

# Assessment and Improvement of *n*-Paraffin Distribution Obtained by HTGC To Predict Accurately Crude Oil Cold Properties

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**ABSTRACT:** Wax precipitation and deposition in crude oils can produce flow assurance problems in production and transportation operations. Knowledge of the wax appearance temperature (WAT) and the amount of wax that precipitates from the crude oil at different temperatures, i.e., the wax precipitation curve (WPC), is necessary for accurate predictions of wax deposition in subsea pipelines. The theoretical study of the wax precipitation process is frequently carried out using thermodynamic models. These models require as input information the molecular weight and the *n*-paraffin distribution of the crude oil. The *n*-paraffin distribution is commonly determined by high-temperature gas chromatography (HTGC) analysis, but it has some limitations such as the low signal/noise ratios, elution and resolution problems in the heavy compounds zone, and discrepancies with regard to the delineation of the baseline to integrate the chromatogram. In this work, three variables have been analyzed to improve the *n*-paraffin distribution obtained by HTGC: the total amount of C<sub>20</sub><sup>+</sup> paraffin, extrapolation of paraffin concentration above C<sub>38</sub><sup>+</sup>, and molecular weight of crude oil. The results predicted were compared to experimental data obtained by fractional precipitation and differential scanning calorimetry, showing great influence of the *n*-paraffin distribution on the model accuracy.

## 1. INTRODUCTION

Paraffin waxes contained in petroleum mixtures can precipitate when temperature decreases during oil production, transport through pipelines, or storage. Such a problem is very well-known within the petroleum industry because the presence of solid waxes increases fluid viscosity, and its accumulation on the wall reduces the flow line section, causing the blockage of filters, valves, and pipelines and reducing or even stopping oil production or transportation. All of these facts increase operational costs and are identified as “flow assurance problems”. Consequently, a great effort has been made to understand, describe, and predict the wax formation process.<sup>1–3</sup>

Crude oils are complex mixtures formed by a great variety of compounds, and the determination of their composition is impossible. The solubility of such different species in a crude oil depends on pressure, temperature, and crude oil composition. Waxes are usually considered to be heavy hydrocarbons (C<sub>20</sub>–C<sub>60</sub>) mainly formed by linear *n*-alkanes<sup>4</sup> and represent the major risks in wax deposition problems because they can precipitate when the temperature of the crude oil decreases due to the reduction of their solubility.

The prediction of the wax appearance temperature (WAT) and the wax precipitation curve (WPC) of crude oils is critical to avoid or minimize flow assurance problems related to wax deposition in flow lines or storage tanks.<sup>5,6</sup> Thermodynamic models should provide that information, while kinetic models should estimate the deposition rate and the thickness of the layer of the deposit. Nevertheless, predicted results by kinetic models are strongly influenced by the reliability of the thermodynamic ones.

Some thermodynamic models of wax precipitation process require as input data the knowledge of the *n*-paraffin distribution,

total wax content (C<sub>20</sub><sup>+</sup>), and molecular weight of the crude oil. Obtaining the distribution of *n*-paraffin is not an easy task. There are several methods to determine it, but the most widely used are those based on high-temperature gas chromatography.<sup>3,7,8</sup>

One of the major unsolved problems in obtaining the *n*-paraffin distribution by HTGC is the uncertainty in the determination of the baseline to integrate the chromatogram because of the low signal/noise ratios and the interference created by other components of different natures, which makes the integration process difficult. In addition, heavy *n*-paraffins can be eluted with difficulty, so the wrong determination of their composition affects the WAT value. To overcome some of these difficulties, the isolation of saturated compounds was proposed in the literature.<sup>9</sup> Also, two integration methods have been tested: valley to valley integration and integration to the baseline of the chromatogram.<sup>10</sup>

Different experimental methods to determine cold properties of crude oils have been reported in the literature.<sup>11–19</sup> Most currently used methods are indirect, i.e., the change in a property of the sample that is known to be affected by wax precipitation is measured. However, the result of such methods is determined by the accuracy in the measurement of the property in question. Differential scanning calorimetry (DSC) is a fast technique that provides good results.<sup>20</sup> It measures the variation in heat flow between a sample of crude oil and a reference or the power that must be provided or removed from the system for both; the sample and reference remain at the same temperature when the crude oil is subjected to a temperature profile in a controlled

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atmosphere. In this work, it has been used to determine the WAT and the WPC of crude oils.

Several procedures exist for the direct determination of the total amount of waxes and the WPC. In most cases, precipitated wax is separated from the rest of the crude oil by filtering and quantifying by gravimetry. One of these is a modification of the traditional Burger's method,<sup>11</sup> which provides the total wax content ( $C_{20}^+$ ) in a crude oil because it is widely accepted that all paraffinic compounds that can lead to flow assurance problems ( $C_{20}$ – $C_{60}$ ) precipitate at  $-20$  °C. Nevertheless, it cannot be used to determine WPC because it presents two limitations: the starting crude oil sample is dissolved, and it can be only used to study wax precipitation at a single temperature. An alternative method, known as the fractional precipitation method, overcomes such limitations.<sup>15</sup> In this method, crude oil is not dissolved in any solvent, and it consists of making consecutive filtration experiments, while reducing the operation temperature. Finally, trapped crude oil into the precipitated paraffinic solid must be quantified to obtain the WPC. For example, proton nuclear magnetic resonance can be used for that purpose.<sup>16</sup>

In this work, the saturate fraction of one crude oil was extracted using a SARA type analysis based on ASTM D2549-02.<sup>17</sup> The *n*-paraffin distribution of the raw crude oil was determined by HTGC from its saturate fraction. The molecular weight of the crude oil was obtained by gel permeation chromatography. A predictive model<sup>21–36</sup> was applied to calculate the WPC of the crude oil using the *n*-paraffin distribution previously determined. Model predictions were checked with experimental data of wax precipitation (WAT and WPC) obtained by fractional precipitation<sup>9,15</sup> and differential scanning calorimetry.<sup>9,20</sup>

Predictions were greatly influenced by the integration method used to determine the *n*-paraffin distribution fed to the model. Apart from the integration method, different variables were studied such as the total  $C_{20}^+$  paraffin content, concentration of *n*-paraffin compounds from  $C_{38}^+$ , and molecular weight of the crude oil.

It was shown that the best agreement was achieved when using the *n*-paraffin distribution obtained by the integration method from valley to the baseline together with the amount of waxes from  $C_{20}^+$ . Elution problems were overcome taking into account the WAT obtained by DSC. The results show that the experimental error in the determination of molecular weight has a negligible effect on the predictions.

## 2. EXPERIMENTAL AND COMPUTATIONAL SECTION

**Materials.** A dead paraffinic crude oil from Asia provided by Repsol was used in this work.

**Gravimetric Determination of Wax Precipitation.** Two procedures have been used for experimental determination of wax precipitation in this work: modified Burger's method<sup>11</sup> and fractional precipitation.<sup>15</sup> In the first method, crude oil is dissolved in *n*-pentane and stirred during 30 min. A mixture of acetone and *n*-pentane (3:1 vol/vol) is added to the mixture and cooled to  $-20$  °C for 12 h. The solid phase present in the oil is separated by filtration in a Buchner funnel using a glass microfibre Whatman filter N° 934. The solid phase is washed with *n*-pentane in order to remove asphaltenes and the filtered liquid evaporated. This solid obtained after solvent evaporation contains the *n*-paraffins and is redissolved in *n*-hexane and filtered again. After solvent removal, the final product is weighted.

The fractional precipitation of paraffins contained in a crude oil consists of making consecutive filtration experiments while reducing the

working temperature. The crude oil sample is cooled in a cryostat at a lower temperature than its WAT for 24 h. It is then filtered using a glass microfibre Whatman filter N° 934 during at least 2 h. The solid phase is collected for further purification of the precipitated waxes, while the liquid phase is used for the next precipitation. The solid phase is washed with acetone to reduce the trapped crude oil. This washing process is carried out at room temperature in a Buchner funnel using vacuum. The remaining solids are recovered by washing the filter with dichloromethane, and after solvent removal by heating at  $50$ – $60$  °C, the final free-solvent product is weighted and stored for further characterization.

**Differential Scanning Calorimetry (DSC).** This technique is usually used to experimentally quantify the amount of wax precipitated in crude oils.<sup>4,11,37</sup> The equipment used to carry out the calorimetric measurements was a DSC822e from Mettler Toledo. In DSC analysis, the sample follows a temperature profile, the heat transfer is registered, and any phase transition is quantified through the involved heat change. The difference between the DSC curve and the baseline is a direct measurement of the total heat involved in the phase change, which is converted into the corresponding mass using a calibration from pure *n*-paraffins. In a previous work,<sup>20</sup> experimental DSC conditions were optimized for these kind of samples. First, the sample is heated from  $20$  to  $80$  at  $3$  °C/min. Then, the sample is cooled from  $80$  to  $-120$  at  $3$  °C/min, and finally, the sample is heated from  $-120$  to  $80$  °C at the same rate.

The baseline is determined by assuming that the sample behaves as a usual liquid at temperatures above the WAT and as a solid at very low temperatures, the two-phase system behavior can be obtained by imposing the continuity of the heat capacity and first derivative. DSC measured heat is converted into mass through the specific melting heat.<sup>4,20,38</sup>

**SARA Type Separation.** The purpose of this method focuses on determining the content of saturated, aromatics, resins, and asphaltenes in a crude oil. It is based on the ASTM D2549-02 standard test method<sup>17</sup> with some modifications related to the removal of asphaltenes and the stationary phases used. In the first stage of SARA type analysis, asphaltenes and insoluble resins should be separated by precipitation with *n*-pentane (crude oil/solvent ratio equal to 1/30 vol.). The filtered sample (malthe fraction) is later split in a chromatographic column to obtain saturated compounds, aromatic, and polar resins.

Chromatographic separation of malthenes is carried out in an installation that comprises three glass columns packed with silica gel (Macherey-Nagel 0.071–0.160 mm/100–200 mesh) and alumina (Merck 0.063–0.200 mm/70–230 mesh). A stream of nitrogen is also used to control liquid flow through the columns. In two of them, crude oil samples are eluted in order to check repeatability. The third column is used as a blank to detect potential problems related to the stationary phases. The different fractions are separated depending on their affinity to the solvent being used at each step of extraction. Saturated compounds are recovered passing through the column 85 mL of *n*-pentane.

**High-Temperature Gas Chromatography (HTGC).** The experiments were carried out in a Varian Chrompack CP-3800 chromatograph, equipped with a Varian CP 7542 column 10 m long, 0.53 mm internal diameter, and 0.17  $\mu$ m thick stationary phase. For detection, a flame ionization detector (FID) with a flame of air and hydrogen at a temperature of  $430$  °C was used. The method is based on the ASTM D-2887 analysis. The samples were diluted in carbon disulfide at a concentration of 5% by weight and injected on column. The carrier gas used was helium, with a flow of 18 mL/min. The initial temperature of the column oven is  $40$  °C, and it is heated to  $425$  °C using a rate of  $16$  °C/min. Then temperature remains constant for 20 min. For calibration of the retention times two different standard *n*-paraffin mixtures were used: a mixture of  $C_5$ – $C_{18}$  *n*-paraffins from Agilent Technologies and a  $C_{20}$ – $C_{70}$  mixture from Supelco called Poliwx 500.

**Proton Nuclear Magnetic Resonance ( $^1\text{H}$  NMR).** The equipment used was a Varian Mercury Plus 400 MHz spectrometer. Samples were dissolved in deuterated chloroform (20 mg in 0.45 mL) using tubes of 5 mm in diameter. A radiofrequency with a pulse of  $30^\circ$  was used. A total of 64 scans with 1 s delay was applied.

In this work, this technique has been used to determine the aromatic content in each fraction. The weight percent of  $\text{H}_{\text{ar}}$  (hydrogen atoms in aromatic rings),  $\text{H}_\alpha$  (hydrogen atoms next to functional groups),  $\text{H}_\beta$  (methylene hydrogen atoms), and  $\text{H}_\gamma$  (methyl hydrogen atoms) were obtained by integration of the corresponding peak areas. The following chemical shift ranges were considered:  $\text{H}_{\text{ar}}$  (9.2–6.5 ppm),  $\text{H}_\alpha$  (3.8–1.8 ppm),  $\text{H}_\beta$  (1.8–1.03 ppm), and  $\text{H}_\gamma$  (1.03–0.4 ppm). The trapped crude oil amount of each precipitated fraction was calculated by comparing the aromatic content of the precipitated fraction and the raw crude oil.<sup>16</sup>

**Chromatographic Separation of Trapped Crude Oil (CS).** This method is based on a modification<sup>43</sup> of the sequential elution procedure proposed by Musser and Kilpatrick,<sup>12</sup> and it is used to determine the total wax content of a crude oil. The precipitated solid obtained by Burger's method (known as  $\text{C}_{20}^+$ ) is dissolved in dichloromethane, and the mixture is adsorbed onto silica gel, previously activated at  $120^\circ\text{C}$  overnight. Dichloromethane is removed in an oven at  $40^\circ\text{C}$ . A glass chromatographic column of 1 m long is used. The bottom of the column is charged with fresh activated silica, and the top is partially charged with fresh activated alumina and the adsorbed organic matter onto  $\text{SiO}_2$  gel. *n*-Hexane is charged in a 250 mL reservoir attached to the top of the column, and it is passed through the column. The cleaned paraffinic compounds are collected after eluting 200 mL of *n*-hexane.

**Gel Permeation Chromatography (GPC).** Molecular weight determination was carried out in a Waters Alliance 2000 GPCV chromatograph equipped with three chromatographic columns: two columns PLGEL 10  $\mu\text{m}$  mixed-B,  $300 \times 7.5$  mm, and a PLGEL 10  $\mu\text{m}$   $10^6$  Å column. The columns and detectors are kept at  $145^\circ\text{C}$ . Solvent was 1,2,4-trichlorobenzene, and a flow rate of 1 mL/min was used. Each sample was analyzed twice in order to check the reproducibility of results.

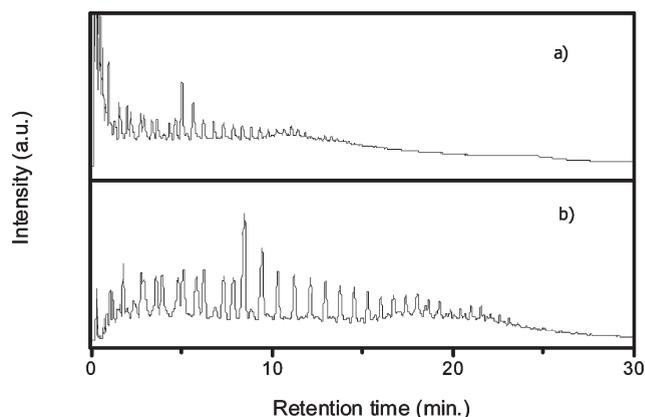
**Thermodynamic Model.** The precipitation of solids in crude oils at low temperatures is described using an approach previously proposed for alkane mixtures.<sup>21–36</sup> The solid–liquid equilibrium equation, relating the composition of component *i* in the solid and liquid phases, their nonideality, and the thermophysical properties of the pure components,<sup>39</sup> is given by the next expression

$$\ln \frac{x_i^s \gamma_i^s}{x_i^l \gamma_i^l} = \frac{\Delta_{\text{fus}} H_i}{RT_{\text{fus},i}} \left( \frac{T_{\text{fus},i}}{T} - 1 \right) - \frac{\Delta_{\text{fus}} C_{p,i}}{R} \left( 1 - \frac{T_{\text{fus},i}}{T} + \ln \frac{T_{\text{fus},i}}{T} \right) \quad (1)$$

where  $\gamma_i$  is the activity coefficient of the *i* compound,  $x_i$  its mole fraction,  $\Delta_{\text{fus}} H_i$  the molar enthalpy of fusion of the pure solute at the melting temperature  $T_{\text{fus},i}$ , and  $\Delta_{\text{fus}} C_{p,i}$  the molar heat capacity change upon fusion, at fusion temperature  $T_{\text{fus},i}$ . The heat capacity change upon fusion is usually regarded as being independent of the temperature, and the bracketed term multiplied with  $\Delta_{\text{fus}} C_{p,m}$  is often considered as being small, as the opposite signs inside the bracket lead to near cancellation.<sup>40</sup> This term was thus neglected in the calculations. The solid phase nonideality is described by the most recent version of the Predictive UNIQUAC model.<sup>26</sup> The UNIQUAC model can be written as

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \ln \left( \frac{\Phi_i}{x_i} \right) + \frac{Z}{2} \sum_{i=1}^n q_i x_i \ln \frac{\theta_i}{\Phi_i} - \sum_{i=1}^n x_i q_i \ln \left[ \sum_{j=1}^n \theta_j \exp \left( -\frac{\lambda_{ij} - \lambda_{ii}}{q_i RT} \right) \right] \quad (2)$$

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad \text{and} \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (3)$$



**Figure 1.** HTGC chromatograms: (a) raw crude oil and (b) saturated fraction separated by SARA analysis.

where  $\Phi_i$  and  $\theta_i$  are the area and volume fractions, respectively, and  $Z$  is the coordination number with a value of 10 as in the original UNIQUAC model.<sup>26,41</sup> The structural parameters,  $r_i$  and  $q_i$  (area and volume parameters, respectively) are obtained from the UNIFAC parameter table.<sup>42</sup>

The predictive local composition concept<sup>21–26</sup> allows the estimation of the interaction energies,  $\lambda_{ij}$ , used by these models without fitting to experimental data. The pair interaction energies between two identical molecules are estimated from the heat of sublimation of the pure component

$$\lambda_{ii} = -\frac{2}{Z} (\Delta_{\text{sub}} H_i - RT) \quad (4)$$

The heat of sublimation is calculated at the melting temperature of the pure component as

$$\Delta_{\text{sub}} H = \Delta_{\text{vap}} H + \Delta_{\text{fus}} H \quad (5)$$

The pair interaction energy between two nonidentical molecules is given by

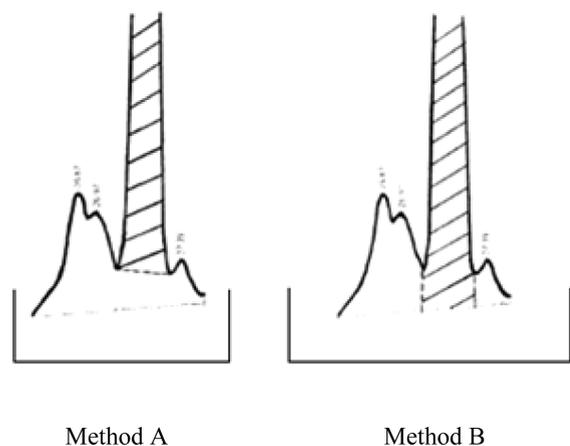
$$\lambda_{ij} = \lambda_{ji} = \lambda_{jj} \quad (6)$$

where  $j$  is the *n*-alkane with the shorter chain of the pair *ij*. The solid–liquid equilibrium model used in this work is thus a purely predictive model that uses only pure component properties for the calculation of the phase equilibria.

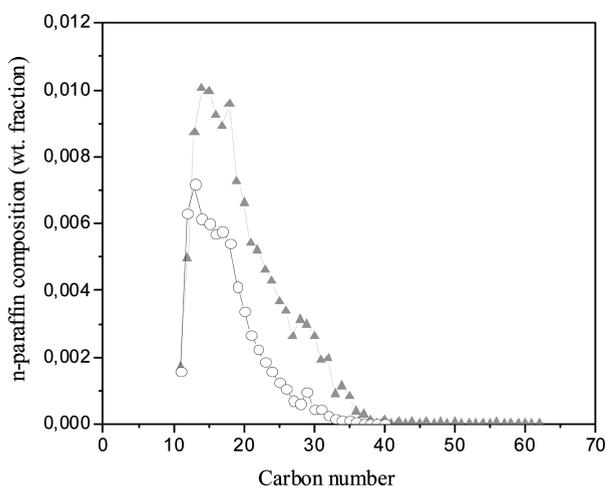
### 3. RESULTS

As previously mentioned, *n*-paraffin distribution is the input parameter fed to the model used in this work. Paraffin distribution was obtained from saturated compounds of the crude oil obtained by SARA type analysis. The saturate content determined for the crude oil used in this study was 33.8% by weight. Figure 1 shows the chromatograms of the raw crude oil and its saturated fraction. Signals with higher intensities correspond to *n*-paraffins. It is clear that the analysis of the saturated fraction increases signal intensity and allows quantifying the heavier compounds with greater precision.

Besides resolution problems, it is not clear which integration method should be used. In fact, two different methods have been proposed in the literature<sup>10</sup> for obtaining the composition of the *n*-paraffins: valley to valley integration (method A) and integration to the baseline of the chromatogram (method B), both are shown in Figure 2. Integration by method A is the most used method in the literature, but because of the scarcity of



**Figure 2.** Different proposed methods of integrating a chromatogram: (a) method A (valley to valley integration) and (b) method B (integration from valley to the baseline of the chromatogram).

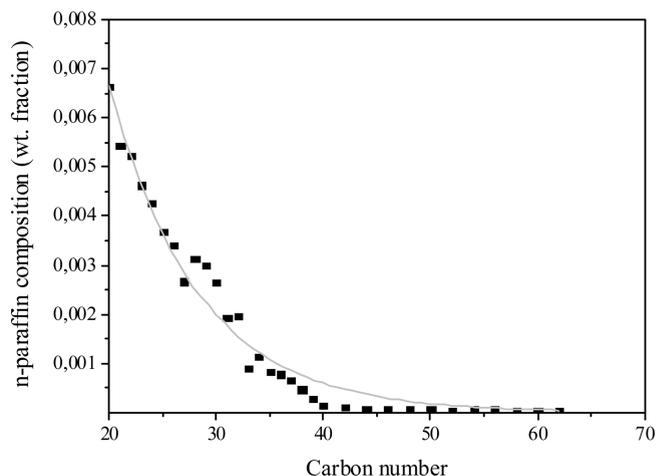


**Figure 3.** Distribution function (in weight fraction) of *n*-alkane like components: integration method A (O) and integration method B (▲).

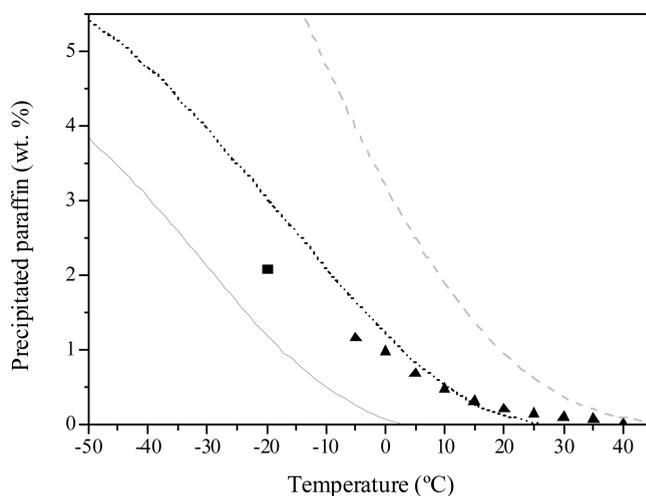
experimental data of wax precipitation in crude oils, predicted results have not been accurately validated.

Figure 3 shows the differences between the *n*-paraffin distribution obtained by the two integration methods used for the studied crude oil. As shown, *n*-paraffin obtained from method B is quantitatively higher. This can be explained because method A only considers the areas belonging to *n*-paraffinic compounds, while, as shown in Figure 1, there is a nonresolved zone in the chromatogram from the baseline to the start of a valley, which belongs not only to *n*-paraffins but also to other compounds that cannot be identified by means of the up-to-date techniques. For that reason, the integration by method A subestimates the content of the *n*-paraffins, while it is overestimated by method B.

In spite of obtaining an enhanced signal/noise ratio when saturated fractions are analyzed, it is not enough to solve the resolution problems for a high carbon number ( $C_{38}^+$ ). This point is critical in flow assurance because heavy paraffins have a great influence on the WAT value. For that reason, extrapolation of paraffin composition from  $C_{38}^+$  is proposed as a possible solution. In Figure 4, the deviation of *n*-paraffin composition for heavy paraffin compounds with regard to the expected exponential decay trend can be observed for the crude oil studied.



**Figure 4.** Exponential decay trend of *n*-paraffin distribution: experimental data (■) and exponential decay fit (solid line).



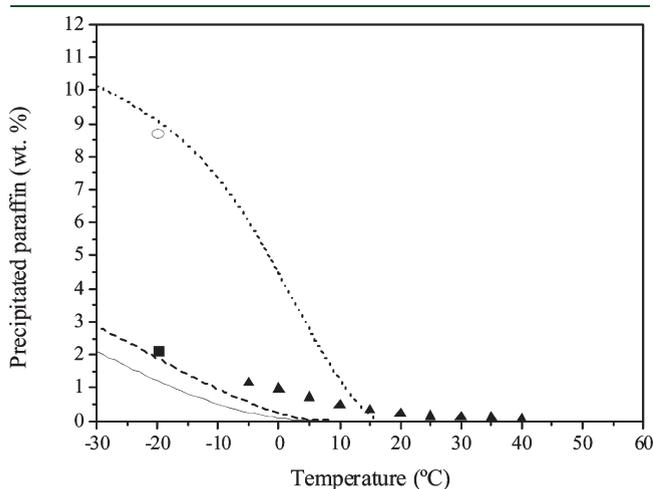
**Figure 5.** Total wax content (■), experimental WPC fractional precipitation (▲), DSC (dotted line), and predicted WPC from both *n*-paraffin distribution: integration method A (solid line) and integration method B (dashed line).

In this work, the model previously described was used to predict the WPC for the selected crude oil. The model requires as input information the *n*-paraffin distribution and molecular weight of the crude oil. In this work, the  $C_{38}^+$  *n*-paraffin distribution, obtained by extrapolation of the results obtained by the HTGC of saturated compounds using the integration methods A and B, in addition to the molecular weight of the crude oil determined by GPC, were used as input information. In Figure 5, experimental WPC obtained by fractional precipitation without trapped crude oil discounted by  $^1\text{H}$  NMR, WPC obtained by DSC, and total wax content at  $-20^\circ\text{C}$  obtained by modified Burger's method are compared to thermodynamic model prediction. As observed, the thermodynamic model underestimates both WAT and WPC when using the *n*-paraffin distribution obtained from integration method A as input data. On the contrary, if the *n*-paraffin distribution obtained by integration method B is used, the thermodynamic model overestimates both magnitudes.

As explained before, the HTGC technique and the equipment used in this work have some limitations, and the results provided by the model depend on them. In this work, three variables have

been analyzed by using the thermodynamic model previously described to improve the  $n$ -paraffin distribution obtained by HTGC: the total amount of  $C_{20}^+$  paraffin, extrapolation of paraffin concentration above  $C_{38}^+$ , and molecular weight of crude oil.

**Correction of  $n$ -Paraffin Distribution Obtained by Integration Method A.** (a). *Effect of Total Amount of Paraffin  $C_{20}^+$ .* The composition of  $C_{20}^+$   $n$ -paraffins obtained by HTGC and integration method A was recalculated in order to check the effect of the total amount of paraffin  $C_{20}^+$  in the WPC predicted by the model. Each individual  $C_{20}^+$   $n$ -paraffin composition was proportionally increased/decreased to make the sum equal to the amount of paraffin obtained experimentally by Burger's method, corrected with the trapped crude oil obtained by  $^1\text{H}$  NMR or CS. The results of the different simulations for the crude oil are shown in Figure 6. As is shown, the model overestimates WPC, compared to the experimental data provided by DSC or fractional precipitation, when  $n$ -paraffin distribution is corrected with the  $C_{20}^+$  value provided by Burger's method and the



**Figure 6.** Effect of  $C_{20}^+$  correction in the WPC. Experimental: total wax content trapped crude oil  $^1\text{H}$  NMR (■), total wax content trapped crude oil CS (○), and WPC fractional precipitation (▲). Predicted by  $n$ -paraffin distribution HTGC (method A): uncorrected  $n$ -paraffin distribution (solid line), corrected with trapped crude oil determined by  $^1\text{H}$  NMR (dashed line), and corrected with trapped crude oil determined by CS (dotted line).

trapped crude oil is obtained by CS. Nevertheless, if  $^1\text{H}$  NMR is used to determine trapped crude oil, the differences between predicted and experimental WPC are lower. The chromatographic separation of trapped crude oil allows determining the total saturated content in the precipitated solid, but not exclusively the  $n$ -paraffin compounds, which are supposed to be the only ones that precipitate by decreasing temperature. For that reason, the  $n$ -paraffin distribution obtained by this method leads to an overestimation of WPC. As is shown in Table 1, predicted WAT values are underestimated in all cases compared to those provided by DSC.

(b). *Effect of Heavy Paraffin Composition ( $C_{38}^+$ ).* To solve the underestimation of the WAT, the distribution of  $n$ -paraffins obtained by HTGC was extrapolated from  $C_{38}^+$ . Figure 7 shows the results obtained by applying the model once the  $n$ -paraffin distribution with the experimental amount of paraffin  $C_{20}^+$  was corrected and the extrapolation of the composition from  $C_{38}^+$  was performed. In this case, as shown in Table 1, the predicted WAT value is closer to that determined by DSC. However, the WPC is also underestimated if compared to experimental data. As has been shown, the extrapolation improves the model predictions, and therefore, the correction should be included in the  $n$ -paraffin distribution obtained by HTGC.

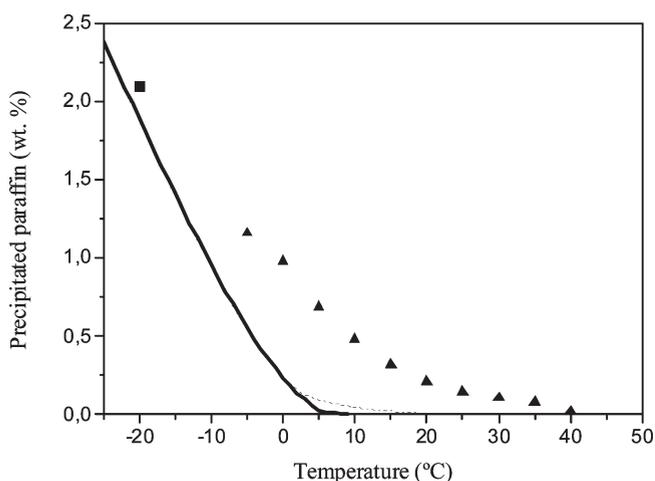
(c). *Effect of Molecular Weight of Crude Oil.* The molecular weight is one of the physicochemical properties of a crude oil that thermodynamic models require to transform the  $n$ -paraffin composition provided by HTGC in percentage by weight into mole fractions used by the model. In this work, the influence of a variation in the molecular weight of about 15% (approximate error of the methods used to determine this parameter) has been studied. Figure 8 shows the effect of such variation in molecular weight over model predictions. As observed, differences between predicted WPC using molecular weights with a variation of 15% are minimal. WAT values differs by only  $\pm 1$  °C.

In spite of the different corrections considered, it was not possible to obtain a good fit between experimental data and predicted values with the  $n$ -paraffin distribution obtained from integration of method A.

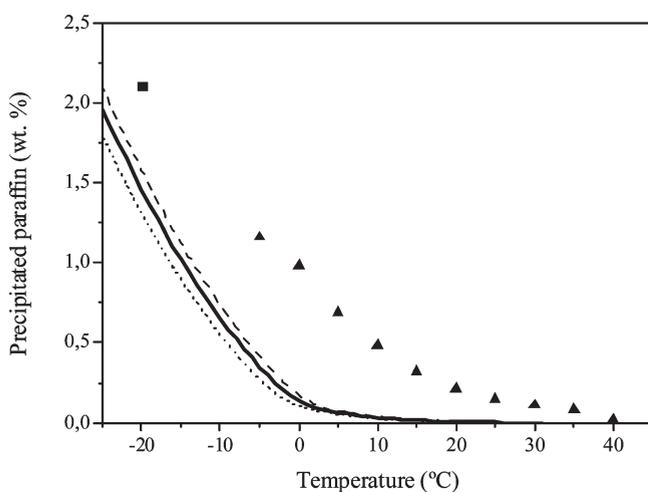
**Correction of  $n$ -Paraffin Distribution Obtained by Integration Method B.** (a). *Effect of Total Amount of Paraffin  $C_{20}^+$  and Extrapolation from  $C_{38}^+$ .* To check the effect of the total amount of paraffin  $C_{20}^+$  in the predicted WPC, the  $n$ -paraffin distribution obtained by integration method B was corrected as explained before for integration method A. Figure 9 compares

**Table 1.** Experimental and Predicted WAT Values and WPC

	DSC		method A		method B	
	WAT (°C)	WPC	WAT (°C)	WPC	WAT (°C)	WPC
experimental	29.4	see Figure 5	—	—	—	—
uncorrected $n$ -paraffin distribution	—	—	7	underestimated	49	overestimated
effect of $C_{20}^+$ correction	corrected with trapped crude oil CS	—	16	overestimated	—	—
	corrected with trapped crude oil NMR	—	9	underestimated	—	—
effect of $C_{38}^+$ correction	$C_{20}^+$ correction with trapped crude oil CS	—	—	—	51	overestimated
	$C_{20}^+$ correction with trapped crude oil NMR	—	—	32	underestimated	45
WAT <sub>DSC</sub> fitting	—	—	—	—	33	✓



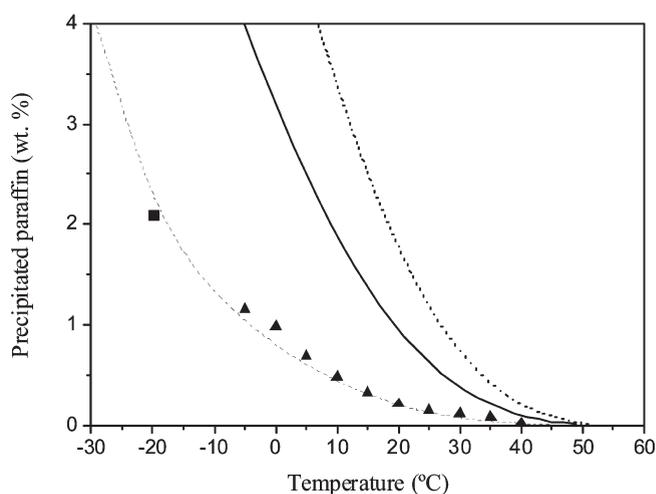
**Figure 7.** Effect of paraffin composition from  $C_{38}^+$  in the WPC. Experimental: total wax content trapped crude oil  $^1\text{H}$  NMR (■) and WPC fractional precipitation (▲). Predicted by  $n$ -paraffin distribution HTGC (method A): corrected  $C_{20}^+$  with trapped crude oil determined by  $^1\text{H}$  NMR (solid line) and extrapolated  $n$ -paraffin distribution (dashed line).



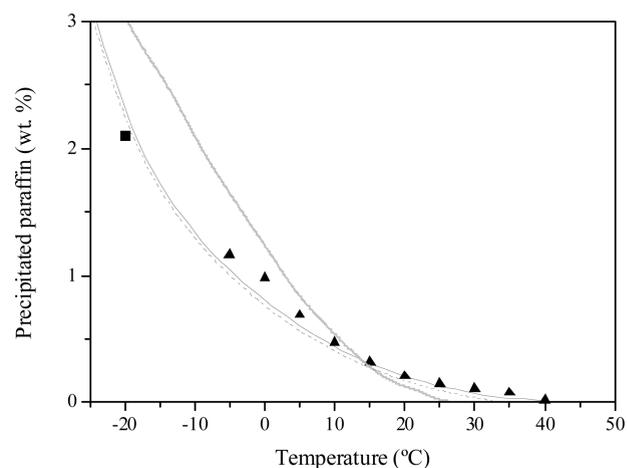
**Figure 8.** Effect of molecular weight of crude oil in the WPC: total wax content (■), experimental WPC fractional precipitation (▲), GPC molecular weight (solid line), molecular weight overestimated 15% (dashed line), and molecular weight underestimated 15% (dotted line).

the predictions provided by the thermodynamic model with the experimental results obtained by fractional precipitation and DSC. The model overestimates WPC with regard to the experimental data provided when  $n$ -paraffin distribution is corrected with the amount of  $C_{20}^+$  provided by Burger's method and the trapped crude oil is corrected by CS analysis. The predicted WAT value in this case is shown in Table 1. Nevertheless, if  $n$ -paraffin distribution corrected with the  $C_{20}^+$  amount provided by Burger's method and the correction of trapped crude oil by  $^1\text{H}$ -NMR is used, predicted WPC at low temperatures fits quite well with the experimental data but not the predicted WAT value, as shown in Table 1.

(b). *Correction by Fitting Experimental WAT Obtained by DSC.* The previous results show that the extrapolation of the  $C_{38}^+$  composition is not enough to minimize the differences



**Figure 9.** Effect of total amount of paraffin  $C_{20}^+$  correction and extrapolation of paraffin composition from  $C_{38}^+$  in the WPC. Experimental: total wax content (■) and WPC fractional precipitation (▲). Predicted by  $n$ -paraffin distribution HTGC (Method B): original  $n$ -paraffin distribution (solid line), corrected with trapped crude oil determined by  $^1\text{H}$  NMR (dashed line), and corrected with trapped crude oil determined by CS (dotted line).



**Figure 10.** Effect of correction of  $n$ -paraffin distribution obtained by method B on predicted WPC. Experimental: total wax content (■), WPC fractional precipitation (▲), and WPC<sub>DSC</sub> (gray solid line). Predicted by  $n$ -paraffin distribution HTGC (method B): corrected with trapped crude oil determined by  $^1\text{H}$  NMR (black solid line) and corrected  $n$ -paraffin distribution with the experimental WAT<sub>DSC</sub> (dotted line).

between the WAT predicted by the thermodynamic model and the experimental one obtained by DSC as a consequence of heavy paraffin elution problems.

For that reason, the  $n$ -paraffin distribution obtained from the previous step was corrected again. This correction was carried out in three steps:

1. The amount of precipitated  $n$ -paraffin at the DSC WAT value was obtained from the predicted WPC.
2. The composition for the heaviest  $n$ -paraffin was set to zero until the sum of discounted  $n$ -paraffin content was equal to the amount determined in point 1.

3. The resulting *n*-paraffin distribution was normalized to a  $C_{20}^+$  value provided by Burger's method correcting the trapped crude oil by  $^1H$ -NMR as described in section (a).

An iterative procedure was not necessary because the new WAT predicted by the model was very similar to that provided experimentally by DSC in the first stage.

The results of the predictions taking into account the WAT obtained by DSC are shown in Figure 10. As observed, the predictions obtained in this case are quite good. Predicted WAT values shown in Table 1 compare favorably with the experimental values provided by DSC.

#### 4. CONCLUSIONS

The *n*-paraffin distribution obtained by HTGC and integration method A was corrected studying the influence of the total amount of paraffin  $C_{20}^+$  and extrapolating heavy *n*-paraffin composition from  $C_{38}^+$  to overcome the limitations of HTGC method, but the prediction in all cases underestimated the WAT and the WPC. However, when integration method B was applied, the predicted WPC compared satisfactory with the experimental curve obtained by fractional precipitation and DSC when correcting the *n*-paraffin distribution with the total amount of paraffins  $C_{20}^+$ . Only the determination of trapped crude oil by  $^1H$  NMR gives a reliable experimental total amount of waxes. The CS method overestimated in all cases the total wax content and led to wrong predictions.

Although the extrapolation of the heavy *n*-paraffin composition from  $C_{38}^+$  improves predicted WAT results, it is additionally necessary to fit the composition of the heavier *n*-paraffin with the WAT value obtained by DSC. The molecular weight variation by 15% does not have a significant effect on the predictions.

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