

The Limitations of the Cloud Point Measurement Techniques and the Influence of the Oil Composition on Its Detection

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Abstract: In the petroleum industry, cloud points are one of the main guides to evaluate the wax precipitation potential of a fluid. The planning of the exploration of a reservoir or the design of its pipelines are based on the measured cloud points for the reservoir oil. It is known that each measuring technique will provide a different cloud point temperature, yet although some of these techniques seem to be more accurate than others, no definite conclusion was established on how cloud points should be measured.

On this work, several cloud point measurement techniques are discussed and compared. It will be shown that some of these techniques, such as viscosity, filter plugging, and differential scanning calorimetry (DSC) can only be used under very favorable circumstances, but it will be argued that because every technique requires some finite, often large, amount of solid to detect the presence of a new phase, the cloud point, defined as the temperature for which the first solid appears in the oil, is not accessible experimentally, and unless a very detailed compositional analysis is available, it is also impossible to predict it accurately with a thermodynamic model. The effect of the paraffin distribution in the oils on the cloud point detection will be discussed, and it will be shown how the compositional information can be used to assess the uncertainty of the measured cloud points.

Keywords: cloud point, wax, paraffins, wax appearance temperature

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INTRODUCTION

Wax formation in crudes and its deposition on reservoirs and pipelines constitutes a major problem in the extraction and transportation of petroleum in offshore systems. The paraffins precipitate from the liquid matrix mainly due to the cooling of the fluid as it is extracted from the reservoir, but changes in composition due to losses in light compounds to the gas phase caused by pressure depletion also contribute to the wax formation. The potential of a fluid-to-wax precipitation is measured by the cloud point of the fluid. The cloud point, a.k.a. wax appearance temperature, is defined as the temperature at which the first solid particles appear in a fluid. Several methods to measure the cloud point were proposed, and a number of them became American Society for Testing Materials (ASTM) standards [e.g., ASTM 2500-98a (1998); ASTM 3117-96 (1998)]. The methods differ in the cooling program used, but their main distinction is the method of detection of the first crystals. In a review of the methods used for cloud point determination, it will be shown how these methods are dependent on the quantity of solid required to produce a detectable signal and how this can affect the cloud point estimation by as much as 20 K. The influence of the oil composition on the cloud point measurements will be examined. The possibility of constructing a model to predict the cloud point from compositional information alone will be discussed, showing how the cloud point estimates are very much dependent on the composition of the very heavy paraffins that can hardly be measured and are seldom available. It will be concluded that the true cloud point, i.e., the temperature at which the very first crystal of paraffin is formed in a fluid, is probably not accessible experimentally and, alone, is not a good indication of the hazardous potential of crude oils.

HOW WAX FORMS IN PETROLEUM FLUIDS

If the cloud point is defined as the temperature for which the very first crystal of paraffin appears in the fluid, then this temperature will depend on the total wax content, the paraffin distribution, and the heaviest paraffin present on the oil. It may be somewhat surprising and counterintuitive, but the nature of oil that could be described by a paraffin naphthenic aromatics (PNA) or a saturated, aromatics, resins (SARA) analysis does not significantly influence the cloud point as discussed by Coutinho and Daridon (2001). The presence of asphaltenes was not proven to have any influence on the cloud point besides becoming crystallization nuclei (Garcia and Carbognani, 2001). Using a model shown to be successful in describing wax formation and cloud points of crudes and distillate fractions (Pauly et al., 2000, 2001; Coutinho and Daridon, 2001; Mirante and Coutinho, 2001; Coutinho et al., 2002), five hydrocarbon mixtures that emulate real crudes in what concerns the main characteristics enounced above (wax content, paraffin distribution, and

Table 1. Oil compositions

Fluid	Total wax content (%)	Mw	Solvent	Paraffin decay (C_{n+1}/C_n)	Heaviest n-alkane
Oil A	15.0	230	C15	0.92	90
Oil B	15.0	230	C15	0.92	50
Oil C	15.0	230	C15	0.88	90
Oil D	15.0	230	C15	0.88	50
Oil E	13.77	230	C15	0.92	50

heaviest paraffin present) are simulated. Compositional information for these mixtures is presented in Table 1. Paraffin distribution and heaviest paraffin present were chosen to be closely related to real oils (Monger-McClure, Tackett, and Merrill, 1999). Simulated results for the wax fraction formed are presented in Figure 1. It is clear that the heaviest paraffin present in the oil has a dramatic effect on the cloud point, and the heavier this is, the more difficult it will be to detect the true cloud point that often will appear at the top of a very long and thin tail.

CLOUD POINT MEASUREMENT TECHNIQUES

Numerous experimental techniques were proposed, patented, and adopted as standards. In fact, looking at the huge number of techniques available, it would be tempting to suppose that cloud points are easily measurable and that adequate methods for their determination are available. The problem with cloud point measurement techniques is that no technique available seems to

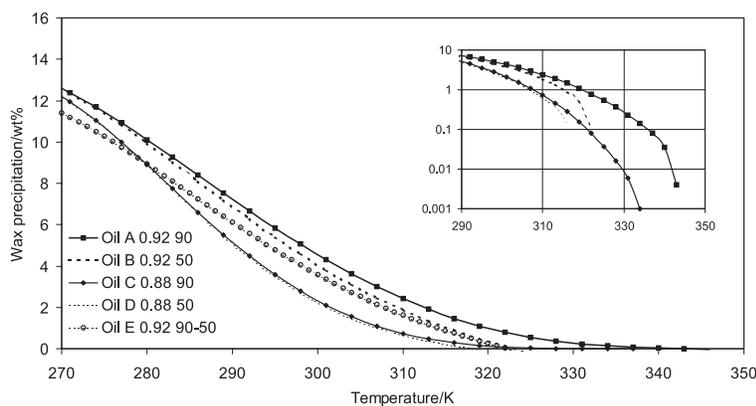


Figure 1. Simulated wax precipitation curves for the oils used in this study. The insert shows the low composition region in semilogarithmic scale.

be able to detect the very first crystal to appear in a representative fluid sample in thermal equilibrium. All techniques will require some amount of solid to be present to produce a detectable signal. Several techniques use temperature-scanning rates that prevent the sample from being in thermal equilibrium, thus adding further error to the measurement. Finally, some techniques produce signals for which interpretation is not straightforward.

ASTM Standard Methods

The ASTM methods for determination of the onset temperature of wax crystallization (D2500 and D3117) rely upon the visual inspection of a 30 mm thick sample to detect crystal formation. This method presents multiple weaknesses in what concerns the cooling rates, temperature measurements, and the subjective judgement of the operator on the cloud point. Even when an automatic optical device replaces the operator, increasing the reproducibility of the measurements, the amount of solids required for a change in appearance of the oil to take place or for a detectable signal to be produced may still be quite important. Besides, these methods can only be used for refined products or clear oils, such as gas condensates, and not black oils. The use of optical devices with other than visible light is discussed below.

DSC

Thermal methods are quite popular for determining the cloud point of petroleum fluids due to the high enthalpies of crystallization of the paraffins. Among these, DSC is the most used. Based on the precipitation curves presented in Figure 1, simulated DSC curves were calculated, and the cloud points were assessed as the crossing point between the tangents to the peak and the baseline (ASTM D4419-96, 1998; Kok et al., 1996). Results are presented in Figure 2a–d. This figure shows how the quality of DSC cloud points is dependent on the paraffin distribution. Comparison between oils A, B and C, D shows that the heavier the higher paraffin present, the longer are the tails and then the further from the true cloud point will be the measurement. For oils with very heavy n-alkanes, such as oils A, C, it will be more difficult to detect the true cloud point, but the cloud point, although with a larger error, is determined for a much lower quantity of solid precipitated than for oils B, D. This result is in agreement with the conclusions of Kok et al. (1996). In all studied cases using DSC, both the errors in the cloud point temperature and the amount of solid required for a change in signal to be detected are important. Simulated DSCs suggest that instead of tangent interception, the deviation from the baseline would be a more precise method to detect solid formation; however, in real DSC measurements, a good baseline may be difficult to obtain, and the deviation from the baseline would be difficult to assess. Moreover, due to its dynamic character, it is not only the crystallization of wax that is responsible for the signal but also the rate of

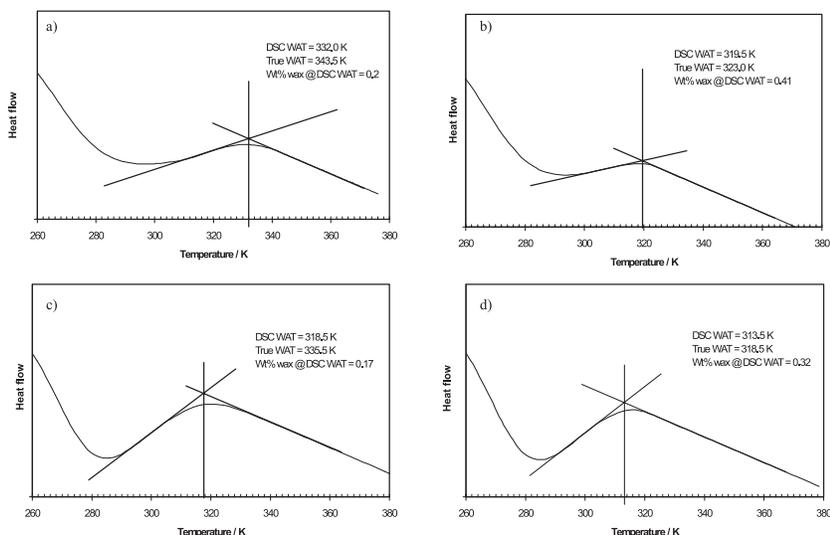


Figure 2. (a) through (d) Simulated DSC thermograms for the oils used in this study.

crystallization. Very low rates of crystallization will be offset by the baseline drifting and noise, or simply will be too difficult to identify, such as in oils A and C. Thus, the quality of the measured cloud points will be very much fluid dependent.

DSC still has the problem of being a dynamic method requiring a temperature-scanning rate to be used that often is far too large for a thermodynamic equilibrium to be achieved, and thus, important supercooling of the sample occurs. Superheating, as discussed below, is less prone to occur, and important differences between wax appearance temperatures (WATs) and wax disappearance temperatures (WDTs) are reported (Rønningsen et al., 1991; Monger-McClure et al., 1999). The differences between WAT and WDT may be due not only to the supercooling effect but also to poor DSC calibration. As shown by Martins and Cruz-Pinto (1999), the failure to calibrate the DSC on cooling and the use of calibrations on heating for measurements on cooling is responsible for many errors on the temperature measurements using a DSC. The low cooling rates required for thermodynamic equilibrium to be achieved cannot be used in DSC, as the signal becomes too weak and the noise of the measurement overshadows the thermal effects (Jiang, Hutchinson, and Imrie, 2001). The cloud point comparison using different techniques presented in Table 2 gives a good indication of the limitation of this technique, although it is interesting to remark that an experienced user of DSC can obtain cloud points by DSC higher than those by cross-polarization microscopy (CPM), as reported by Kok et al. (1996).

The application of temperature modulated differential scanning calorimetry (TMDSC) to the measurement of WATs was done by Jiang et al. (2001), but the results reported do not seem to improve over conventional DSC.

Table 2. Comparison of cloud point detection techniques. Average temperature differences and standard deviations (*in italics*) are reported between the technique on the line and the technique on the column

	Viscosity	DSC	Light transmittance	Filter plugging	ASTM 2500	Acoustic	FTIR
CPM	6.0 (4.7) ^a , 13.2 (8.4) ^c , 5.4 (6.9) ⁱ , 0.7 (3.9) ^j	9.0 (6.9) ^a , 14.6 (9.7) ^c , 1.3 (3.1) ^e , 6.0 (7.8) ⁱ , -1.2 (5.2) ^j	10.4 (0.6) ^b	6.1 (4.7) ^d , 0.1 (3.1) ^e	-4.4 (-) ^f		-1.8 (3.6) ^g
Viscosity		3.0 (5.6) ^a , 1.0 (3.6) ^c , 0.7 (0.9) ⁱ , 2.9 (4.0) ^h , -1.9 (7.2) ^j					
DSC				-1.2 (2.5) ^e	-5.6 (-) ^f , -5 (8.9) ^j , -3.8 ^k 2.8 (-) ^f		-3.1 (2.9) ^e
Light transmittance							
Filter plugging							
ASTM 2500							-1.6 (3.4) ^e
Acoustic							2.2 (0.6) ^g
FTIR							

^aRønningesen et al. (1991); ^bHammami and Raines (1997); ^cErickson et al. (1993); ^dRønningesen et al. (1997); ^eMonger-McClure et al. (1999); ^fKruka et al. (1995); ^gSivaraman et al. (1998); ^hElsarkawy et al. (2000); ⁱCazaux et al. (1998); ^jNoel (1972); ^kClaudy et al. (1986); ^lKok et al. (1996).

Viscosity

Determination of cloud points through viscosity changes is a technique used by several authors (Rønningsen et al., 1991; Erickson, Niesen, and Brown, 1993). Due to the formation of wax crystals in suspension, the fluid develops a non-Newtonian behavior with temperature. Newtonian fluids follow an exponential temperature dependence of the Arrhenius type known as the Andrade equation:

$$\eta = \eta_o \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

The cloud point could thus be detected by a deviation of the experimental data from linearity in a $\ln \eta$ versus $1/T$ plot.

The dependence of viscosity on the amount of solids in dilute suspensions is given by the Einstein equation:

$$\eta = \eta_f(1 + 2.5\Phi) \quad (2)$$

In the following analysis, the crystals are assumed to be spherical, and because the density of the solid wax is not much different from the fluid, the volume fraction is taken to be similar to the mass fraction. If a deviation of 2.5% from the Newtonian fluid viscosity is required to detect a non-Newtonian behavior, and this is a conservative estimate given the exponential dependence of the viscosity on the temperature, this corresponds to a mass fraction of crystals of 1%. This value of solids is often enough to produce a pour point and not the cloud point (Claudy et al., 1993; Coutinho et al., 2002, 2003; da Silva and Coutinho, 2004).

The viscosity cloud point cannot be detected within the dilute region. Only when the volume fraction of crystals is large enough for the viscosity to increase no longer linearly but exponentially will a change in signal be large enough to be detected. The critical volume fraction that separates the dilute and semidilute regions is as follows (Cazaux, Barrs, and Bruey, 1998):

$$\Phi = \left(\frac{R}{L}\right)^2 \quad (3)$$

Although no exhaustive study has ever been presented in the literature, the evidence available from microphotographs indicates that the paraffin crystals have axis ratios of about 15–20. This would mean critical volume fractions of 0.3–0.5%. This value is in agreement with the values proposed by Rønningsen for the mass fraction of paraffins at the viscosity cloud point (Rønningsen et al., 1991). This amount of solids may seem small, but even very small amounts of solids can represent serious production problems. With only 0.5 wt% solids detected in the laboratory, more than 600 kg of solid phase will be formed in the field for every 1000 bbl produced (Thomas and Bennion, 1999). Unlike DSC, this technique seems to detect cloud points

using a coherent solid volume fraction. Although the measured cloud point would be far from the true cloud point, it would present a lower error for oils with paraffin distributions similar to oils B, D than to oils A, C.

Filter Plugging

This technique is based on the continuous monitoring of the pressure drop across a filter while the oil flows through a temperature-controlled flow-loop. It has a number of interesting features, because it is applicable to both live and dead oils at low or high pressures, unlike most other techniques that are restricted to dead oils at low pressures. Filters with a $0.5 \mu\text{m}$ size are commonly used along with very low flow rates (inferior to $0.5 \text{ cm}^3/\text{min}$) to minimize the shear stress at the filter promoting the deposition and the pressure buildup.

Using the Carman–Kozeny equation to describe the flow in porous media (Foust et al., 1980), it is possible to show that the pressure drop across a filter is proportional to the cube of the inverse of the porosity, ε^{-3} , and thus to the cube of the solids concentration, w_s^3 :

$$\Delta P \propto \varepsilon^{-3} \propto w_s^3. \quad (4)$$

Figure 3 shows the pressure drop with the temperature for oils A through D. The exact cloud point temperature would be dependent on the accuracy of the pressure measurements, but it is clear that the temperature identified would be not far from 320 K for oil A or even lower, this is to say an amount of solid of 1%, probably closer to the pour point than the cloud point, as mentioned before.

A significant quantity of crystals with size larger than $0.5 \mu\text{m}$ must develop before the filter plugs. Filter plugging cloud points must thus be

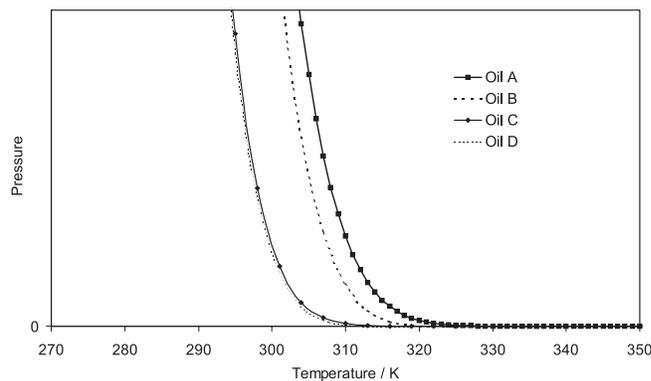


Figure 3. Pressure drop across a filter plugged by the oils used in this study as a function of the temperature.

dependent on the flow rate used. The higher the flow rate, the more difficult it will be for large particles to form and to deposit in the filter, as the shear stress produced by the flow will contribute to reducing the size of the particles, thereby increasing the quantity of solid required to plug the filter and, thus, reducing the measured cloud point.

Light Transmission Measurements

Multiple light transmission techniques were proposed to detect the cloud point. It minimizes the uncertainty associated with the visual inspection techniques and, depending on the light source used, can be applied, unlike ASTM standards, to black oils. It measures the variation on light transmission due to the appearance of crystals as the sample is cooled. It seems to improve the results over the visual inspection technique (Kruka, Cadena, and Long, 1995), but an important quantity of crystals must be required to produce a detectable reduction on the light transmitted. Hammami and Raines (1997) reported that differences on the order of 10 K between light transmission and CPM are found. McMullin et al. (1999) remark that “the drop in transmission of laser light through a sample does not actually measure the wax appearance temperature but rather the initiation of the growth stage” (p. 1775).

The simulation of a light transmission curve as was done to DSC and filter plugging is too complex to be attempted. At the beginning of the precipitation, crystals can be assumed independent and small enough for Beer’s law to be used in the description of the attenuation of light due to scattering. However, as temperature drops, there is an increase of not only the crystal number but also of the crystal size and shape and aggregation of crystals into a three-dimensional (3D) network. The extinction coefficient must then also change due to these factors, and quickly, the crystals become too large compared to the wave length, so that Beer’s law is no longer valid. The shapes of the curves presented by Hammami and Raines (1997) do not show the exponential decay of Beer’s law, but a sudden drop on the light transmitted and the photomicrographs presented by Hammami indicate that the size of particles is more than 20 times the wavelength of the radiation used. The drop in signal will thus be produced by large crystal aggregates and not the small crystal particles leading to important cloud point detection errors.

Because the light transmittance can be measured across a high-pressure cell, this method was used to measure high-pressure cloud points.

Acoustic Resonance Techniques

Acoustic resonance techniques for the determination of the appearance of a solid phase in oils were proposed (Ruffier-Meray et al., 1993; Colgate and Sivaraman, 1996; Sivaraman, Thomas, and Bennion, 1999; Carrier et al., 2000). These techniques have not yet been extensively compared against other conventional techniques, and the response to the presence of a new solid phase

appears to be of some complexity, requiring some experience to be able to distinguish between the different signals (Sivaraman et al., 1999). Like its precedent, this method was extended to high pressures and to the analysis of live oils. The results available indicating that it may be more sensitive than infrared (IR) techniques (Sivaraman et al., 1999) are too scarce. Our personal experience with this technique for wax appearance temperatures is not favorable. The interpretation of the signal output is not straightforward, the measurements do not seem to be reproducible, and large fractions of solid are required for a detectable change in the signal to occur due to the very small size of the crystals comparing to the wavelengths used.

IR Techniques

The cloud points are measured by detection of the increase in energy scattering due to wax solidification. The wavelengths used may vary with the approach, and live oils at high pressure can be studied with this technique. Although in a comparison of cloud point measurement techniques Fourier transform infrared (FTIR) analysis consistently produced the most conservative values (Monger-McClure et al., 1999), even in comparison to CPM it would be going too far to say that this is the most sensitive technique for cloud point detection. Their microscopy values seem to be underestimated when compared to the calorimetric values. The most extensive application of FTIR to measurement of wax formation in oils was developed by Roehner and Hanson (2001). The determination of the cloud point is obtained by identification of a break on the absorbance of the $735\text{--}715\text{ cm}^{-1}$ peak area with temperature. The problem, akin to what happens with DSC, is the identification of the linear regions to obtain the cloud point by intersection of the two lines. For model systems, when a large amount of solid forms in a narrow temperature range below the cloud point, it is easy to identify the cloud point and the limits of the linear region. This may be far more complex for fluids with long n-alkane distributions and with low total n-alkane content where the precipitation of the solid is gradual and the departure from the linear baseline is subtle and difficult to detect. In particular, for the TAPS Mix reported by Roehner and Hanson (2001), it is clear that the liquid baseline is dependent on the number of points used to define it. The choice of the absorbance points and the regression used significantly influences the cloud point measured. As discussed above for other techniques, for oils with very small amounts of solid forming just below the cloud point, the effect of the solid formation on the FTIR spectra is within the sensitivity of the experimental method.

CPM

CPM is one of the most widely used cloud point techniques and one that often seems to give the most conservative results for cloud point measurements when carefully applied. It is based on the capacity that wax crystals, unlike liquid hydrocarbons, have to rotate the plane of polarization of transmitted

polarized light. The limit of detection is a crystal with a size between 0.5 and 1 μm depending on the magnification used. It should be more accurate than the filter plugging technique, because it can detect particles with a similar size but in much less quantity, as a single crystal is enough to be detected. CPM seems to be sensitive to the thickness of the film used (Rønningsen et al., 1991), and different authors have been using different approaches—from no spacer as in Monger-McClure et al. (1999) to 50 μm of Rønningsen et al. (1991) and the 150 μm of Cazaux et al. (1998)—which may contribute to uncertainties on the evaluation of the technique. Moreover, given the very small sample volume used, the sample may not be representative, and the restricted field view may also make it difficult to detect the first crystals. Although typically used for low pressures, this technique has been extended to high pressures using a high-pressure microscope stage (Brown, Niesen, and Erickson, 1994; Daridon, Pauly, and Milhet, 2002).

Recent results on the morphology of paraffin crystals in crude oils using transmission electron microscopy (Kané et al., 2003) indicate that the first crystals forming under quiescent conditions have sizes of just 50 nm in length and a thickness of about 2–3 nm with aggregates forming with a size of 150 nm. Under shear, the size of individual crystals is about 20–30 nm, and aggregates have no more than 100 nm. These are well below the detection limit of the CPM technique. The sizes of crystals forming on oils are much smaller than in synthetic mixtures or refined products, such as diesels. Although some of this can be attributed to the complexity of the mixture crystallizing, as discussed by Anderson et al. (2001), this effect alone cannot explain the extremely small size of the crystals. This must be due to the presence of natural crystal growth inhibitors present on the oil that prevent the growth of the crystals. This may also explain the poor behavior of CPM for some oils, although, in general, it seems to be one of the most conservative techniques for measuring cloud points.

A number of other methods based on densitometry (Kruka et al., 1995), x-ray (Karacan, Demiral, and Kok, 2000) and other techniques have been reported or patented. In general, all the cloud point methods suffer from limitations akin to those discussed above (Kruka et al., 1995), either the crystals must be large or a large quantity of crystals is required.

TESTING MEASUREMENT TECHNIQUES USING N-ALKANE SOLUTIONS

Often, techniques proposed for cloud point detection are tested using solutions of one or a few n-alkanes to emulate the wax formation in real fluids (Majeed, Bringedal, and Overa, 1990; Ruffier-Meray et al., 1993; Monger-McClure et al., 1999). This approach is not acceptable, because cloud point detection techniques often rely on the rate of appearance of crystals or on the quantity of solid to detect a new phase. Most techniques perform very well for high rates of precipitation and when important quantities of solid form just below

the cloud point. These conditions are easily met by simple synthetic solutions of n-alkanes, but as shown in Figure 1, although waxes are constituted by n-alkanes due to the long paraffin distribution, they do not behave in this way, and thus, the ability of a technique to detect n-alkane crystallization on a synthetic mixture is by no means a guarantee of success in the detection of cloud points of real oils. Moreover, the paraffin crystal size distribution is strongly influenced by the complexity of the alkane mixture, as shown by Anderson et al. (2001). Methods that rely on the size of the wax crystals to detect the cloud point will report good results for simple mixtures for which large crystals may grow but not necessarily for complex mixtures for which the crystals will have much smaller dimensions.

EFFECT OF THERMAL HISTORY AND SCANNING RATES

The simulated curves used in the previous analysis are the curves for equilibrium conditions, and it was shown that, even under equilibrium, measured cloud point temperatures may be far from the true cloud point. The generality of the essays are, however, done not under static conditions but under dynamic conditions. In some cases, the temperature scanning rates [0.1–0.5 K/min (Hammami and Raines, 1997; Sivaraman et al., 1999; Monger-McClure et al., 1999)] are low enough to consider that deviations to equilibrium are negligible if the sample cell is small enough. Often, very large scanning rates [5–10 K/min (Rønningsen et al., 1991; Erickson et al., 1993; McMullin et al., 1999)] are used, leading to considerable superheating/cooling effects. An empirical correction in cloud point temperatures equal to the cooling rate in K/min has been used (Monger-McClure et al., 1999), but the results reported by Rønningsen et al. (1991) indicate that this effect may be much more important. Moreover, most of these techniques use cooling cycles rather than heating cycles in the determination of the cloud point, and sometimes the cooling rate is not constant, such as in ASTM D2500. Due to difficulties associated with crystal growth, the detection of crystal formation in cooling cycles is far less rigorous than under a heating cycle. Determination of the melting of the last crystal is easier and more reproducible than the formation of the first crystal. Evidence for the differences between WATs and WDTs using DSC (circa 15 K) and microscopy (circa 10 K) clearly express this problem often associated with important supercooling effects due to the large cooling rates used. Interestingly, data by Rønningsen et al. (1991) on WAT and WDT differences support the analysis of the cloud points' dependence on the paraffin distribution done in this work. It would be reasonable to expect that faster paraffin decays, with the long precipitation tails, would have more difficulties in crystallizing and would thus produce larger WAT–WDT differences. This is what the data by Rønningsen presented in Figure 4 reveals. Recently, Bhat and Mehrotra (2004) established the WDT as the thermodynamically variable, showing this to be the appropriate measure for the liquidus temperature of wax–solvent mixtures or crudes.

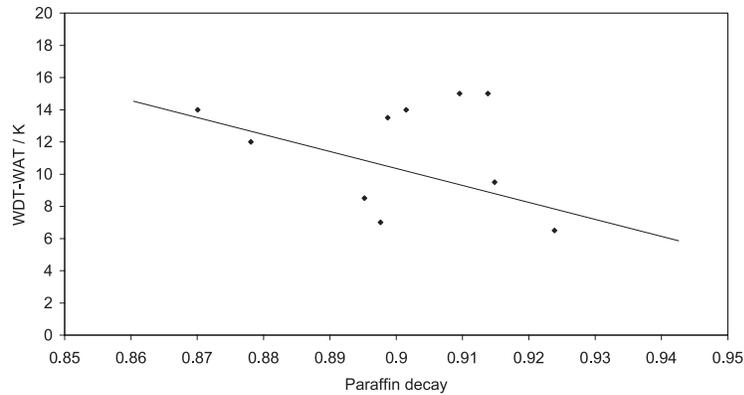


Figure 4. Dependence on the paraffin decay of the difference between the wax disappearance and appearance temperatures after Rønningsen et al. (1991).

EFFECT OF CRUDE OIL SAMPLING, SAMPLE HANDLING, AND TREATMENT

The analysis of the cloud point measurement techniques reveals the importance of the paraffin distribution, and the limits of this distribution on the wax formation. Noticing that most measured cloud points of waxy crudes (Rønningsen et al., 1991; Monger-McClure et al., 1999) are around 315 K, and that, as this study has shown, true cloud points are probably even larger, it is easy to realize how oil sampling, sample handling, and sample pretreatment may have a huge influence on the measured data. Most of the published data are measured properties of crude oils collected at the separator. These types of fluids may not be representative of downhole fluids if the true cloud point temperatures are above those maintained at the separators (i.e., the heaviest paraffin molecules would likely drop out or stick to the production tubing and not reach the separator as the temperature cools from the well bore to the well head and eventually the separator). Oil A will be taken as an example. If during sampling this oil was cooled to a temperature of 320 K, it would have lost all the paraffins above C50 turning into oil E. The resulting oil would have a completely different cloud point and precipitation curve, as shown in Figure 1. Loss of this material would hardly be detected. The reduction in total wax content of about 1% is within the accuracy of experimental techniques. Results obtained from this sample would be completely meaningless in what concerns the identification of depth of deposition on the field or amount of precipitated wax. Such a loss of heavy material can easily occur at any step given the cloud point temperatures of crudes being well above room temperature. For obtaining a representative sample and meaningful measurements, utmost care must be taken during sampling, sample handling, and measuring so as not to lose any heavy material. This analysis is done in accordance with the recommendations of Monger-McClure et al. (1999).

MODELING OF CLOUD POINTS

A number of models were reported in the literature to describe the cloud point of oils (Coutinho et al., 2004). They are usually based on the thermodynamic description of the solid–liquid equilibrium of heavy paraffins. Although some claim to be predictive, generally, these models are fitted to experimental data, typically to cloud points that are the most commonly available data for the low-temperature behavior of oils. Given the uncertainties associated with the cloud point measurements discussed above, it is not surprising that models fitted to experimental cloud points cannot produce an adequate description of the wax precipitation in the oil. As discussed above, an adequate description of the wax formation of an oil by a thermodynamic model requires a detailed description of the oil composition in what concerns the paraffins present: total amount of paraffins, paraffin distribution, and largest paraffin present in the oil in a concentration above its solubility threshold. Figure 1 clearly shows the effect of these three quantities on the wax precipitation curves. If for large paraffin decays (C_{n+1}/C_n below 0.9) the heaviest paraffin influences only the cloud point but not significantly the wax precipitation curve for small paraffin decays (C_{n+1}/C_n above 0.9), the knowledge of the large paraffin changes not only the cloud point but also the precipitation curve. A detailed composition analysis is not only a tool for the analysis of the cloud point reliability along the lines discussed above but is also a must for an adequate modeling of wax formation and of wax deposition from live or dead oils.

That paraffin distributions have such a dramatic effect on cloud point measurements and modeling is well illustrated by a counterexample. Although cloud points for crudes are quite difficult to measure and predict, cloud points for refined products, such as jet fuels or diesels, have their cloud points easily detected, and their modeling is easy and quite reliable (Coutinho, 2000; Mirante and Coutinho, 2001). Due to the narrow paraffin distributions on these fluids and very large paraffin decays (typically of about 0.5), the solubility threshold of heavy paraffins is quickly attained, leading to a fairly well-defined and well-behaved system.

CONCLUSIONS

The paraffin distribution on crude oils and its breadth has a dramatic effect on wax formation and, in particular, on detection of cloud points. Oils with paraffin distributions leading to the precipitation of large quantities of solids just below the cloud point can have their cloud points easily identified, and most techniques are adequate for their measurement. Unfortunately, most oils have very low precipitation rates close to the cloud point, making difficult a reliable measurement of the cloud point. It was shown here that all the currently available techniques present shortcomings that prevent the detection of the true cloud point, and that the incertitude of the measurements is as much oil as technique dependent, as the error is not only associated with the

technique but also with the oil composition. Due to the poor reliability of the cloud point measurements, they should not be considered alone as a good indicator of the hazardous potential of a crude oil. Nevertheless, a detailed compositional analysis, when available, can provide insight on the accuracy and reliability of the cloud points measured using different techniques, and other information can complement or replace cloud points in the evaluation of the wax formation potential of an oil with advantages as discussed elsewhere (Hammami et al., 2003).

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