

# Influence of Ethylene-co-Vinyl Acetate Copolymers on the Flow Properties of Wax Synthetic Systems

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**ABSTRACT:** Wax crystallization can cause serious damage to petroleum flow because as the viscosity increases, there is organic deposition in the pipe lines, which causes oil production reduction. Ethylene–vinyl acetate copolymers (EVA) are used as an alternative to prevent such problems. The influence of EVA copolymers on the properties of wax synthetic systems, composed of a solvent mixture and paraffin and petroleum asphalt residue (PAR), was evaluated in this work. The performance of EVA as a wax inhibitor depends on the molecular weight and vinyl acetate content of the copolymer and on the presence of the asphalt fraction. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1337–1348, 2002

## INTRODUCTION

There is a great amount of natural paraffin, but paraffins can also be obtained as primary or secondary products of some industrial processes. For examples, natural gas is mainly constituted of low molecular weight paraffin and, depending on the temperature and pressure conditions, paraffins are also found in crude oil composition.<sup>1</sup> Paraffin can be classified as either macrocrystalline or microcrystalline. Macrocrystalline paraffin is composed of paraffin with linear chain length of 18–30 carbons. This class of paraffin has well defined crystals, which are visible to the naked eye. Branching paraffin with > 40 carbons is classified as microcrystalline.<sup>1</sup>

Depending on petroleum composition and temperature and pressure conditions, paraffin can crystallize and this solid phase can cause several problems during oil production. The temperature

at which the first crystal is formed is called the cloud point or wax appearance temperature (WAT).<sup>2,3</sup> Paraffin molecules are incorporated onto this first crystal, thereby increasing its size.<sup>4,5</sup> The crystals can present as different forms depending on the growing conditions.<sup>5</sup> Chichakli and Jansen<sup>6</sup> have reported two main morphologies; they are plates (or lamella) and needles.

The wax deposition depends not only on the wax crystallization but also on the transportation of the crystallized material from the solution to the pipe wall. The main problems caused by wax crystallization are wax precipitation in the reservoir rock, which blocks the pores; wax precipitation in the column and/or flow lines of the production, which causes reduction of the flow section; and increase in the viscosity of the petroleum, which causes flow reduction.<sup>7</sup>

The chemical composition of the paraffin deposits shows that it is mainly composed of paraffin, but others factions, such as asphaltenes and resins,<sup>8</sup> are also present. In addition to these organic fractions, some inorganic material has also

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**Table I** Characterization Data of the Poly(ethylene-co-vinyl acetate) (EVA)

EVA	Vinyl Acetate (wt %) <sup>a</sup>	Molecular Weight <sup>b</sup>		
		$\bar{M}_n$	$\bar{M}_w$	Polydispersity
EVA 22	22 ± 1	40100	183100	4.56
EVA 32	32 ± 1	44800	141500	3.16
EVA 40	40 ± 1	45600	112000	2.46
EVA82	82 ± 1	231600	626800	2.71

<sup>a</sup> Determined by hydrogen nuclear magnetic resonance (<sup>1</sup>HNMR).

<sup>b</sup> Determined by size exclusion chromatography (SEC).

been detected in the deposits (e.g., sand, clay, and residues from corrosion process<sup>9</sup>).

Several techniques can be used to solve the problems caused by wax deposition, one of which is chemical inhibitor injection. These inhibitors are polymer compounds, with structures containing long or medium hydrocarbon chains, that interact with the paraffin and modify the crystal morphology. Consequently, the inhibitors are known as wax crystal modifiers. The following polymers are mentioned in the literature<sup>10</sup> as wax crystal modifier: polyamides of linear or branched acids; ethylene-co-vinyl acetate copolymers (EVA); copolymers of  $\alpha$ -olefins, and maleic anhydride. To date, the inhibition mechanism and the influence of polar oil components are not well understood.

This work presents the results of a study of the influence of the EVA composition on the flow behavior of the wax synthetic systems that was conducted to gain information related to the process of wax deposition inhibition. The influence of paraffin content and polar components in the synthetic system on the EVA copolymers performance was evaluated in terms of pour point and wax deposition trend.

## EXPERIMENTAL

### Materials

The kerosene oil, the paraffin mixture and the petroleum asphalt residue (PAR) were obtained from the Duque de Caxias Refinery of PETROBRAS (Rio de Janeiro, Brazil). Poly(ethylene-co-vinyl acetate) copolymers were obtained from POLITENO S.A. (Bahia, Brazil), and their characterization data are summarized in Table I.

### Characterization of the Petroleum Asphaltic Residue (PAR)

The weight average molecular weight ( $\bar{M}_w$ ) was obtained by vapor pressure osmometry (VPO) with a 233 WESCAN instrument and benzyl as calibration standard.

Characterization of the composition (saturated, aromatic, resin, and asphaltene) was carried out by thin layer chromatography-flame ionization detection (TLC-FID), using a MK-5 Latorscan apparatus. Hexane, toluene, and dichloromethane : methanol (95 : 5 v/v) mixture were used as solvent, at a temperature of 20 °C.

The elemental analysis was carried out on a 2400 Perkin Elmer-serial II. The carbon, hydrogen, and nitrogen contents were determined with software that compares the signals related to each element of the sample with the signals obtained by analyzing a standard at the same conditions. The amount of oxygen plus sulfur was calculated by subtracting the C, N, and S from the total.

### Characterization of the Paraffin Mixture

#### *Distribution by Number of Carbon Atoms*

A solution of paraffin in carbon disulfide was injected in a capillary column of steel (CHROMPACK), using an injector on-column. The initial and final temperatures were, respectively, 40 and 380 °C, the detector temperature was kept at 420 °C, and the temperature was changed at a rate of 10 °C/min.

#### *Differential Scanning Calorimetry (DSC)*

The wax sample was analyzed on a DSC 7 Perkin Elmer, at a heating rate of 10 °C/min, from zero to 100 °C.

**Table II** Composition of the Synthetic Systems

System	Paraffin (wt %)	PAR (wt %)	SOLMIX (wt %) <sup>a</sup>
1	3.0	0.0	97
2	5.0	0.0	95
3	3.0	2.0	95
4	5.0	2.0	93

<sup>a</sup> SOLMIX = solvent mixture toluene, cyclohexane, and kerosene oil (25, 25, and 50 wt %, respectively).

### Synthetic Systems Preparation

Four synthetic systems, containing paraffin, PAR, and SOLMIX in different compositions, were prepared (Table II).

### Preparation of the Solution of the EVA Copolymer in Toluene

Solutions of 5.0% p/p copolymer in toluene were prepared. The complete dissolution of the copolymer was achieved after 2 h at 70 °C. This methodology ensured the total solubilization of the system at room temperature.

### Pour Point of the Systems with and without using EVA Copolymer as Additive

The pour points of the four pure systems and the systems 1 and 2 containing EVA as additive were determined as follows. The crude oil sample was warmed to 71 °C and then slowly cooled to 30 °C. From this temperature, the oil was cooled, and the flow capacity was verified every 2 °C. To verify the flow capacity, the tube containing the sample was slight tilted. The pour point was determined by adding 2 °C to the temperature at which the sample stopped flowing.

### Wax Deposition Simulation

The test of static simulation of wax deposition, also known as the cold finger test, was performed at the CENPES/PETROBRAS. This test consists of wax deposition by inducing a contact between the warmed oil and a cold metallic surface. Although this test does not take in account dynamic parameters associated with a real situation, such as shear rate and Reynolds number, it has been used to evaluate and screen chemicals with results in good accordance with their field performance because the main mechanism of mass transport (molecular diffusion) at wax deposition

phenomena is mimicked in this cold finger apparatus. The test procedure is described in the literature.<sup>11</sup> The temperatures of the metallic surface and the oil sample were kept at 4 and 40 °C, respectively.

The copolymer efficiency was expressed as a relation between the deposit obtained from the pure oil and that from the oil containing additive, and was calculated by eq. 1:

$$\text{Efficiency (\%)} = \frac{W_{s.i.} - W_{c.i.}}{W_{s.i.}} \times 100 \quad (1)$$

where  $W_{s.i.}$  and  $W_{c.i.}$  are the weight of the organic deposit obtained without and with adding inhibitor, respectively.

### Characterization of the Wax Deposits Obtained from the Synthetic Systems

#### *Paraffin Distribution by Number of Carbon Atoms and Thermal Properties of the Deposits*

The methodologies used were the same as those used for paraffin mixture.

#### *Wax Deposit Characterization by Fourier Transform Infrared Spectrometry (FTIR)*

The analysis were carried out on a Magana 550 Nicolet. KBr pellets were prepared to analyze the samples in the range 400–4000  $\text{cm}^{-1}$ , at room temperature ( $\sim 25$  °C).

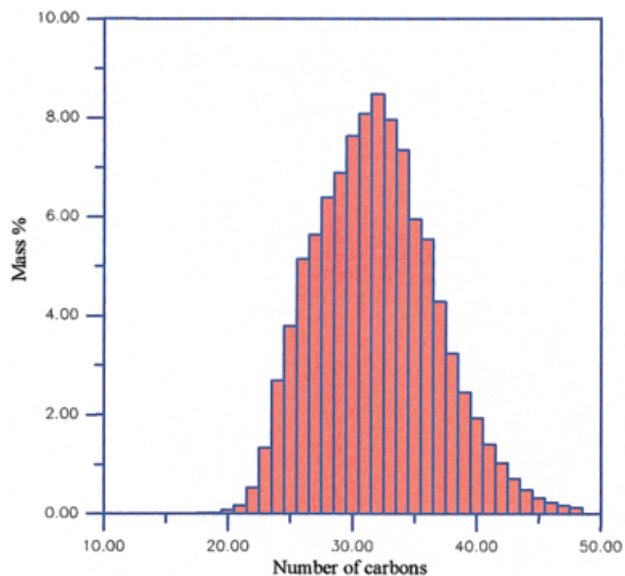
## RESULTS AND DISCUSSION

### Characterization of the Petroleum Asphaltic Residue (PAR)

The PAR is also composed of heteroatoms, as verified by elemental analyses, and the literature<sup>8</sup> cites heteroatoms in the structure of the asphaltenes and resins.

The following composition was determined by TLC-FID: resins (38% m/m), aromatic fraction (30% m/m), asphaltenes (20% m/m), and saturated compounds (3% m/m).

The number average molecular weight ( $M_n$ ) is 1380. This value is relatively low, probably because the aromatic compound plus resins represent 68% of the PAR.



**Figure 1** Distribution by the number of carbon atoms of the paraffin that constitute the paraffin mixture.

### Characterization of the Paraffin Mixture

Characterization of the paraffin (from REDUC) became necessary to gain information about structures, physical properties, and composition of the mixture. Such information is important to evaluate the influence of the EVA copolymer on the paraffin properties.

#### *Distribution by Number of Carbon Atoms*

The distribution (mass %) of the paraffin as a function of number of carbon atoms is shown in Figure 1. The paraffin mixture is composed of paraffin containing a number of carbon atoms in the range 18–48, and the largest fraction represents 32 carbons. These results were used to calculate the weight-average molecular weight ( $M_w$ ) of 588.28, which is related to the molecular weight of  $C_{42}H_{86}$ . The contents of linear and

branched paraffin are 83.82 and 16.18 wt %, respectively.

### Thermal Properties

Thermal properties of paraffin were determined by DSC. The melt was observed in the temperature range 30–67 °C. According to the distribution by number of carbons, one would expect the melting to begin at 28 °C (which corresponds to the melting point of the octadecane) and the final temperature to be at 90.3 °C (which corresponds to the melting point of the octatetracontane). Such a difference can be understood if the paraffin mixture is considered a solid solution and its behavior depends on the molecular interactions; that is, the smallest paraffin can interact with the largest one, and a solubilization phenomena takes place. This solubilization results in the reduction of the highest melt temperature observed for the mixture compared with the melting of the pure largest component. The melting enthalpy is 357.85 J/g.

### Pour Point of the Systems with and without Adding EVA Copolymer

The crude oil is a complex mixture and thus it is difficult to interpret the experimental results in terms of contribution of each component. To evaluate the influence of EVA copolymer and also the influence of polar fractions (PAR) on paraffin behavior, synthetic systems were prepared. A solvent mixture (called SOLMIX; Table II) was used as the liquid phase so that each component represents a petroleum fraction: kerosene oil, toluene, and cyclohexane represent the aliphatic hydrocarbons fraction of low and medium boiling points, the aromatic hydrocarbons, and naphthenic hydrocarbons, respectively.

The pour points determined for the synthetic systems are shown in Table III. System 1 (com-

**Table III** Pour Point of the Synthetic System without Additive

System	Paraffin (wt %)	PAR (wt %)	SOLMIX (wt %) <sup>a</sup>	Pour Point (°C) ± 1
1	3.0	0.0	97	+18
2	5.0	0.0	95	+20
3	3.0	2.0	95	< -26
4	5.0	2.0	93	< -26

<sup>a</sup> The SOLMIX composition is described in Table II.

**Table IV Pour Point Reduction for System 1 with Addition of EVA Copolymers**

Copolymer	Additive Concentration (ppm)	Pour Point Reduction ( $^{\circ}\text{C} \pm 1$ )
EVA22	5	2
EVA22	50	> 40
EVA22	500	> 40
EVA22	5000	> 40
EVA32	5	2
EVA32	50	> 40
EVA32	500	> 40
EVA32	5000	> 40
EVA40	5	2
EVA40	50	> 40
EVA40	500	> 40
EVA40	5000	> 40
EVA82	5	0
EVA82	50	0
EVA82	500	0
EVA82	5000	0

**Table V Pour Point Reduction of system 2 with Addition of EVA Copolymers**

Copolymer	Additive Concentration (ppm)	Pour Point Reduction ( $^{\circ}\text{C} \pm 1$ )
EVA22	5	0
EVA22	50	8
EVA22	500	> 42
EVA20	5000	> 42
EVA32	5	0
EVA32	50	36
EVA32	500	> 42
EVA32	5000	> 42
EVA40	5	0
EVA40	50	10
EVA40	500	> 42
EVA40	5000	> 42
EVA82	5	0
EVA82	50	0
EVA82	500	0
EVA82	5000	0

posed of 3% paraffin and 97% SOLMIX) has a pour point of  $+18^{\circ}\text{C}$ , and system 2 (composed of 5% paraffin and 95% SOLMIX) has a pour point of  $+20^{\circ}\text{C}$ . Increasing the paraffin content by 2% did not significantly increase the pour point, probably because the minimum amount of precipitated paraffin to achieve the pour point did not vary by changing the concentration.

The pour points obtained for the systems 3 and 4 were lower than  $-26^{\circ}\text{C}$ . Systems 3 and 4 contain, respectively, the same paraffin amounts as systems 1 and 2, plus 2% PAR. So, when PAR is added to the systems, it provokes a reduction of  $> 30^{\circ}\text{C}$ , probably because of the co-precipitation of some polar fractions containing aliphatic segments, which obstructed the perfect arrangement of the paraffin crystals.

The pour points for systems 1 and 2, with EVA copolymer added at 5, 50, 500, and 5000 ppm are shown in Tables IV and V, respectively. EVA 82 (as observed in previous work<sup>12</sup> for the crude oil) did not present good efficiency in any system. This result confirms the explanation suggested for the petroleum system; that is, according to the polymer/paraffin interaction tests, this copolymer modifies the wax crystals, but its solubility behavior is not suitable because due to the difference between the solubility parameter, EVA 82 exhibited phase separation at a temperature higher than the cloud points found for the others copol-

ymers. In fact, EVA 82 does not precipitate with the paraffin, which can reduce its performance.

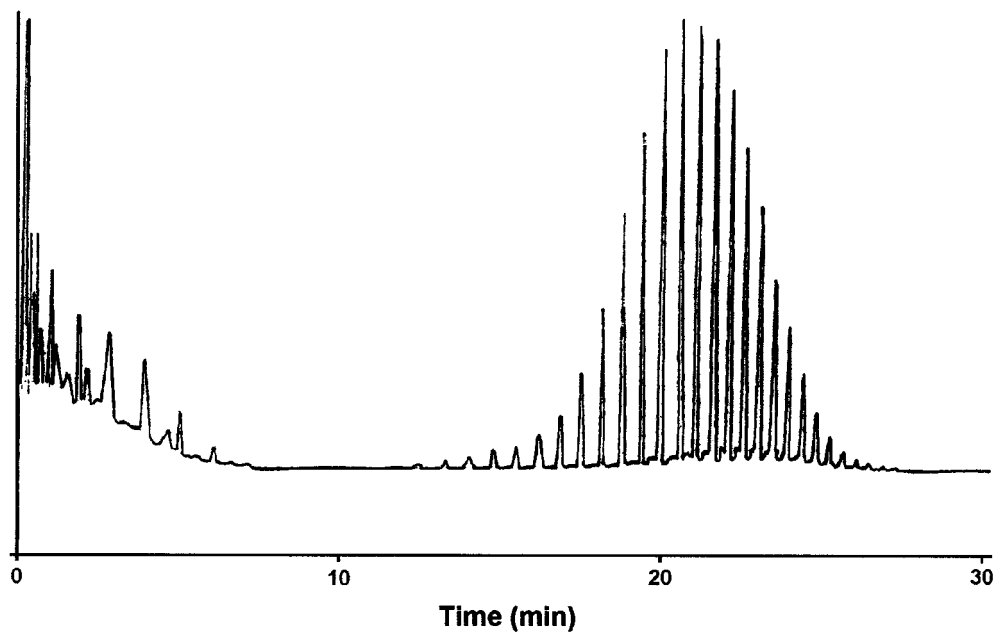
EVA 22, 32, and 40 exhibit the same effect on system 1 (see Table IV). These copolymers, at 5 ppm, provoked a pour point reduction of  $2^{\circ}\text{C}$ . At higher concentrations (50, 500, and 5000 ppm), the additive induced to a pour point reduction of  $> 40^{\circ}\text{C}$ . Such results show that the concentration of 50 ppm for system 1 is enough to achieve good performance and it is independent of the pour point of the system without additive.

EVA 22, 32, and 40 perform differently in testing system 2, which contains more paraffin than system 1 (see Table V). At 5 ppm, the behavior was similar for both systems; that is, good perfor-

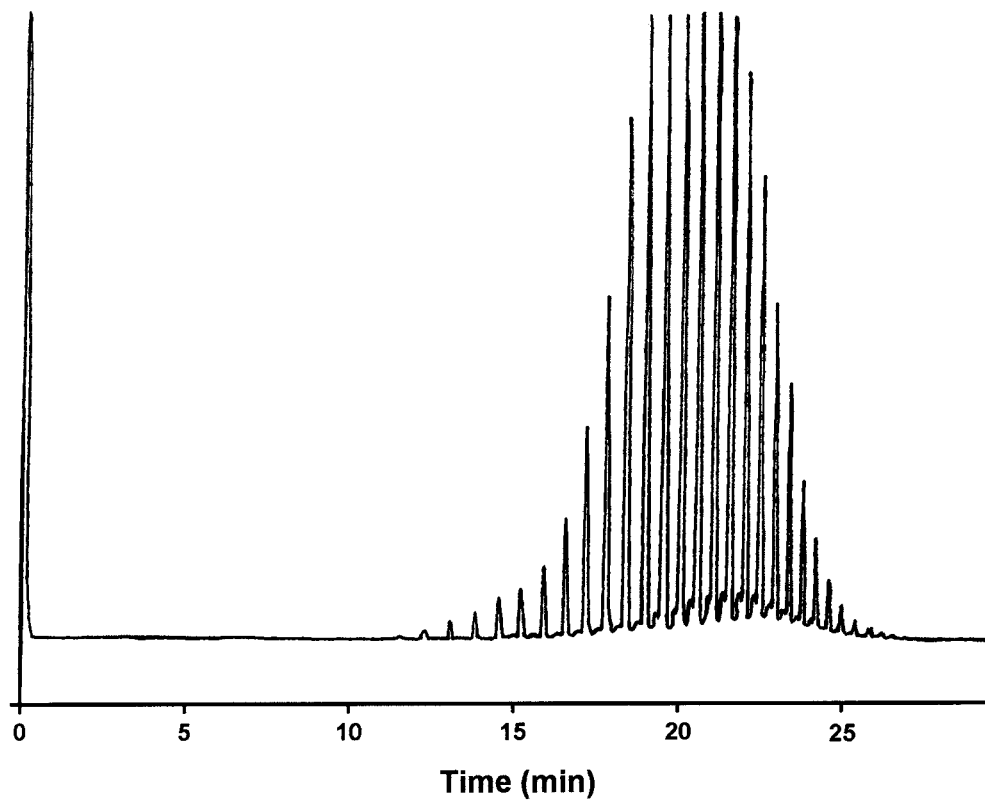
**Table VI Results of Static Simulation of the Wax Deposition for Systems 1 and 3 with the Addition of EVA 32**

System	EVA 32 Concentration (ppm)	Inhibition Efficiency (%)
1	50	48
1	500	83
1	5000	76
3	50	29
3	500	54
3	5000	59

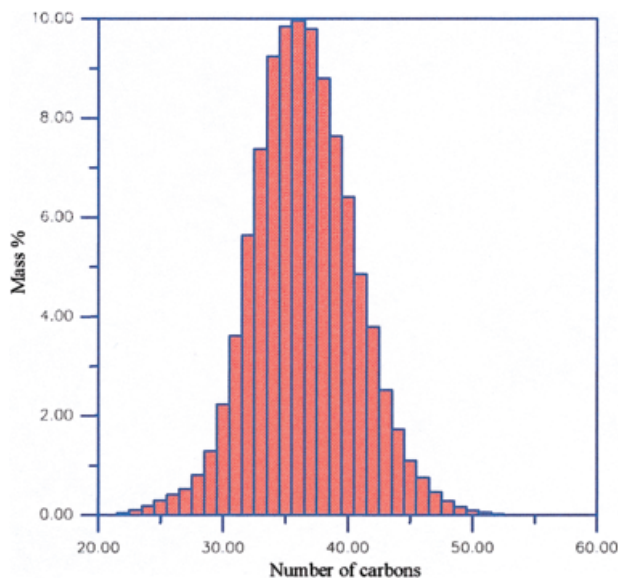




**Figure 2** Chromatogram of the deposit obtained from the static simulation test of system 1 without adding additive.



**Figure 3** Chromatogram of the deposit obtained from the static simulation test of system 1 with adding EVA 32 at 500 ppm.



**Figure 4** Distribution by the number of carbon atoms of the paraffin that constitutes the deposit obtained from system 1 without adding additive.

mance is not observed for any copolymer, indicating that this concentration is not enough to provoke an efficient wax crystal modification. EVA 32 achieved good performance at 50 ppm, and EVA 22 and EVA 40 achieved good performance at higher concentration (500 ppm). These results show that EVA 32 gives the best pour point reduction for both synthetic systems and crude oil.<sup>12</sup> Similar behavior has also been observed for others crude oils of different composition.<sup>4,13,14</sup> So, although the polar/nonpolar balance of the additive depends on the oil composition, the best EVA composition seems to be ~ 35 wt % vinyl acetate for most cases.

Excluding EVA 82, the copolymers performance was better for the synthetic systems than for the crude oil.<sup>12</sup> It is possible that other oil components, such as polar fractions, can induce a lower efficiency. However, the results obtained for synthetic systems containing polar fractions did not provide clear conclusions about the influence of the polar fractions on the copolymer efficiency to reduce the pour point.

#### Wax Deposition Simulation FROM THE Systems with and without Adding EVA Copolymer

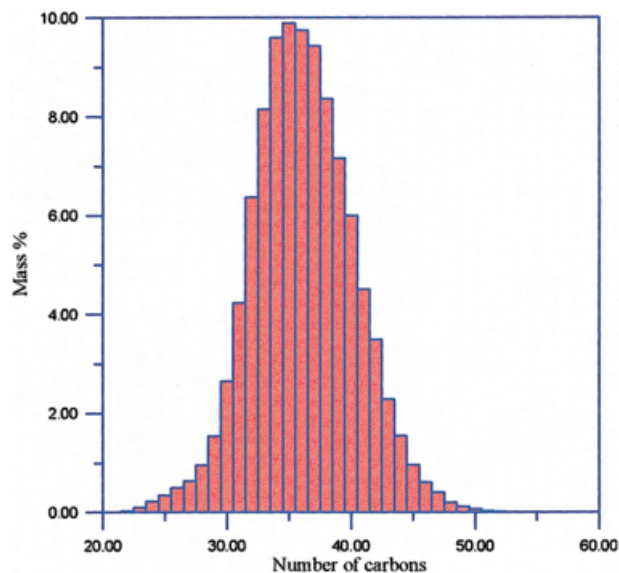
The EVA 32 efficiency as a wax deposition inhibitor for systems 1 and 3 is shown in Table VI; EVA 32 was chosen because it performed the best in

pour point tests at 50, 500, and 5000 ppm. The results obtained for system 1 were better than those obtained for the crude oil.<sup>12</sup>

The EVA 32 efficiency in system 1 was better than that in system 3. The worst performance in system 3 is related to the presence of the polar fractions from the PAR. In addition, the highest efficiency for system 3 was achieved at 5000 ppm, showing that the addition of the asphalt fraction resulted in the system behavior being more similar to that of petroleum. PAR interacts with and co-precipitates with the paraffin, causing modification of the crystals, which is evident from the pour point results. However, the effect of crystal modification caused by PAR is less efficient than that caused by the copolymer. So, when PAR competes with the copolymer, less copolymer interacts with the wax crystals and the copolymer efficiency is reduced.

#### Characterization of the Wax Deposits Obtained from the Static Simulation Tests of the Synthetic Systems

To obtain more information about the copolymer mechanism as a wax deposition inhibitor, the deposits produced from system 1 with and without adding EVA 32 (at 500 ppm) were analyzed. The 500 ppm concentration was chosen because at this concentration the additive exhibited the maximum



**Figure 5** Distribution by the number of carbon atoms of the paraffin that constitute the deposit obtained from system 1 with adding EVA 32 at 500 ppm.

**Table VII Characteristics of the Paraffin Mixture and the Deposits Obtained from the Static Simulation Tests of System 1 without and with the Addition of EVA 32 at 500 ppm**

Characteristic	Paraffin Mixture	Deposit Obtained without Adding Additive	Deposit Obtained with Adding EVA 32 at 500 ppm
C <sub>&lt;32</sub> -C <sub>32</sub> (wt %)	56.85	15.14	17.55
C <sub>33</sub> -C <sub>41</sub> (wt %)	40.11	73.90	72.71
C <sub>42</sub> -C <sub>&gt;42</sub> (wt %)	3.04	10.96	9.74
Isoparaffin (wt %)	16.18	8.42	8.39
Average molar mass (g/mol)	588.28	652.76	648.19

efficiency. The aim of this study was evaluate the main differences between these two deposits.

### Visual Appearance and Consistency

The deposit produced from system 1 without adding additive is amorphous and look likes paste, suggesting that there is a liquid phase associated with the paraffin solid phase. On the other hand, the deposit obtained from system 1, with adding EVA 32, is more compact, probably because there is not enough of the liquid phase to create the softness observed for the system 1 without additive. The liquid phase is related to some solvent (SOLMIX) retained in the crystalline agglomerate produced from the crystallization without additive.

### Distribution of Deposit Paraffin by Number of Carbon

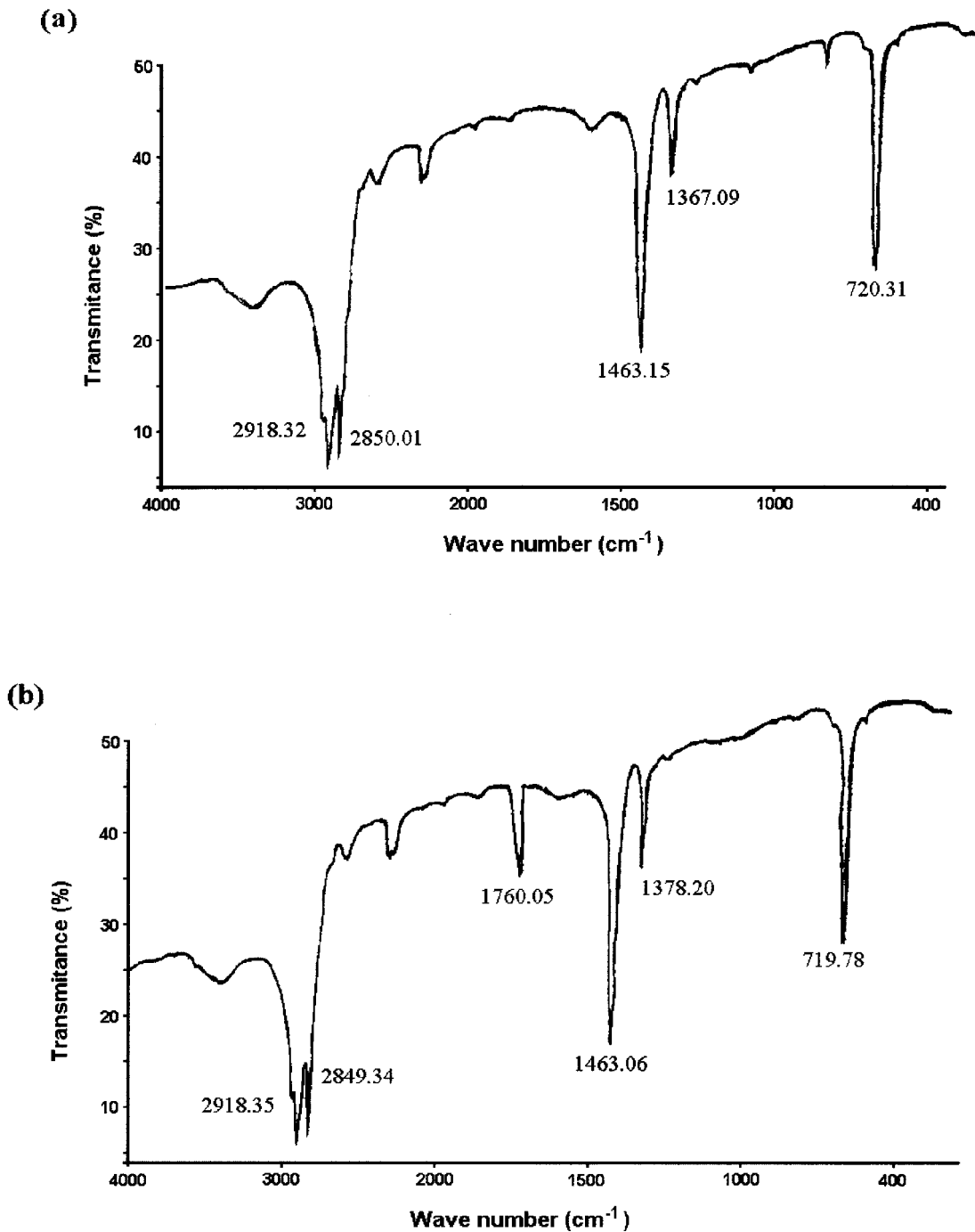
The chromatograms of the deposits obtained from system 1 without and with adding EVA 32 (500 ppm) are shown in Figures 2 and 3, respectively. The chromatogram of the deposit obtained without adding additive presents peaks at the region of the low molecular weight hydrocarbons, which are the same as those observed for the kerosene oil, indicating solvent in the deposit.

The distribution by number of carbon of the paraffin compounds (coming from paraffin mixture) in the deposits obtained with and without adding additive are shown in Figures 4 and 5, respectively. By comparing these figures to that related to the paraffin mixture (Figure 1), an enrichment of the higher molar mass fractions in the deposits is observed. A great similarity is observed for the paraffin distribution for both deposits, suggesting that the copolymer action mechanism is not related to an interaction with a specific paraffin type.

The accumulated mass percentage of the paraffin (divided in three ranges), the isoparaffin content, and the average molecular weight for the paraffin mixture and for the deposits obtained from system 1 without and with adding EVA 32 (500 ppm) are summarized in Table VII. The paraffin mixtures are divided into three types: C<sub><32</sub>-C<sub>32</sub>, which is related to the paraffin containing 32 carbons and less; C<sub>33</sub>-C<sub>41</sub>, which is related to the paraffin containing carbons at the range 33-41; and C<sub>42</sub>-C<sub>>42</sub>, which is related to the paraffin containing 42 carbons and more. By comparing the results obtained for the paraffin mixtures with those obtained for the deposits, it is observed that in the deposits, the C<sub><32</sub>-C<sub>32</sub> fraction was reduced, the C<sub>33</sub>-C<sub>41</sub> and C<sub>42</sub>-C<sub>>42</sub> fractions were increased, and the isoparaffin content was reduced. These results indicate that the C<sub><32</sub>-C<sub>32</sub> fraction does not present a great tendency to constitute the deposit; the C<sub>33</sub>-C<sub>41</sub> fraction is the main component of the deposit; the C<sub>42</sub>-C<sub>>42</sub> fraction has a greater tendency to deposit than the C<sub>33</sub>-C<sub>41</sub> one; and the crystallization of the linear paraffin is easier than that of the isoparaffin. The molecular weights of the deposits are higher than that of the paraffin mixture because the concentration of the higher paraffin was increased in the deposits.

As previously mentioned, the compositions of the deposits produced from synthetic system with and without adding EVA 32 were very similar, suggesting that there is not an additive preferential interaction with a specific paraffin fraction. Nevertheless, the values in Table VII show that the additive induces a slight reduction of the higher molar mass paraffin in the deposit, that is, the additive is more effective on this kind of paraffin. Based on this observation, it is possible to suggest that this additive would not be efficient as a lubricant oil for the systems containing lower





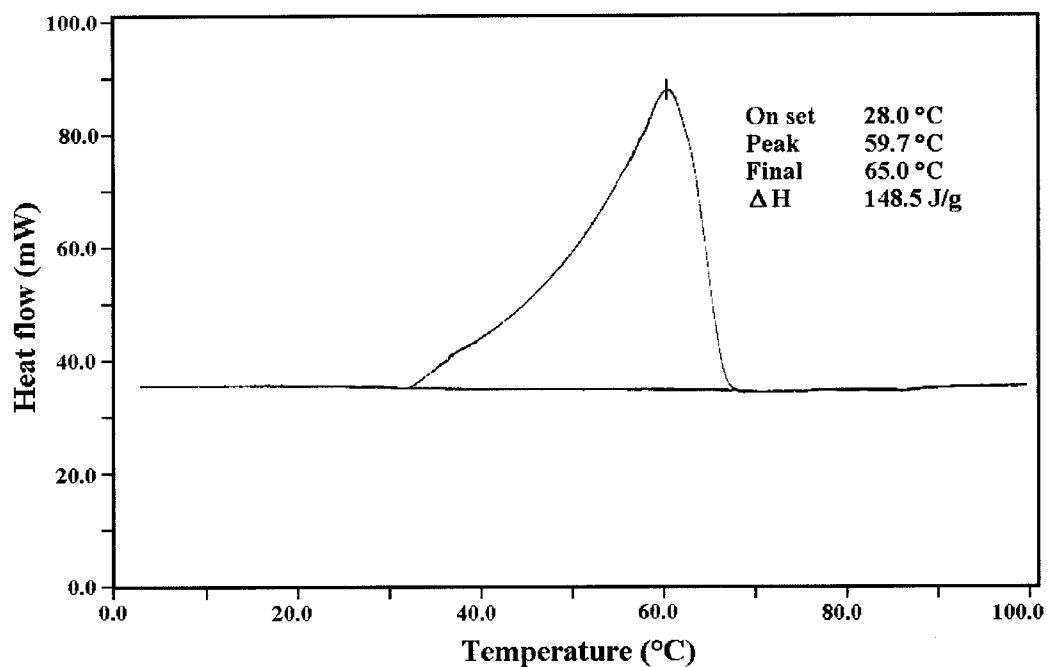
**Figure 6** Infrared spectra of the deposit obtained from the static simulation test of system 1: (a) without adding additive; (b) with adding EVA 32 at 500 ppm.

molar mass paraffin. Such behavior can be explained by the additive solubility parameter, which is similar to that of the higher molar mass paraffin. This kind of study is very useful to foresee problems related to wax deposition.

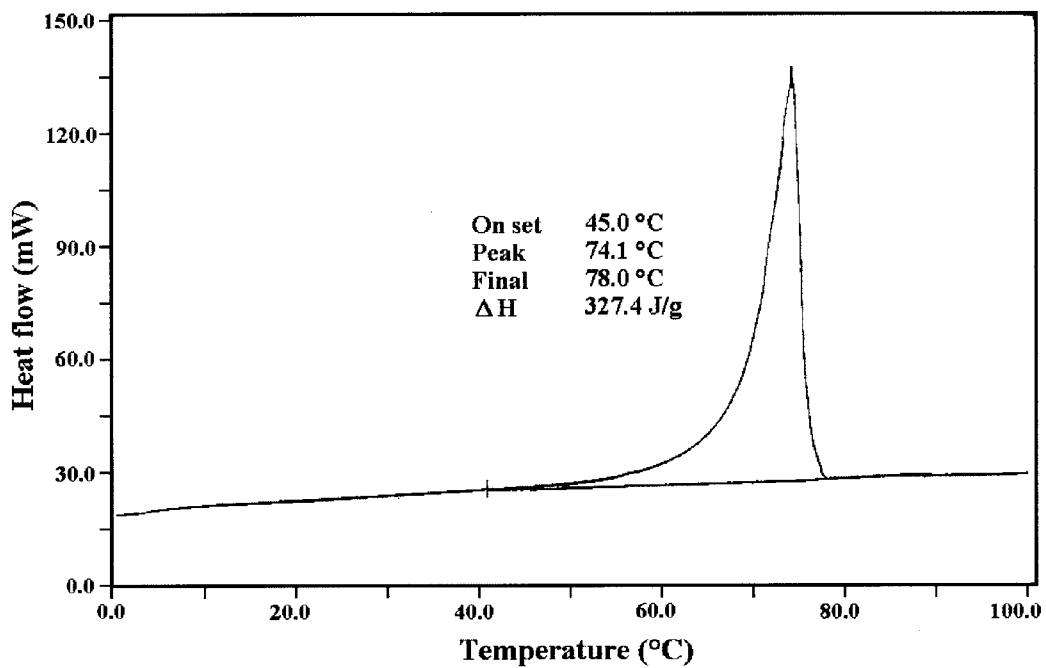
#### *Deposits Characterization by Fourier Transform Infrared Spectrometry (FTIR)*

This characterization was carried out to identify EVA copolymer in the wax crystal produced by

(a)



(b)



**Figure 7** DSC curves exhibiting the melting of the deposit obtained from the static simulation test of system 1: (a) without adding additive; (b) with adding EVA 32 at 500 ppm.

the wax deposition simulation test. The spectra of the deposits obtained from system 1 without and with adding EVA 32 are shown in Figures 6a and 6b, respectively; the latter presents the same peaks observed for system 1 without EVA and also a peak at  $1760\text{ cm}^{-1}$  related to EVA because the pure synthetic system does not have carbonyl compounds. This result confirms that the EVA crystallizes together with paraffin.

### *Thermal Properties of the Deposits*

Because the deposits produced are different, a study was carried out to evaluate the influence of such a difference on the thermal properties of these deposits. First, it is important to mention that the melting temperature range of the pure EVA 32 is  $28.0\text{--}65.0\text{ }^{\circ}\text{C}$ , and the melt enthalpy is  $33.5\text{ J/g}$ . The DSC curves for the deposits produced from wax deposition simulation tests for system 1 without and with adding EVA 32 (500 ppm) are shown in Figures 7a and 7b, respectively. The melting temperature range of the deposit produced without additive (Figure 7a) is  $28.0\text{--}65.0\text{ }^{\circ}\text{C}$ , and the melt enthalpy is  $1485\text{ J/g}$ . The melting temperature range of the deposit produced with adding additive (Figure 7b) is  $45.0\text{--}78.0\text{ }^{\circ}\text{C}$ , and the melt enthalpy is  $327.4\text{ J/g}$ . Because the paraffin distribution of both deposits is similar (shown by gas chromatography), it would be expected that the thermal properties were also similar. However, it was suggested by visual appearance that the deposit without additive presents a certain amount of solvent. This result is in good agreement with the differences detected by DSC because the solvent can reduce the melting temperature and also the melt enthalpy. The melting point onset of the deposit containing EVA 32 ( $45\text{ }^{\circ}\text{C}$ ) is higher than that for the pure EVA 32 ( $28\text{ }^{\circ}\text{C}$ ). In fact, EVA was used in a very low concentration (500 ppm), and the crystals are formed by paraffin modified by the EVA copolymer.

By comparing the thermal properties of the deposits (produced with EVA 32) with those of the paraffin mixture, it is observed that the deposit melt occurs at a higher temperature range than the paraffin mixture because the deposit presents a higher concentration of higher molecular weight paraffin. On the other hand, the melt enthalpy of the paraffin mixture ( $\Delta H_m = 357.8\text{ J/g}$ ) is higher than that of the deposits ( $\Delta H_d = 148.5\text{ J/g}$  and  $\Delta H_{d\text{EVA}} = 327.4\text{ J/g}$ ). The deposit produced without additive presents a lower enthalpy due to the presence of the liquid phase. The deposit produced using

additive contains paraffin and also EVA copolymer (as confirmed by FTIR), which is semi-crystalline and contributes to the reduction of the deposit crystallinity. The sample that contains additive presents narrower crystal size distribution because the rate of crystallization is high.

## CONCLUSIONS

The systematic study of the influence of polar fractions on wax crystals modification provided important information about the behavior of the additives on the crude oil. The behavior of a paraffin mixture depends on the interactions that occur in the system. The lowest molecular weight paraffin can solubilize the highest one by specific interactions, and then the upper limit of mixture melt is lower than that of the highest component when in a pure state.

In general, the copolymer performance as a pour point depressor was better for the systems than for the crude oil because of the influence of the polar fractions. Although some components of the petroleum asphalt residue (PAR) can interact with the paraffin, the effect of the competition between the copolymer and the PAR reduces the copolymer performance.

The action mechanism of the EVA32 copolymer is related to the preferential interaction with the higher molecular weight paraffin ( $C_{<32}\text{--}C_{32}$ ). So, this additive will be efficient for the systems containing paraffin of higher molecular weight (for example, crude oil) and it will not exhibit good performance for the systems containing paraffin of low molecular weight (for example, lubricant oils).

The EVA copolymer was detected in the deposit by FTIR.

## REFERENCES

1. Freund, M.; Csikós, R.; Keszthelyi, S.; Mózes, G. Paraffin Products; Elsevier: New York, 1982.
2. Létóffé, J. M.; Claudy, P.; Kok, M. V.; Garcin, M.; Volle, J. L. Fuel 1995, 74 (6), 810–816.
3. Ronningsen, H. P.; Pedersen, W. D. Energy Fuels 1991, 5 (6), 895–907.
4. Petinelli, J. C. Ver Inst Franç Du Petrole 1979, 34 (5), 771–790.
5. Edwards, R.T. Ind Eng Chem 1957, 49 (4), 750–757.
6. Chichakli, M.; Jansen, F. W. Ind Eng Chem 1967, 59 (5), 86–98.

7. Wattenbarger, R. A.; Maggard, J. B. In 1<sup>st</sup> International Symposium on Colloid Chemistry in Oil Production: Asphaltenes and Wax Deposition, Rio de Janeiro, 1995; pp. 74–79.
8. Long, R. B. ACE Adv Chem Series 1981, 195, 17–26.
9. Oliveira, R. C. G. Louvise, A. M. T. “Deposição de parafina para petróleos dos campos de Albacora e Marlim e sua inibição mediante o uso de aditivos químicos”. III E.T.I.E.A.P., PETROBRAS, Rio de Janeiro, 1991; pp. 137–150.
10. Sanine, P.I. Rev Inst Franç du Pétrole 1961, XVI, 468–484.
11. Machado, A. L. C.; Lucas, E. F. Petrol Sci Tech 1999, 17(9 & 10), 1029–1041.
12. Machado, A. L. C.; Lucas, E. F. Petrol Sci Tech 2001, 19 (1 & 2), 197–204.
13. Jamaluddin, A. K. M. Soc Petrol Eng 1995, 28994, 513–521.
14. Holder, G. A.; Thorne, J. Polym Chem 1979, 20 (1), 766–769.