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A new experimental setup for the liquid–solid phase transition determination in crude oils under high pressure conditions

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Abstract

A high pressure apparatus based on two sapphire windows high pressure cell coupled with a detection system of the reflected and refracted light intensities coming from a laser beam was designed to determine the phase transitions by the measurement of the light intensity change. The setup was used to measure the wax disappearance temperature under pressure up to 100 MPa in pure component, synthetic complex mixtures made up of distributions of *n*-paraffins ranging from *n*-C_{20} to *n*-C_{42}. Finally a real stabilized condensate was successfully investigated and the sensitivity of the detection system was demonstrated on a dark crude oil.

Keywords: Solid–liquid equilibrium; Pressure; Wax

1. Introduction

Among all the challenges that the oil industry have been facing for many years, the prediction of solid formation is one of the major. Production, transportation and treatment facilities of most of the produced fields should be designed to allow preventive or curative processing in the event of appearance of organic deposits. The fitting of those designs with the real operating situations clearly have a great impact on the rate of profit.

A number of experimental techniques for predicting the onset of crystallisation of wax on synthetic and real systems under pressure have been proposed in the literature. It is possible to classify them in two main categories: the analytic approach and the synthetic ones. A non exhaustive lists of these experimental procedures can be briefly presented as a state of the art.

The calorimetric techniques as the DSC method (Differential Scanning Calorimetry) are some of the most employed to describe liquid–solid equilibrium in paraffinic systems because of the important values of their crystallisation enthalpies [1–3]. Some authors have the conviction that theses techniques applied for crude oils can provided better results than the other ones [4]. In fact the pressurization of the setup, the shape of the distribution of *n*-alkanes in crude oils or the potential presence of metastable phase [5] can make the results of the experimentation inaccurate [6].

Among the other procedures some of them are based on a visual detection of the Wax Appearance Temperature (WAT) in crude oils, we can notice the ASTM standards D2500 and D3117 [7] but also the complete visibility high pressure cell developed in our laboratory [8,9]. Important drawbacks can be cited as the non homogenisation of the system, the non control of the cooling speed and above all the important volume of the cell making the study of opaque fluids impossible [10].

To improve the detection of the crystals it is possible to use an optical setup to replace the human operator [7,11]. The solid detection system is then based on light transmittance through an optical cell. The crystallisation of the wax

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induces a huge reduction of the light intensity. Nevertheless even if it is possible to throw of disadvantage related to the opacity, the problem of the small size of the crystals remains. In the same category, the techniques of Cross Polarization Microscopy (CPM) are usually used to measure the liquid–solid transition at atmospheric pressure [12] and is considered as one of the most accurate approach in the investigation of liquid–solid transition [6,13,14]. Recently this setup has been extended with success under high pressure [15]. Even if the volume of the sample can be decreased at its minimum the opacity encountered in real crudes stays a major problem for the determination of wax disappearance temperature under pressure.

Mechanical dynamic procedures can also be considered for determining the presence of solids in a fluid. They are based on a ''Filter Plugging'' leading to a strong change of the differential pressure ΔP measured at both sides of the filter [14] or simply based on a visual observation of the deposit on the surface of the filter [16] as reported for asphaltenic systems for example. When applied for the WDT determination those techniques can only be used during a cooling procedure meaning that the subcooling effects which are very important in such dissymmetric systems can not be avoided.

Many other approaches like viscosity [7,10] and acoustic measurements [17], FT-IR spectroscopy [18], can be considered for the determination of the liquid–solid phase equilibrium at atmospheric pressure or under high pressure conditions. But the majority leads to important uncertainties due to the fact that they are unable to detect correctly the disappearance of the last crystal (WDT) or the appearance of the first one (WAT) for the following reasons:

(i) the amount of solid just below the WDT is very small;
(ii) in real fluids the size of the crystal is particularly small (<0.1 μm);
(iii) the high opacity of the system.

Then despite the economical tasks, few precise data have been reported in the open literature due to the limitations of most of the techniques. Following the investigations conduced in our group on organic deposit characterization under high pressure conditions, we have developed a new equipment allowing phase transition detection in crude oils and derivatives.

The experimental setup is able to work over the pressure interval 0.1–100 MPa in the temperature range from 243 to 373 K, and comprises an apparatus for the emission–reception of a laser beam used with a two sapphire windows high pressure cell connected to a manual high pressure pump. A detector is placed in front of each window and they are used to monitor the intensity of the reflected and refracted light from the laser (1.3 mW, 635 nm). In order to study dark oils, the thickness of the fluid confined in the optical cell is reduced to 1 mm. Results for synthetic mixtures and diesel obtained with this equipment are compared to those already obtained [19,20] with a high pressure microscope and reveals excellent agreement. The influence of the pressure on the wax disappearance temperature are also reported and analyzed up to 100 MPa for paraffinic crudes.

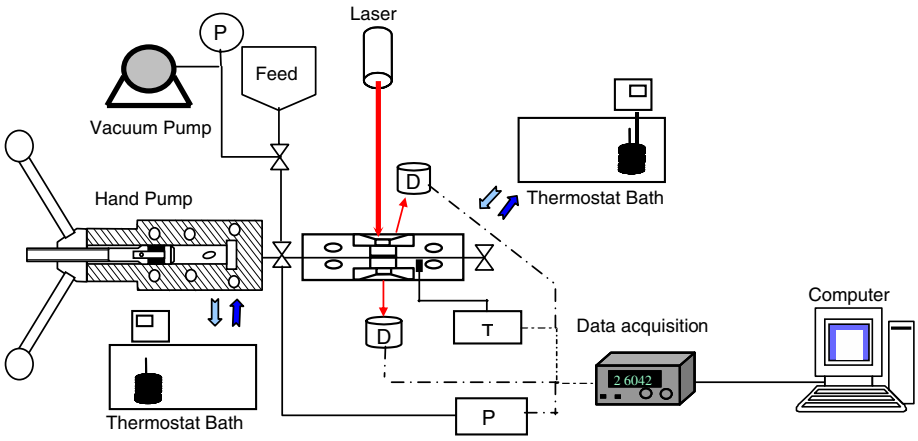
2. Experimental device

The experimental apparatus is composed of a high pressure cell made up of a stainless steel autoclave block in which two transparent sapphire windows are positioned face to face. The geometric characteristics chosen for this cell offer a useful volume of 30 mm^3 and make possible to carry out measurements at pressures up to 100 MPa over a temperature range of between 243 K and 373 K. As previously mentioned, in order to study dark colored oils by light transmission, the thickness of the fluid confined in the optical cell was reduced to 1 mm. The temperature of the cell was controlled by the flow of a heat-carrying fluid, regulated with a temperature stability of 0.1 K by a thermostat bath (Huber ministat CC1), in four flow lines embedded in the metal block of the cell. The temperature was measured with a calibrated Pt 100 probe (0.1 K), inserted inside the cell close to the sample. The fluid was pressurized with a high pressure pump made up of a stainless steel autoclave cylinder in which a mobile piston can move in such a way as to transfer the pressure to the fluid. The maximum volume of the high pressure pump is equal to 25 cc. During the run, the hand pump was thermo regulated above the maximum solid–liquid transition temperature to preserve the homogeneity of the system (Huber Polystat CC1). In order to avoid solid formations in the connecting lines these were heated with an electrical heating ribbon. The pressure was measured with a Keller pressure gauge PA-33X, calibrated within the range 0–100 MPa with a dead-weight balance Bunderberg, giving an uncertainty better than 0.02 MPa over the experimental range. Fig. 1 shows a schematic representation of the experimental setup whereas Fig. 2 concerns a description of the high pressure cell.

The technique used for the WDT determination is based on the measurement of light intensity change during phase transition. This approach has been successfully applied for synthetic systems in a large range of pressure as previously reported by [21–23].

Two detectors placed at both sides of the double sapphire windows cell were used to monitor reflected and refracted light intensities. The incident light was emitted by a diode laser MC 6305 (635 nm wavelength and 1.3 mW power supplied by Melles Griot) temperature control to preserve a constant wavelength and power during an all day experiment. Incident, reflected and refracted lights are carried to the cell or to the detectors by optical fibers, 1 m length and 1 mm of diameter.

The detectors were home made detectors and comprise a BPW21 silicon photodiode (Siemens) especially suitable for applications from 350 to 820 nm. Delivered signals are amplified using high precision compounds, in order to



T- Temperature sensor ; P- Pressure transducer ; D- detector

Fig. 1. Schematic representation of the experimental setup.

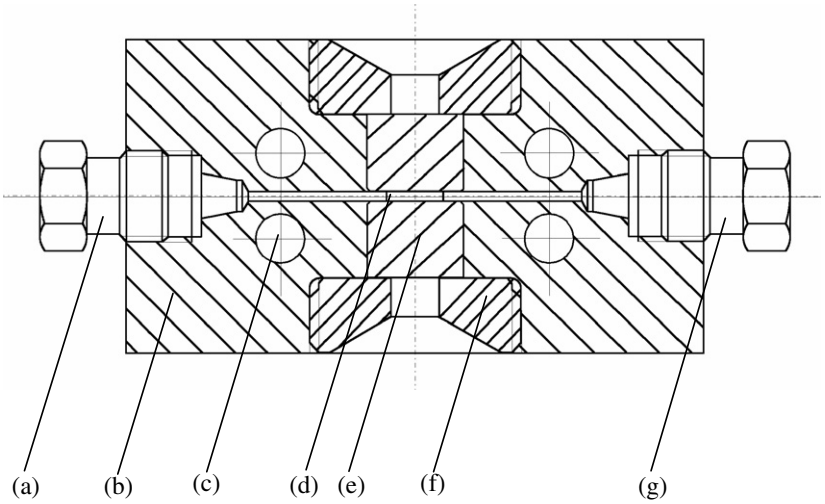


Fig. 2. Scheme of the high pressure cell: (a) fluid inlet; (b) high pressure block; (c) heat carrying flow line; (d) fluid sample; (e) sapphire window; (f) plug with a conic orifice; (g) fluid inlet.

avoid voltage shift due to room temperature changes. They are calibrated to deliver 8 V when directly illuminated by the laser's light. Reflected and refracted light intensities as well as pressure and temperature values are acquired through a data acquisition card with a PC.

3. Experimental procedure

Prior to any study, a high vacuum was made in the cell, in the pump and in the connecting lines using a vacuum pump (Leybolg Trivac D 4B, 10^{-3} Pa). Once this preliminary operation was done, the distance between sensors and windows was adjusted for each sample, because it has been demonstrated [24] that part is essential to determine the sensitivity and the accuracy of the setup. The detectors were positioned in order to give a collected intensity in the range from 5 to 6 V.

To illustrate how the fluid solid disappearance temperature is determined from experimental curves, Fig. 3 shows a representation of reflected light intensity as a function of temperature, at constant pressure, during a heating process.

The first part of the reflected intensity curve is almost flat traducing very small changes of medium refractive index with temperature. Part II displays the phase transition from a solid phase to the homogenous fluid phase. The third part starts when the signal reaches a plateau, also related to small changes attributed to the temperature effect on the refractive index of an homogenous liquid. Thus, a calculated line is adjusted to the linear segment representative of the third part. To determine the melting temperature the following criterion is then applied:

$$\left|\frac{I_{\mathrm{exp}} - I_{\mathrm{calc}}}{I_{\mathrm{calc}}}\right| > 1\%,$$

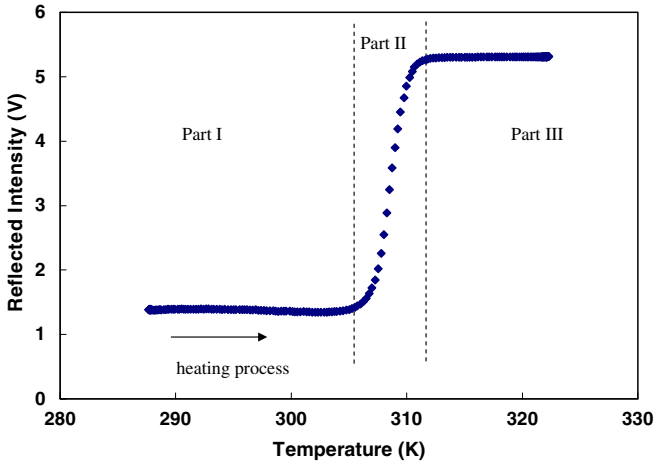


Fig. 3. Representation of reflected light intensity as a function of temperature, at constant pressure, during a heating process.

where I_{calc} and I_{exp} are, respectively, the calculated intensity and the experimental one.

The temperature obtained following the proposed procedure is perfectly matching that observed visually for the disappearance of the last crystal in transparent systems.

4. Results and discussion

4.1. Chemicals

Concerning the pure components, both octadecane and tetradecane used are from Aldrich Company and have a mole fraction purity of 0.99. The paraffin wax was purchased from Prolabo Company. It is a commercial paraffin called Prolabo 52–54 °C, composed by *n*-alkane ranging from C_{20} to C_{42} for which the C_n distribution was determined by gas chromatography and mass spectrometer (Table 1).

4.2. Pure component tests

Before any attempt at experimental investigation on a complex mixture for which there is no data in the literature, the reliability of measurements were checked on a pure substance. With this view in mind, a set of experiments were carried out on octadecane, a substance for which several references are available on the literature [25–27]. Measurements were carried out from atmospheric pressure to 80 MPa every 20 MPa so as to describe the phase boundary between the homogeneous liquid phase and the solid–liquid phase domain with no less than six points. This very simple system allows us to determine the best experimental procedure concerning in particular the influence of the speed of heating. Due to important subcooling effects the phase change was not determined by measuring the wax appearance conditions but by measuring the conditions of disappearance of the last crystals in the system. Fig. 4 illustrates

Table 1
Composition (mass%) of the system studied and of the wax Prolabo

	Feed composition (mass%)
Solvent	83.66
Wax content	6.34
Composition of the wax	
n-C_{20}	0.05
n-C_{21}	0.59
n-C_{22}	3.74
n-C_{23}	10.81
n-C_{24}	17.68
n-C_{25}	16.79
n-C_{26}	13.95
n-C_{27}	9.3
n-C_{28}	6.93
n-C_{29}	5.15
n-C_{30}	3.86
n-C_{31}	2.59
n-C_{32}	1.19
n-C_{33}	0.47
n-C_{34}	0.22
n-C_{35}	0.12
n-C_{36}	0.08
n-C_{37}	0.05
n-C_{38}	0.04
n-C_{39}	0.03
n-C_{40}	0.02
n-C_{41}	0.02
n-C_{42}	0.01
PNA[a]	6.32

[a] Paraffinic (nonlinear), Naphtenic and Aromatic.

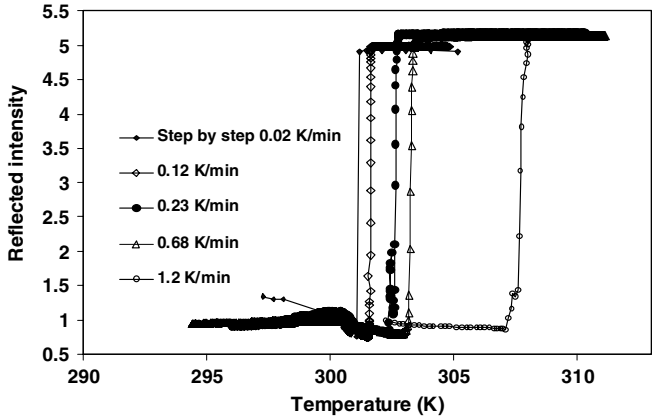


Fig. 4. Influence of the speed of heating on the solid–liquid phase transition of octadecane at atmospheric pressure.

the speed of heating influence demonstrating a significant difference on the wax disappearance temperature observed between data sets. Then the selected procedure follows the different steps:

- Heat at 0.3 K per minute to get roughly the wax disappearance temperature,
- Reduce the heating power of the regulator and then operate a step-by-step procedure in which the speed of heating is less than 0.02 K per minute.

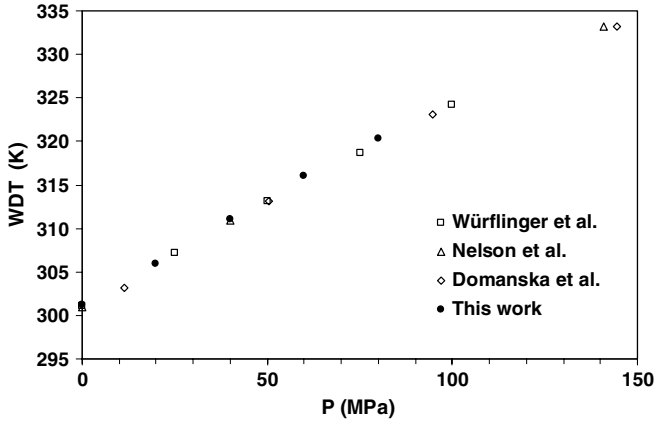


Fig. 5. Melting temperature of octadecane: (△) from [25], (□) from [26], (◇) from [27] and (•) from our work.

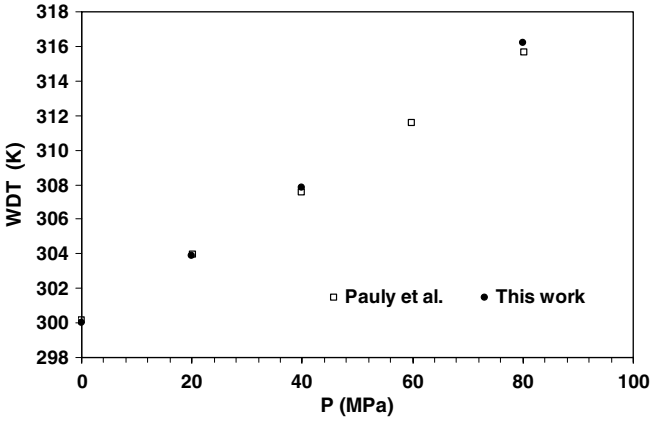


Fig. 7. Comparison of the wax disappearance temperature of the synthetic system tetradecane + wax distribution (C_{20}–C_{42}) with the data published by Pauly et al. [29].

Results are plotted in Fig. 5 on which the experimental points representing values from the literature [25–27] have also been added. Comparison of our measurements under higher pressure with those already published in the literature also revealed a very good agreement.

4.3. Complex synthetic systems

To study the influence of the components number on the formation of waxy solid phase, the wax disappearance temperature was determined as a function of pressure in a synthetic complex system tetradesane + (multiparaffinic commercial wax ranging from C_{20} to C_{42}) already investigated both at atmospheric conditions [28] and under high pressure [29]. The composition of the studied mixture is detailed in Table 1.

The experimental procedure used was described in the previous item. Fig. 6 represents the reflected intensity versus the temperature. When compared to the pure component the signal break appears to be less strongly marked. Actually this behavior can be explained by considering that the melting of mixture does not take place at constant T and P. It is then possible to detect from the obtained signal the beginning and the ending of the melting of the system.

In Fig. 7 the experimental wax disappearance temperature points shows a good fit with experimental points obtained from a high pressure microscopy [29].

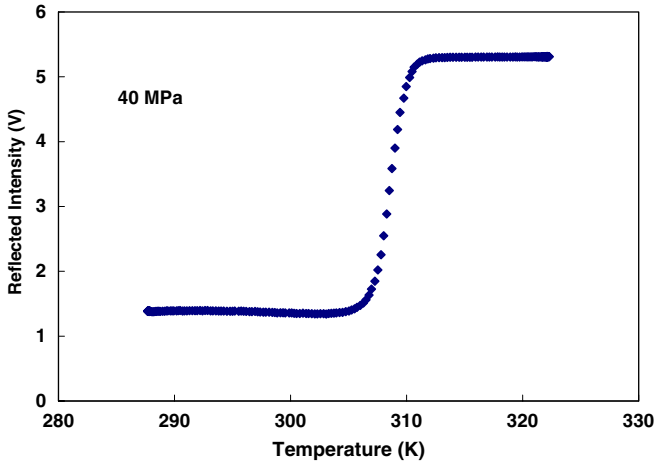


Fig. 6. Reflected intensity versus temperature for synthetic wax at 40 MPa.

4.4. Real fluids

Both of the previous systems presented are synthetic model systems. It has already shown that the size of crystals are more important in model systems than in real crude oil even if this mixture are made of a large distribution of *n*-alkanes. Then the measurement of liquid–solid transition is fairly more simple and can be obtained accurately with most of the conventional techniques. The real problems concern the investigation of real fluid due to two different aspects. The size of the crystal which does not exceed in most of the case 0.1 μm [30] as well as the high opacity induced a huge difficulty to detect the disappearance or presence of waxy crystals in the solution.

Then to validate our experimental technique a real stabilized condensate was tested. Most of the conventional techniques do not give any accurate results probably because crystal size is too small to detect appearance of the first crystal or disappearance of the last one. The analysis of Fig. 8 shows clearly the sensitivity of our detection technique even when the crystal size does not exceed 0.1 μm. Then the set of data obtained on this system is compared in Fig. 9 to the one from high pressure microscopy technique. The difference between both set of melting temperature does not exceed 0.5 K in all the pressure range.

Finally our experiment has been tested on a dark heavy oil for which no accurate information are available due to the high difficulties to study this oil:

- Low % paraffin content (<5%).
- High opacity.
- Small crystal size.

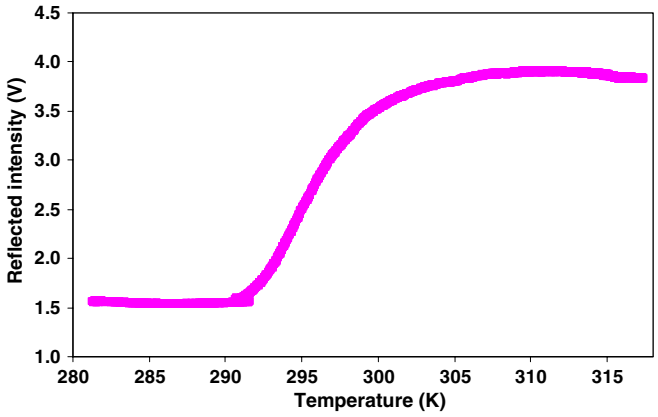


Fig. 8. Influence of the temperature on the reflected intensity with a stabilized condensate at 40 MPa.

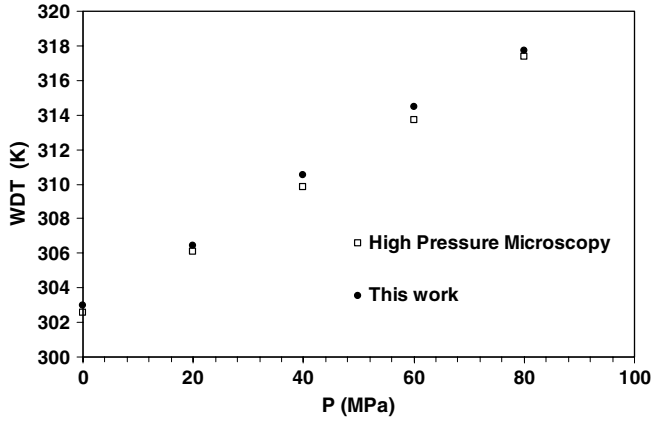


Fig. 9. Influence of the pressure on the WDT of the stabilized condensate.

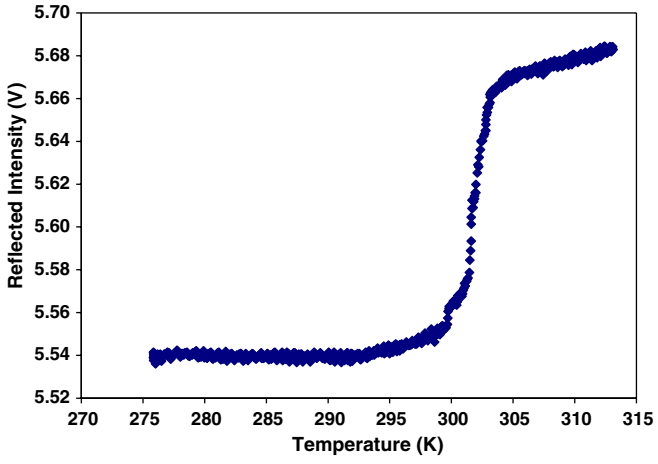


Fig. 10. Reflected intensity versus temperature at 20 MPa for crude oil.

Fig. 10 clearly shows that the signal presents a major break even when the system studied presents all the drawbacks listed above.

5. Conclusion

During this work different tests have been successfully performed on pure components and on complex synthetic system. Then the technique has been used on real complex systems for which the opacity associated to the small size of the crystals make the measurements perilous. The results clearly show that the setup designed and developed for detecting structural modifications is very accurate when the system is opaque fluids. Thus this experimental device will be used to provide reliable characterisation of real paraffinic oil in the exploration and production range of pressure of interest. It also seems that this procedure should be successfully applied in the detection of the onset of flocculation of asphaltenic crudes.

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References

[1] Chevallier V, Petitjean D, Bouroukba M, Dirand M. Polymer 1999;40:2129–37.
[2] Achour Z, Sabour A, Dirand M, Hoch M. J Therm Anal Calorim 1998;51:477–88.
[3] Briard AJ, Bouroukba M, Petitjean D, Huber N, Moise JC, Dirand M. Fuel 2006;85:764–77.
[4] Kok MV, Létoffé JM, Claudy P, Martin D, Garcin M, Vollet JL. Fuel 1996;75(7):787–90.
[5] Milhet M, Pauly J, Coutinho JAP, Dirand M, Daridon JL. Fluid Phase Equilibr 2005;235:173–81.
[6] Coutinho JAP, Daridon JL. Pet Sci Technol 2005;23(9–10):1113–28.
[7] Kruka VR, Cadena ER, Long TE. J Petrol Technol 1995;47:681–7.
[8] Daridon JL, Xans P, Montel F. Fluid Phase Equilibr 1996;17:241–248.
[9] Pauly J, Daridon JL, Coutinho JAP, Lindeloff N, Andersen SI. Fluid Phase Equilibr 2000;167:145–59.
[10] Rønningsen HP, Bjørndal B, Hansen AB, Pedersen WB. Energ Fuel 1991;5:895–908.
[11] Hammami A, Raines M. SPE 1997;38776:273–87.
[12] Hollander FFA, Stasse O, van Suchtelen J, van Enckevort WJP. J Cryst Growth 2001;233:868–80.
[13] Ji HY, Tohidi B, Danesh A, Todd AC. Fluid Phase Equilibr 2004;216:201–17.
[14] Monger-McClure TG, Tackett JE, Merrill LS. SPE Prod Facil 1999;14:4–16.
[15] Daridon JL, Pauly J, Milhet M. Phys Chem Chem Phys 2002;4:4458–61.
[16] Verdier S, Carrier H, Andersen SI, Daridon JL. Energ Fuel 2006;20:1584–90.
[17] Carrier H, Plantier F, Daridon JL, Lagourette B, Lu Z. J Petrol Sci Eng 2000;27:111–7.
[18] Roehner RM, Hanson FV. Energ Fuel 2001;15:756–63.
[19] Pauly J, Daridon JL, Coutinho JAP. Fluid Phase Equilibr 2004;224:237–44.
[20] Pauly J, Daridon JL, Sansot JM, Coutinho JAP. Fuel 2003;82:595–601.
[21] Chun Chan AK, Russo PS, Radosz M. Fluid Phase Equilibr 2000;173:149–58.

[22] Chun Chan AK, Hemmingsen PV, Radosz M. J Chem Eng Data 2000;45:362–8.
[23] Luszczyk M, Radosz M. J Chem Eng Data 2003;48:226–30.
[24] Castillo J, Canelón C, Acevedo S, Carrier H, Daridon JL. Fuel 2006;85:2220–8.
[25] Nelson RR, Webb W, Dixon JA. J Chem Phys 1960;33:6.
[26] Würflinger A, Schneider GM. Ber Bunsen-Ges Phys Chem 1973;77:121–8.
[27] Domanska U, Morawski P. Fluid Phase Equilibr 2004;218: 57–68.
[28] Chevallier V, Bouroukba M, Petitjean D, Dirand M, Pauly J, Daridon JL, et al. Fuel 2000;79:1743–50.
[29] Pauly J, Daridon JL, Coutinho JAP, Dirand M. Fuel 2005;84(4):453–9.
[30] Anderson T, Scott Peters H, Torres RA, Nagy NA, Schruben DL. Fuel 2001;80:1635–8.