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Is There any Relation Between the Solubility of a Polymeric Additive and its Performance as a Pour Point Reducer?

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Summary: In this work, polymeric additives based on poly(ethylene-co-vinyl acetate) were chemically modified by inserting different contents of hydrocarbon chains (C14). The performance of the modified copolymers as organic deposition inhibitors (ODI) was evaluated using a model system composed of different types of paraffins by measuring the pour point and viscosity of these systems. The phase behavior of the modified copolymers was evaluated in systems with different solubility parameters in order to correlate the additive's performance as ODI and the esteem solubility parameter of these modified copolymers. The results show that the EVA modified copolymers performed better ODI than those obtained for non-modified copolymer. However, the molecule must retain a hydrophobic-lypophobic balance in order to keep its capacity to modify the paraffin crystal. Moreover, copolymers with similar solubility parameters did not present the same pour-point values, which suggests that the solubility of the additive is important, but is not the only factor that influences the additive performance.

Keywords: additives; EVA; paraffin; pour point; solubility parameter; viscosity

Introduction

One of the problems related to exploration and production of oil and gas reservoirs is paraffin deposition, especially when the crude oil has a high content of aliphatic hydrocarbon chains that induce, by temperature change, the crystallization of normal or n-paraffins.[1,2] The temperature at which the paraffin crystallization begins is called the wax appearance temperature (WAT).[3] This crystallization process often leads to the formation of wax deposits. Alternatively, when the concentration of wax particles is enough to form a stable three-dimensional network within the system, the oil is able to reach its pour point, the minimum temperature at which the oil flows under the influence of gravity.

In the production, storage and transportation of paraffinic petroleum, it is important to maintain the oil at a temperature higher than its natural pour point. Several kinds of treatment (mechanical, physical and chemical) have been applied to control paraffin separation and its adverse consequences. Chemical products, known as flow improvers, crystal modifiers or pour point reducers, are used to reduce the apparent viscosity, the yield point and the pour point of crude oils. Furthermore, during production operations, these additives minimize problems related to wax deposition in the production pipelines and other facilities. In the pipelines, the addition of a suitable additive may result in an increase of the oil's fluidity, enabling the reestablishment of oil flow after temporary deactivation of the lines.[4–7]

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The literature[6–13] shows that among the basic requirements for good flow performance, the additive chemical structure is especially important. The additives must have structures similar to paraffins, in order to co-crystallize with them. However, they must also contain dissimilar groups or segments in order to promote the modification of wax crystals to prevent crystals aggregation for the formation of organic deposits. Regarding this co-crystallization phenomenon, it is not clear yet whether the additive must co-precipitate with paraffin or if it is the already precipitated additive that becomes part of the paraffin particles.

In this work, we obtained a family of additives by chemical modification of poly (ethylene-co-vinyl acetate) (EVA) with the introduction of different amounts of hydrocarbon chain containing fourteen hydrocarbon groups (C14). In this way, it was possible to obtain molecules with similar overall structure but having different solubility behavior. The main objective of the work was to establish a relationship between this property, described by the Hildebrand solubility parameter, and the performance of molecules as paraffin crystal modifiers or wax deposition inhibitors. To do this, we selected an EVA sample containing 20%w/w of vinyl acetate and myristyl chloride, ($C_{14}H_{29}OCl$) to insert hydrocarbon chains containing fourteen carbon atoms into the EVA structure. This chemical structure was chosen based on previous results showing that EVA samples containing from 20 to 40%w/w of vinyl acetate performed well when applied in some petroleum samples.[1,2] Moreover, EVA containing long side chains (from C12 to C18) has also presented good performance for other kinds of oil.[14]

Experimental Part

Materials

EVA copolymer (~20% of vinyl acetate), used in the reactions of chemical modification, was supplied by Politeno Indústria e Comércio S.A., Bahia-Brazil. The method for the chemical modification of the EVA is described in a previous work.[14] The reactions consist of two steps: (1) the complete hydrolysis of the EVA copolymer, obtaining EVA-OH; (2) followed by its esterification by using different amounts of myristyl chloride. The myristyl chloride was purchased from SIGMA ALDRICH Corporation, Steinheim-Germany. The solvents (toluene, xylene, cyclohexane, n-hexane and n-decane) were purchased from VETEC Quimica Fina Ltda, Rio de Janeiro, Brazil.

The paraffins P120, P130 and P140 were supplied by Duque de Caxias Refinery - Rio de Janeiro, Brazil, and eicosane 99% was purchased from Acros Organics, New Jersey, USA.

Methods

Chemical Characterization of Modified Copolymers

The vinyl acetate content of the commercial EVA copolymer, the hydrolysis degree of the EVAOH, and the C14 chain contents of the modified copolymers were determined by hydrogen nuclear magnetic resonance (^{1}H NMR) in a Varian spectrometer, Model Mercury 300. The experiments were carried out at a frequency of 300.067 MHz. Trimethylsulfoxide (TMS) was used as internal reference. The solutions were prepared by dissolving about 15 mg of copolymer in 1 mL of deuterobenzene.

Characterization of the Paraffin Samples

The characterization of the commercial paraffins was done by gas chromatography, using a gas chromatograph with an on-column injection system and a steel capillary - Chrompack. The oven operated at a temperature range from 40 °C to 380 °C, and the temperature of the detector remained at 420 °C during the analysis. The heating rate of the oven was 10 °C/min. The paraffin samples were dissolved in a paraffinc solvent before the experiment.

Model Systems

In order to simulate the fractions normally present in crude oil, the solution, called

model system, contained 10% w/v of paraffin dissolved in a solvent containing normal aliphatic, cyclic and aromatic hydrocarbons at concentrations of 50% n-decane, 20% cyclohexane and 30% toluene. This model system was used for the pour point and viscosity measurements. In the tests using copolymers, these compounds were added as a 2% w/v. solution in toluene.

Solubility Test of the Products

The EVA, EVA-OH and modified EVA copolymers (EVA-C14) were evaluated in terms of their solubility behavior in solvent systems having different solubility parameters by measuring the temperature at which the copolymer became insoluble. At this temperature, designated hereafter as the *Cloud Point (CP)*, the solution becomes cloudy or slightly turbid. The cloud points were determined by visual observation of the solutions in a test tube while heated in a water bath. The temperature was increased using a heating plate and measured using a thermometer positioned inside the test tube. The cloud point was defined as the average value between the temperature at which the solution became cloudy by heating and that at which the solution became clear by cooling. One percent w/v copolymer solutions were used in all tests and the cloud points were measured twice.

The solubility parameter (δ) values of the various solvents used were 18.2; 18.0; 16.8; 14.9 and 13.5 $MPa^{1/2}$ respectively, for toluene, xylene, cyclohexane, n-hexane and n-decane.[15] Some mixtures (binary and ternary) of these solvents were also used and their solubility parameters were calculated by the weighted average of the pure solvents' solubility parameters.

Pour Point Test

A modification of the ASTM D97/93[16] method was used to determine the pour point. The wax solution model system, containing additive or not, was heated in a water bath to about 71 °C. An appropriate volume of this solution was transferred to a test tube. The tube was then sealed with a stopper containing a thermometer and the solution was slowly cooled. When the temperature reached around 25 °C, the thermometer bulb was immersed in a wax solution and the test tube was positioned in a ThermoHaake C40P apparatus. The instrument was programmed to achieve −40 °C. During cooling, we verified whether the wax solution still flowed at intervals of 2 °C. The temperature plus 2 °C at which the system fails to flow by gravity action for 5 seconds corresponds to the pour point.

Viscosity Test

The viscosity measurements of the model systems, containing additive or not, were carried out in a Haake RS-600 rheometer, using a cone-plate system (cone diameter = 60 mm and angle = 1°).

First, the viscosity tests were carried out as a function of time, at different temperatures and 30 s^{-1} was establish for further measures. At this shear rate the systems present Newtonian behavior. In order to melt the wax crystals completely, all systems were heated and then cooled. The measurements were performed at each 2 °C, with the system remaining at each temperature for ∼10 minutes, and the viscosity measurement was taken during the following five minutes.

The viscosity versus temperature graphs were prepared using Microsoft Excel.

Results and Discussion

Characterization of Modified Copolymers

The commercial EVA copolymer and the hydrolyzed EVA (EVA-OH) were characterized by hydrogen-nuclear magnetic resonance (H^1-NMR), in order to determine the vinyl acetate content and the hydrolysis degree, respectively. In both cases, we used the relation among the peak areas, related to to each hydrogen nucleus.[14] The vinyl acetate content of the commercial EVA copolymer was 23 wt%, and the hydrolysis degree for the EVA-OH was nearly 100%.

The esterification reaction of the EVA-OH with myristyl chloride produced macromolecules containing branches of hydrocarbon chains. Table 1 shows the molar percentages of the hydrocarbon chains fed into the reaction and the respective molar percentages of the hydrocarbon chains effectively incorporated in the EVA molecules. The percentage values are related to the hydrolyzed repetitive unities. These calculations were also done through the relation of the areas obtained from the NMR spectra.[14] In general, the content effectively incorporated into the copolymer is very similar to that added to each reaction. The differences observed in some reactions can be related to the errors in the feeding.

Characterization of Commercial Paraffins

Three kinds of paraffin were chosen: P120, P130 and P140. The paraffins were characterized by gas chromatography. The results show that they are different in terms of average molar mass and molar mass distribution. The alkanes that predominate in paraffins P120, P130 and P140 are, respectively, C27, C29 and C36. The distribution of molar mass was expressed in terms of the difference between the carbon number of the greater alkane and the carbon number of the minor alkane, which constitutes the paraffin. The distribution of molar mass varies in increasing order P130 < P140 < P120. The paraffin samples were essentially normal. Insignificant amounts of branched paraffins were detected for P120 and P130, indicating that these samples are suitable to study the crystallization of normal paraffin.

Table 1.
Molar percentage of C14 hydrocarbon chains incorporated into the EVA, related to the hydrolyzed repeating unities.

Sample	Theoretical molar[a)]	Calculated molar[b)]
	%	%
EVA-29% C14	25	29
EVA-30% C14	29	30
EVA-33% C14	33	33
EVA-39% C14	40	39
EVA-45% C14	35	45
EVA-64% C14	50	64
EVA-71% C14	51	71
EVA-56% C14	55	56
EVA-80% C14	80	80
EVA-85% C14	90	85
EVA-93% C14	100	93

[a)] Molar % of C14 chains added in the modification chemical reactions.
[b)] Molar % of C14 chains effectively incorporated into the EVA-OH copolymer, calculated by 1H NMR.

Solubility of the Modified EVA Copolymers

In order to obtain a comparative estimation of the solution behavior of EVA, EVA-OH and EVA-C14 copolymers, two solvents having different solubility parameters (hexane and xylene) and their mixtures were selected. By this procedure, solvent systems with solubility parameters in a range of 14.9 to 18.0 $MPa^{1/2}$ and similar characteristics in terms of the hydrogen bond, dipole-dipole and van der Waals contributions were obtained. Table 2 presents the results for the unmodified commercial EVA copolymer in the various solvent media. Similar to most polymers, EVA copolymers in nonpolar solvents present an upper critical solution temperature. Therefore, as the temperature decreases, the polymer-solvent interactions decline, and at the cloud point, the copolymer separates as a different phase. In this context, lower cloud points represent higher affinity between the polymer and the solvent media. The cloud point obtained for commercial EVA in hexane was 38 °C. This value decreased for the mixtures, attaining 10 °C for pure xylene. In the solubility parameter range analyzed, it is possible to infer that commercial EVA presents its highest solubility in xylene; therefore its solubility parameter should be close to or higher than 18 $MPa^{1/2}$. This result agrees well with data reported in the literature[17] for EVA with 20% of vinyl acetate ($\delta = 19$ $MPa^{1/2}$).

Figure 1 shows the cloud point curves for the various EVA-C14 copolymers at a solution concentration of 1g/L, as a function of the percentage of C14 incorporated into the EVA-OH by the esterification

Table 2.
Cloud point of the commercial EVA in different systems of different solubility parameters (solution concentration: 1000 ppm).

Solvents	Hexane	Xylene	Solubility Parameter	Cloud point of commercial EVA
	%	%	δ ($MPa^{1/2}$)	(±1 °C)
Hexane	100	0	14.9	38
Hexane-xylene (65:35)	65	35	16.0	26
Hexane-xylene (50:50)	50	50	16.5	22
Hexane-xylene (30:70)	35	70	17.1	19
Xylene	0	100	18.0	10

reactions. Zero percent C14 denotes the results for EVA-OH. As expected, the substitution of all the vinyl acetate groups by hydroxyls increases the polymer polarity, resulting in an increase of the cloud point in xylene from the original value of 10 °C for commercial EVA to 60 °C for EVA-OH.

In general, all EVA-C14 samples exhibited higher solubility in xylene and their cloud points decreased as the substitution degree increased, indicating that the copolymers become more soluble in the solvents by insertion of C14 chains in the EVA-OH structure. It is interesting to note that for the solvent mixture containing 70% xylene and for pure xylene, the cloud point passed through a minimum, as can be observed by the curve obtained. Higher degrees of substitution result in copolymers with lower solubility parameters, whose solubility in aromatic solvents is lower. For substitution degrees of 85% and 93%, the resulting copolymers are more soluble in predominantly aliphatic solvents.

Thus, based on these results, it is possible to infer that: (1) the copolymers containing C14 chains around 65 mol% present δ values similar to that of the commercial EVA; (2) copolymers containing C14 chains equal to or greater than 70 mol% present lower δ values; and (3) copolymers containing C14 chains equal and below 60 mol% present δ values higher

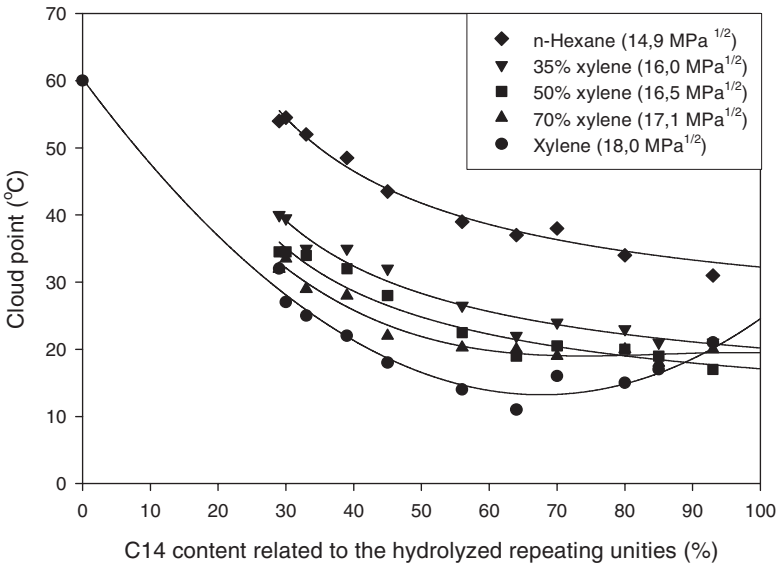

Figure 1.
Cloud points (±1 °C) of the modified EVA dissolved in systems with different solubility parameters.

than that for the commercial EVA. However, the EVAOH presents the highest δ value.

Since the solvent mixture of toluene: n-decane:cyclohexane (30:50:20) presents δ equal to the solvent system, that is, $\delta = 16.5$ MPa$^{1/2}$, the cloud points for the copolymers dissolved in this ternary solvent mixture were measured and compared with the values obtained for xylene:hexane (50:50). The results presented in Figure 2 show that within the standard deviation of the analysis (± 1 °C), the results are almost identical, indicating that the solution behavior of the copolymers is entirely determined by the solubility parameter of the solvent media.

Evaluation of the Additives' Efficiency as Wax Deposition Inhibitors

The additives' efficiency was evaluated by two tests: pour point and viscosity as a function of temperature reduction.

The two tests are different and reproduce different operational conditions, thus providing complementary information. Pour point is a static test in which the temperature at which the sample stops flowing is determined. The flow reduction is associated with the decrease of kinetic energy caused by the temperature reduction. Through rheological measurements as a function of decreasing temperature, it is possible to follow the viscosity increase, also because of the decrease of the kinetic energy. In this case, the precipitation of wax particles may be detected as a discontinuity in the curve.

Pour Point

Table 3 shows the pour point results for the three model systems containing paraffin P120, P130 and P140 and for eicosane, with and without the addition of polymer. We selected the additive concentration of 3000 ppm, since this concentration has already been used for additives based on EVA copolymers.[12,13] As shown in Table 3, in the absence of additives, for the four systems the pour point correlates with the molar mass of the alkane that predominates in each paraffin sample. Regarding the additives' performance, the results indicate that for wax samples P120 and P140, the copolymers were ineffective as pour point depressants. Similar results were obtained at a concentration of 300 ppm. For wax sample P130, EVA-30%C14 shows a

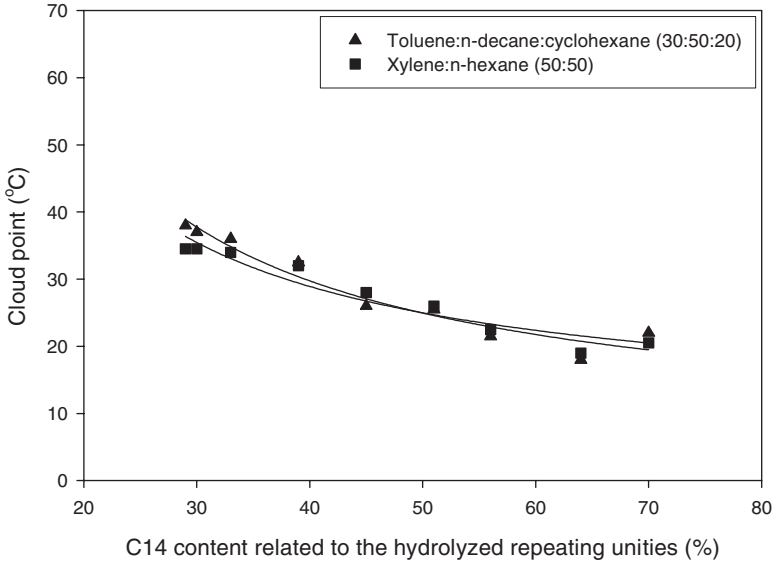

Figure 2.
Solubility behavior of copolymers in two different solvent-systems, both having $\delta = 16.5$ MPa$^{1/2}$.

Table 3.
Pour point of the three model systems containing paraffin P120, P130 and P140 and eicosane, with and without the addition of polymer at a concentration of 3000 ppm.

Additive	Wax			
	P120	P130	P140	Eicosane
	Pour point (±2 °C)			
None	12	22	26	0
EVA	12	20	26	−2/−8*
EVA-30%C14	12	17	27	−18/−12*
EVA-33%C14	12	—	24	0
EVA-45%C14	10	20	27	−3
EVA-64%C14	—	—	—	−3*
EVA-71%C14	8	20	27	−7

* Measured at 300 ppm.

reduction in the pour point from 22 to 17 °C at a concentration of 3000 ppm and to 19 °C at 300 ppm. This reduction may correlate with the narrower molar mass distribution of the P130 (Table 4). In order to check the influence of the molar mass distribution, we used eicosane, which is a linear aliphatic hydrocarbon monodisperse in terms of molar mass, containing 20 carbons ($C_{20}H_{42}$). In this case, good performance was also observed for this same copolymer, as it reduced the pour point by 18 °C at a concentration of 3000 ppm and by 12 °C at 300 ppm. There was also a small effect for EVA-71%C14 and EVA-45%C14, where it reduced the pour point by 7 and 3 °C, respectively.

Correlating the data shown in Table 3 for eicosane with the solubility results shown in Figure 1 and Table 2, it is possible to verify that copolymers having similar solubility parameters (commercial EVA and EVA-64%C14) may not exhibit the same pour point reduction, suggesting that the solubility of the additive is important. However, even for similar structures, it is not the only factor that contributes to the additive performance.

Table 4.
Pour point of model system and size characterization of paraffins.

Paraffin	Chain size[a)]	Distribution of molar mass[b)]	Pour point of the model system
			(°C ± 2)
P120	27	21	12
P130	29	12	22
P140	36	18	26

a) Expressed in terms of the number of carbons of the alkane that predominates in the paraffin.
b) Expressed in terms of the difference between the number of carbons of the greatest and the smallest alkane that constitutes each paraffin.

Viscosity

The main objective of the rheological measurements was to evaluate the influence of the additives on crystal growth. Besides this, it was possible to obtain data on wax appearance temperature (WAT). This kind of experiment is not the most advisalbe for determining WAT, when analyzing complex systems like crude oil plus wax inhibitor.[18] In this work we studied simple model systems, so we used rheological measurements to determine WAT.

Crude oil and paraffin mixtures exhibit Newtonian behavior when they are monophase. That is, the viscosity depends on the temperature but is independent of the shear rate. When the crystals start forming, the rheological behavior changes, and the system is not Newtonian at any shear rate.

Analyses for the pure model systems and also for these systems containing 3000 ppm of commercial EVA were done at two temperatures: (1) close to the pour point of each system, and (2) from 8 to 15 °C above the pour point. The lowest shear rate at which the system still presented Newtonian behavior (30 s^{-1}) was selected for the tests. At this shear rate all systems present Newtonian behavior and the probability of destroying the wax crystals formed is very low, because this shear rate is relatively low.

Figures 3, 4 and 5 present the results of viscosity as a function of temperature for the systems containing commercial EVA, EVA-30%C14, EVA-45%C14 and EVA-71%C14. These additives were selected in order to analyze molecules having low, medium and high content of C14. These systems did not show thixotropic behavior.

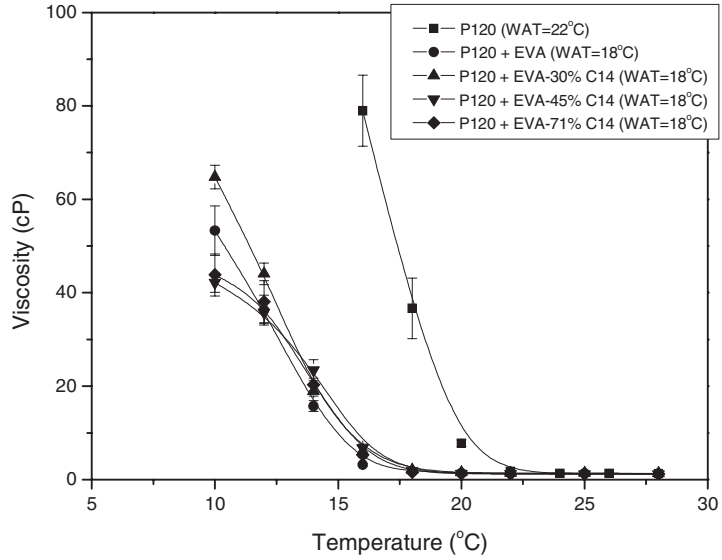

Figure 3.
Viscosity as a function of temperature for the model systems containing paraffin P120, with and without additives: commercial EVA and modified EVA. Additive concentration = 3000 ppm.

The points represent a temporal average value obtained in a period of five minutes and the standard deviations depend, in all cases, on temperature and viscosity, due most likely to the heterogeneity of the system beyond the paraffin precipitation point.

Figure 3 shows the viscosity against temperature for the model system containing paraffin P120, with and without additives. As expected, the system without additives has low viscosity and a very small variation with the reduction in temperature. At a certain temperature,

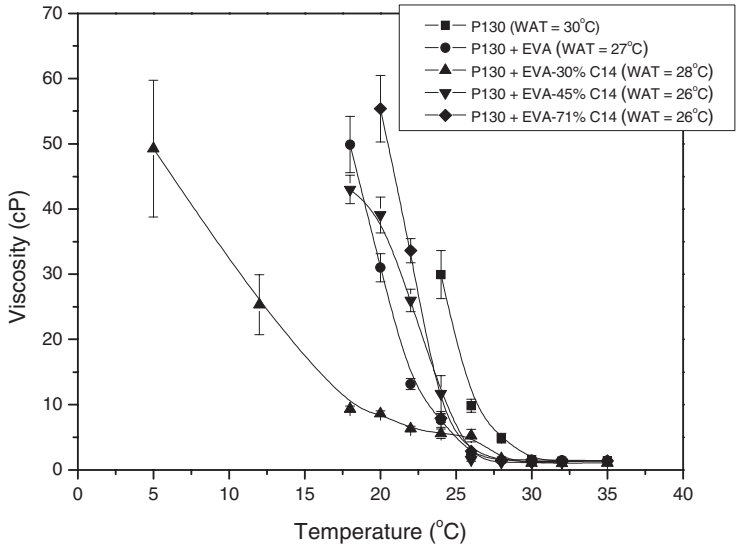

Figure 4.
Viscosity as a function of temperature for the model systems containing paraffin P130, with and without additives: commercial EVA and modified EVA. Additive concentration = 3000 ppm.

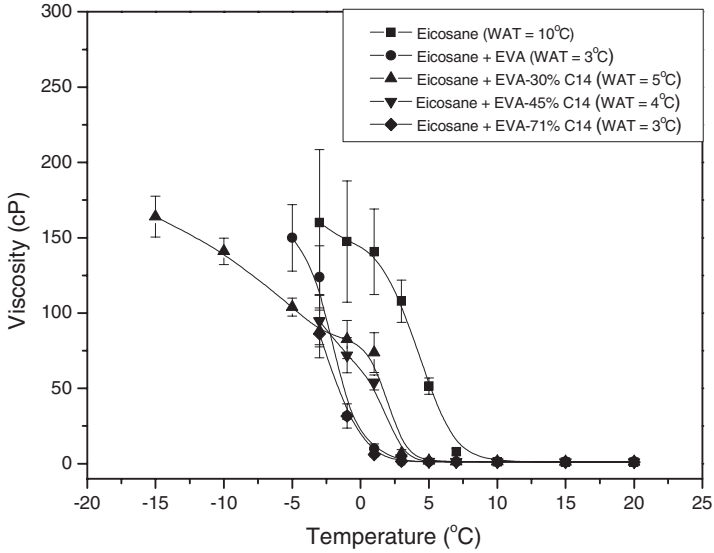

Figure 5.
Viscosity as a function of temperature for the model systems containing eicosane, with and without additives: commercial EVA and modified EVA. Additive concentration = 3000 ppm.

the WAT, viscosity increases drastically as wax crystals appear in the solvent medium. For this system, the WAT was 22 °C. The same behavior was observed for the system containing additives at a concentration of 3000 ppm, however the WAT values decreased to around 18 °C. This change may be ascribed to the paraffin- additive co-crystallization. In the presence of additives, at temperatures below the WAT for the pure system, the viscosity is significantly lower than the corresponding value for the system without additives. Similar behavior was observed for the other systems, P130 and eicosane (Figures 4 and 5).

It is interesting to note that for all pure model-systems the pour point was observed at a temperature around ten degrees lower than their WAT. This indicates that a fair amount of solid particles are necessary to interrupt the flow ability of the system and that these particles probably also need to grow to a certain size for this to occur. In all the viscosity diagrams, when additives are present, a small reduction was observed in the wax samples' WAT, but this modification does not correlate with the changes in the pour point. These diagrams also permit assessing the effect of the polymers at temperatures below the pour point. In this case, the additives that promote the lowest pour point also produce the highest reduction in viscosity at lower temperatures. This is clearly associated with the additive's ability to provide for the formation of small wax crystals dispersed in the solvent medium.

For P130 wax, good performance in viscosity reduction was obtained with EVA-30%C14, which in the model solvent presents a cloud point of 35 °C (Figure 2), five degrees above the wax WAT. The other copolymers present cloud points that are very similar or below the wax WAT. For P120 wax, which exhibits a WAT of 22 °C, all the copolymers show good performance in reducing viscosity, as they have cloud points near or above the P120 WAT. Similar behavior was observed for eicosane, but in this case a clear correlation between the polymer solubility and WAT reduction was obtained (Figures 2 and 5).

Conclusions

Commercial ethylene-vinyl acetate copolymers (EVA), chemically modified by inserting different contents of long hydro-

carbon chains, produce structures with different solubility parameters, whose values can be higher, lower or equal to that of commercial unmodified EVA.

The procedure for determining cloud points of polymer solutions prepared by dissolving the polymer in solvent-systems with different solubility parameters, but similar in nature, allows establishing the solubility parameters of the copolymers by comparison.

The molar mass distribution of the paraffin affects the performance of the organic deposition inhibitors: the broader the molar mass distribution, the lower the additive performance.

The performance of the organic deposition inhibitor is related to its interaction with the paraffin and, as a consequence, to the co-crystallization phenomenon. However, better performance was observed when the additive was already precipitated in the solvent media.

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[1] A. L. C. Machado, E. F. Lucas, G. González, *Journal of Petroleum Science and Engineering* **2001**, *32*, 159.
[2] A. L. C. Machado, E. F. Lucas, *Petroleum Science and Technology* **2001**, *19*, 197.
[3] M. Chichakli, F. W. Jessen, *Ind. Eng. Chem.* **1967**, *May:59*(5), 86.
[4] B. F. Towler, S. Rebbapragada, *Journal of Petroleum Science and Engineering* **2004**, *45*, 11.
[5] G. G. McClaflin, AIME Annual Technical Conference and Exhibition, paper SPE 12204, **1983**, San Francisco, California.
[6] D. Groffe, P. Groffe, S. Takhar, S. I. Andersen, E. H. Stenby, N. Lindeloff, M. Lundgren, *Petroleum Science and Technology* **2001**, *19*, 205.
[7] M. Cristante, J. L. Selves, G. Grassy, J. P. Colin, *Analytica Chimica Acta* **1993**, *274*, 303.
[8] M. Cristante, J. L. Selves, G. Grassy, J. Orrit, F. Garland, *Analytica Chimica Acta* **1990**, *229*, 267.
[9] J. W. Qian, G. R. Qi, D. L. Han, S. L. Yang, *Fuel* **1996**, *75*, 161.
[10] J. S. Weingarden, J. A. Euchener, 61st Annual Conference of the Society of Petroleum Engineers, paper SPE 15654, **1988**, New Orleans, L. A.
[11] G. E. Oliveira, L. B. Passos, C. R. E. Mansur, G. González, E.F. Lucas, 40 th International Symposium on Macromolecules, World Polymer Congress (MACRO 2004), **2004**, Paris, France.
[12] G. T. Woo, S. J. Garbis, T. C. Gray, Annual Conference of the Society of Petroleum Engineers, paper SPE 13126, **1984**, Houston.
[13] L. Fusi, *Nonlinear Analysis* **2003**, *53*, 507.
[14] C. X. Silva, D. R. S. Alvares, E. F. Lucas, *Energy & Fuels*, **2004**, *18*, 599.
[15] E. A. Grulke, in: *Polymer Handbook*, 4th ed.,J. Brandrup, E. H. Immergut, E. A. Grulke, Eds., John Wiley & Sons, New York, 1999, VII–688.
[16] ASTM D97 "Standard test method for pour point of petroleum products" (1993), V05.01, appendix X1, ASTM International. www.astm.org, visited on 1 August 2005.
[17] *Polymer Handbook*, James E. Mark, Ed., Oxford University Press, New York, **1999**.
[18] S. Amadi, A. Dandekar, G. Chukwu, S. Khataniar, S. Patil, W. Haslebacher, J. Chaddock, *Energy Sources* **2005**, *27*(9), 831.

