina Ltd., Xerém, Brazil. All samples were used as received, except the toluene, which was distilled at 110°C and dried with alumina before using.

### 2.2 Methods

The efficiency of the asphaltene dispersants was determined by precipitation onset tests in a near-infrared (NIR) spectrophotometer at 1600nm. With the addition of n-heptane the absorbance decreased because of the dilution. When the volume of n-heptane was enough to provoke the asphaltene aggregation, the absorbance increased since the size of the particle was bigger. So, the asphaltene precipitation onset was taken at the n-heptane volume, in which the absorbance had its lowest value, and the result was expressed as mL of n-heptane/mL of oil (Carbonezi et al., 2009; Garreto et al., 2010; Garreto et al, 2013; Sousa et al., 2004). The concentrations of the dispersant were evaluated ranging from 250 to 5000ppm. The additives were blended in the oil with the product dispersed in toluene at a concentration of 10m/v%. The tests were conducted with 10mL of petroleum system. The flocculant solvent (n-heptane) was mixed with the petroleum system with and without additive using a chromatographic pump (flow rate = 2 mL/min). Plots of absorbance as a function of flocculant volume were obtained. The volume of n-heptane at the lowest absorbance was divided by

10 to obtain the asphaltene precipitation onset. The error of this analysis was ± 0.5mL of n-heptane, so the error of asphaltene precipitation onset is ± 0.05mL of n-heptane/mL of oil system.

The performance of the EVA33 as a wax deposition inhibitor, at concentrations of 50, 100, 500 and 1000 ppm, was evaluated by measuring the pour point and the wax appearance temperature (WAT), determined by differential scanning microcalorimetry (μDSC). The EVA33 was added to the oil as a solution in dry toluene at 10 m/v%. The method of determining the pour point was adapted from the ASTM D97-93 standard, utilizing a Thermo Haake C40P refrigerated circulator bath. First, the crude oil samples were heated to 50°C to eliminate any crystalline structure of the waxes. Then, they were transferred to cuvettes coupled to a thermometer and cooled. At each 2°C decrease in temperature the cuvettes were removed from the bath and slowly placed in an horizontal position to check whether the solution was still fluid. The temperature at which fluidity was no longer observed plus two degrees was considered the pour point. The WAT was obtained by μDSC using a SETARAM model μDSC III microcalorimeter. First, the oil was heated in a chamber at 80°C for one hour to eliminate any organized paraffinic structure. Then, the samples were weighed and sealed in the stainless steel cells. At this stage, 0.400g of oil were placed in sample cells and 0.3680g of n-undecane (n-C11) were placed in the reference cell. The analyses were carried out under dry nitrogen (N<sub>2</sub>) flow at a pressure of 1 bar, at a cooling rate of 0.6°C/min.

## 3. RESULTS AND DISCUSSION

### 3.1 Evaluation of the efficiency of EVA33 as wax deposition inhibitor

The efficiency of EVA33 as a wax deposition inhibitor was evaluated by determining the pour point (PP). This is a static test to determine the temperature at which the oil sample ceases to flow. The reduction of flow is directly associated with the reduction of kinetic energy due to the decline in temperature. Table 1 reports the pour point results for the petroleum with and without the addition of varied concentrations of EVA33.

**Table 1.** Pour point of crude oil with and without adding EVA33.

Additive	Concentration (ppm)	Pour point (°C)
	-	12
EVA33	50	2
	100	- 8
	500	< -20°C
	1000	< -20°C

The oil without EVA presented a pour point of 12°C. EVA33 was a good pour point reducer, considering that addition of 50ppm was sufficient to lower the pour point by up to 10°C, and with 100ppm a reduction of 20°C was obtained. With EVA concentrations greater than 500ppm it was not possible to determine the exact pour point temperature of the crude oil studied due to the limited scale of the thermometer used in the experiments. The pour point value for EVA concentrations of 500 and 1000ppm were below -20°C. The aim of these analyses was to select concentrations of EVA33 to be utilized in preparing the combo formulations, which were 100 and 500ppm.

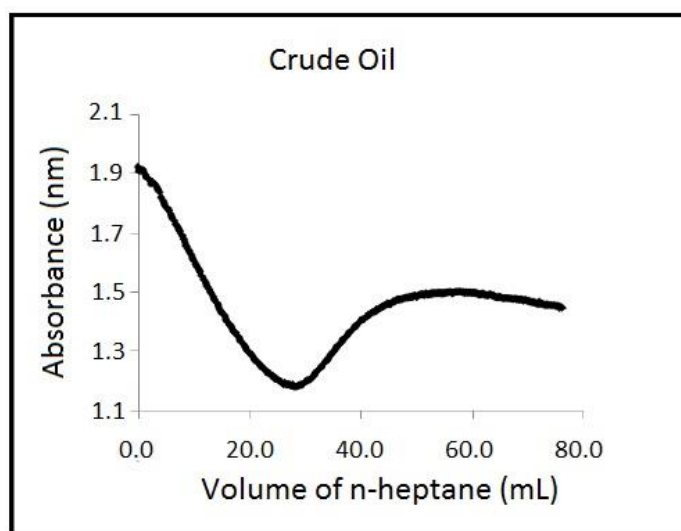
### 3.2 Efficiency of the dispersants in stabilizing asphaltenes

Figure 1 shows the curve of absorbance against volume of n-heptane for the pure oil. Since 10 mL of oil were used, the precipitation onset was 2.52mL of n-heptane/1 mL of oil. The higher the

precipitation onset, the more stable the oil is in terms of asphaltenes precipitation.

Table 2 summarizes the onset precipitation results obtained for the pure oil and with addition of the different dispersants (DBSA, cardanol, INH1 and INH2) at varying concentrations. The results obtained for the DBSA indicated that it is efficient in inhibiting asphaltenes deposition at a relatively low concentration, since it retarded this precipitation in comparison to the crude oil without additive. The asphaltenes precipitation onset rose from 2.52mL to 2.82mL when adding only 100ppm of DBSA. However, a super-dose (greater than 1000ppm) led to the inefficiency of this product, probably due to DBSA self aggregation.

Cardanol was more efficient at inhibiting asphaltenes depositions than DBSA, at all the concentrations studied. And, differently from the DBSA, cardanol was more efficient at higher concentrations, reaching its best performance at

**Figure 1.** Absorbance against volume of n-heptane for the pure crude oil.

**Table 2.** Precipitation onset obtained by NIR for crude with and without additive.

Additives	Concentration (ppm)	Precipitation onset (mL of heptane/mL of oil)
Pure crude	-	2.52
DBSA	100	2.82
	500	2.80
	1000	2.80
	2000	2.74
	3000	2.50
	5000	2.50
Cardanol	250	2.90
	500	2.88
	1000	2.88
	2000	2.96
	3000	3.04
INH1	1000	2.96
	3000	2.74
INH2	1000	2.88
	3000	2.64

5000ppm, where the precipitation onset was shifted to 3.34mL of n-heptane per 1mL of oil. Some authors (Ibrahim & Idem, 2004; Kraiwattanawong et al., 2009) have mentioned that the efficiency of asphaltenes dispersants is directly related to the acid-base interaction between the dispersants and the asphaltenes molecules.

The literature (Al-Sahhaf et al., 2002) compares resorcinol (DR), DBSA, and nonylphenol (NP) as asphaltene dispersants and observing the following order of efficiency: DR > DBSA > NP, stating that this is related to the acidity of these compounds. Resorcinol is listed as the best dispersant because its hydroxyl groups that are linked to the aromatic ring make it more acidic than the other dispersants. The chemical structure of NP is very similar to that of cardanol, and their performances were found to be very similar when evaluated in model systems (Moreira et al., 1998). Based on the performance results already reported (Moreira et al., 1998; Al-Sahhaf et al., 2002; Ibrahim & Idem, 2004; Kraiwattanawong et al., 2009), cardanol

exhibits a higher performance than DBSA due to the differences in their hydrocarbon chains, since the DSBA sulfonic group has a higher acid character than the cardanol hydroxyl group. Analyzing the hydrocarbon chains (DBSA – saturated C12 and cardanol – unsaturated C15), cardanol has a longer segment than DBSA, containing from one to three double bonds. Such characteristics make cardanol rank as the best perform as an asphaltenes deposition inhibitor, which could be related to higher hydrophobicity of the hydrocarbon chain and/or to the double bonds, exhibiting sp<sup>2</sup> hybridization, that provides higher acidity and electronegativity to the carbon.

Both the commercial dispersants (INH1 and INH2) shifted the asphaltene precipitation onset, acting as inhibitors. At a concentration of 1000ppm, it took 2.96 and 2.88mL of n-heptane per 1mL of oil, respectively. These inhibitors exhibited lower performance at 3000ppm, which was considered a super-dosage. By comparing the results, one can observe that, at 1000ppm, INH1 exhibited the best performance (2.96mL of n-

**Table 3.** Asphaltenes precipitation onset of the crude with and without adding combo formulation at different concentrations.

Formulation (ppm)		Asphaltenes precipitation onset (mL heptane/mL oil)
Pure oil		2.52
DBSA 1000	EVA 0	2.80
	EVA 100	2.62
	EVA 500	2.82
DBSA 3000	EVA 0	2.50
	EVA 100	2.40
	EVA 500	2.58
Cardanol 1000	EVA 0	2.88
	EVA 100	2.50
	EVA 500	2.78
Cardanol 5000	EVA 0	3.34
	EVA 100	3.16
	EVA 500	3.22
INH1 1000	EVA 0	2.96
	EVA 100	2.70
	EVA 500	2.78
INH1 3000	EVA 0	2.74
	EVA 100	2.82
	EVA 500	2.86
INH2 1000	EVA 0	2.88
	EVA 100	2.40
	EVA 500	2.58
INH2 3000	EVA 0	2.64
	EVA 100	2.74
	EVA 500	2.72

heptane/mL of oil), followed by equal performance of cardanol and INH2 (in both cases 2.88mL of n-heptane/mL of oil). However, the greatest shift in the precipitation onset, corresponding to the best performance in stabilizing asphaltenes, was obtained at a concentration of 5000ppm of cardanol.

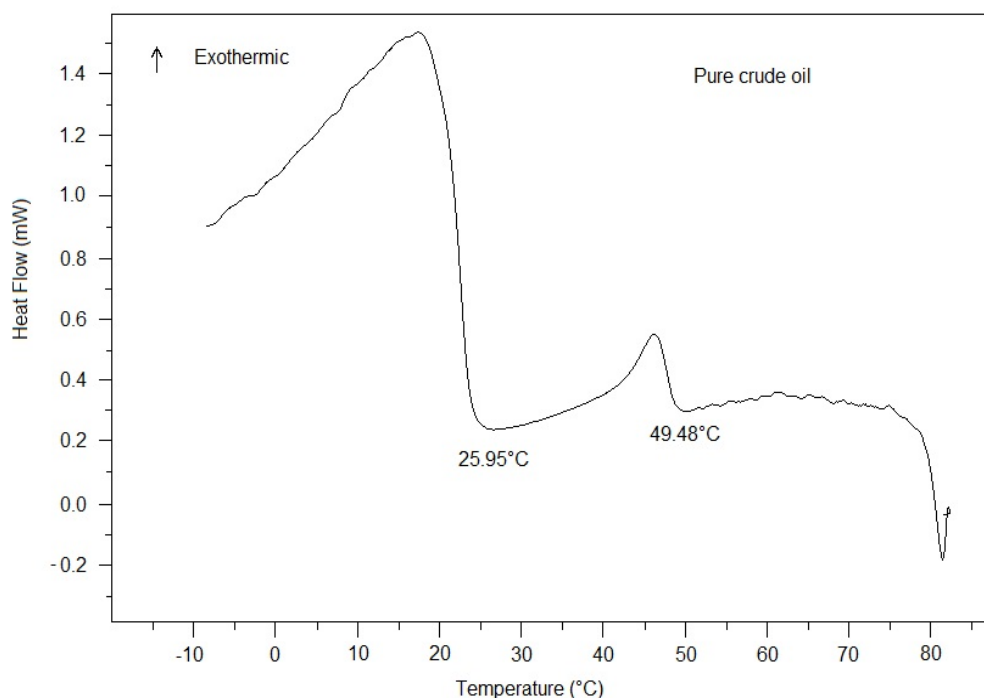
### 3.3 Evaluation of the efficiency of the combo formulations in inhibiting deposition of asphaltenes and waxes

The concentrations of each additive to prepare the combined formulations composed of two products (EVA and an asphaltenes dispersant) were selected based on the results for pour point and

precipitation onset of waxes. The EVA concentrations chosen to prepare the formulations were 100 and 500ppm, at which the oil had presented pour points of  $-8^{\circ}\text{C}$  and  $< -20^{\circ}\text{C}$ , respectively. The asphaltenes dispersants were used at concentrations of 1000 and 3000ppm, except for the cardanol, which had concentrations of 1000 and 5000ppm. For all these formulations, the pour point values remained the same as those obtained with pure EVA33. This result indicates that the asphaltenes dispersants employed did not have any interaction with the waxes, so they did not affect (negatively or positively) the inhibition of wax deposition.

The same behavior was not observed for the influence of EVA33 on the performance of the





**Figure 2.** Heat flow against temperature of the crude oil obtained by microcalorimetry.

asphaltenes dispersants. The precipitation onset results for all the formulations prepared, presented in Table 3, show that in some cases the EVA33 shifted the onset to lower values, thus, reducing the dispersant's efficiency. For example, for INH2 at the concentration of 1000ppm, which before the addition of EVA33 presented a precipitation onset of 2.88mL of n-heptane/mL of oil, the amounts of n-heptane fell to 2.40 and 2.58mL at EVA33 concentrations of 100 and 500ppm, respectively. This same behavior was observed for all the formulations except for INH1 and INH2 at 3000ppm, which presented a slight increase in the asphaltenes precipitation onset when used together with EVA33 at the two concentrations tested (100 and 500ppm). In all cases of a negative influence of EVA33 on the stabilization of asphaltenes, the lowest EVA33 concentration (100ppm) had the mildest negative effect, indicating the EVA33 concentration of 500ppm in the formulation as being the most adequate for inhibiting waxes and asphaltenes deposition. Formulations containing 5000ppm of cardanol reduced the asphaltenes precipitation onset from 3.34mL of heptane/mL of oil to 3.16 and 3.22mL of n-heptane/mL of oil, when used in the formulations containing, respectively, 100 and

500ppm of EVA33. However, these formulations still presented the best performances. Moreover, the cardanol is a natural product extracted from cashew nutshells, a renewable source.

### 3.4 Determination of the wax appearance temperature (WAT) of the combo formulations by microcalorimetry

Differential scanning microcalorimetry ( $\mu$ DSC) is widely used to measure the wax appearance temperature (WAT) (Vieira et al., 2010; Bai & Zhang, 2013). The basic principle of this technique is the detection of the latent heat of solidification released during the crystallization process of the paraffin molecules present in crude oil, by cooling the samples. Figure 2 shows the curve obtained for the pure crude oil, where two events can be observed: the onset of each event was detected at 49.48°C and 25.95°C.

Table 4 summarizes the results obtained for all the formulations studied. As reported in the literature, EVA does not inhibit the formation of wax crystals (Machado et al., 2001). Instead it modifies the crystalline morphology, so the process of reducing the pour point is not necessarily

**Table 4.** Results obtained from microcalorimetry for the crude oil with and without adding “combo” formulation.

Formulation (ppm)		1° Crystallization event (WAT)	2° Crystallization event
Pure oil		49.48	25.95
DBSA 1000	EVA 100	46.49	25.01
	EVA 500	46.70	26.10
DBSA 3000	EVA 100	46.48	25.01
	EVA 500	49.29	25.65
Cardanol 1000	EVA 100	46.65	25.53
	EVA 500	47.60	25.18
Cardanol 5000	EVA 100	48.08	26.01
	EVA 500	47.01	25.86
INH1 1000	EVA 100	46.40	25.10
	EVA 500	47.50	25.45
INH1 3000	EVA 100	46.20	26.05
	EVA 500	48.10	25.36
INH2 1000	EVA 100	46.55	25.10
	EVA 500	46.60	25.50
INH2 3000	EVA 100	48.03	25.35
	EVA 500	47.50	25.45

associated with a variation in the system's WAT. The objective of the  $\mu$ DSC analyses was to check whether the asphaltene dispersants, mixed with EVA33, affected the WAT. The results showed that the crude oil used has two exothermic peaks, related to two crystallization events, as observed in previous studies (Singh et al., 2000; Soni et al., 2005). The WAT was taken as the onset temperature of the first crystallization event during cooling. The results presented in Table 4 indicate that in general the formulations tested did not cause a significant variation of the oil's WAT. Concerning to the 2nd event, the results were essentially the same since the error of these analyses was  $\pm 0.5^\circ\text{C}$ . These results corroborate the observation that the asphaltene dispersants did not affect the crystallization of the paraffin molecules in the petroleum.

#### 4. CONCLUSIONS

The EVA33 performed well in reducing the pour point of the crude oil studied, since at concentrations of around 50 ppm it reduced the pour point from  $12^\circ\text{C}$  to  $2^\circ\text{C}$ . An even better performance was obtained with the concentration

of 500ppm, when the pour point declined to a temperature below  $-20^\circ\text{C}$ .

In relation to the asphaltene dispersants, cardanol performed better than the dodecylbenzenesulfonic acid and the two commercial dispersants, shifting the asphaltene precipitation onset from 2.52mL to 3.34mL of n-heptane/mL of oil with 5000ppm of cardanol. With respect to the combo formulations, the asphaltene dispersants did not influence the performance of the EVA33 as a reducer of the pour point, and the WAT values confirmed this behavior. The EVA33, in turn, had little influence on the performance of the asphaltene dispersants in shifting the precipitation onset, with this influence being mildest at the EVA33 concentrations of 500ppm than at 100ppm. The crude oil mixed with the formulations containing 5000 ppm of cardanol/100 ppm of EVA33 and 5000 ppm of cardanol/500 ppm of EVA 33 performed the best, with asphaltene precipitation onset values of 3.16 and 3.22 mL of n-heptane/mL of oil, respectively. Additionally, cardanol has the advantage of being a product that comes from a renewable source.

This work evidences the potential of developing multifunctional formulations, which can lead to



lower costs and greater facility in applying products in the petroleum industry. Moreover, novel formulations can prevent problems related to the incompatibility of additives.

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