USE OF PULSED NMR SPECTROSCOPY TO MEASURE THE AMOUNT OF SOLID IN WAXY CRUDES

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INTRODUCTION

Wax deposition is a major operating problem during production of oil and condensate in cold environment. Heavy components and more precisely heavy normal alkanes, with high melting temperatures, precipitate in a function of temperature. In this work, we have developed a low resolution NMR method for measuring the crystallized fraction as a function of temperature. The method was first evaluated using pure samples and was then applied to crude oils. The results were compared to those obtained both from differential calorimetry and from the model.

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pipelines or storage facilities. A better understanding of the crystallization process and the capacity to model the wax formation would help to overcome this problem. Thermo-dynamic models have been developed in order to calculate the Wax Appearance Temperature (WAT) and the amount of solid fraction versus temperature. In order to evaluate the model capabilities to calculate these properties, experimental data are necessary. Several methods exist to determine the WAT of the sample but very few are available to measure the amount of solid versus temperature. The work presented here is focused on the assessment of the Pulsed NMR spectroscopy method to measure the amount of solid versus temperature. The method has been developed, and the experimental procedures were set out together with the operating parameters. It has been used to measure amount of solid versus temperature on pure component mixtures and on crude oils. Results have been compared with those obtained by the Differential Scanning Calorimetry method and by modeling.

1 NMR SPECTROSCOPY

Measurements were performed with a Bruker Minispec PC 20 pulsed NMR spectrometer, operating at 20 MHz. In this method we used the fact that the relaxation speeds of protons belonging to a solid phase or a liquid one are different.

It can be seen on Figure 1 that solid protons have completely relaxed at 70 µs and that, in contrast, relaxation of liquid protons can be neglected in this delay and even upto 300 µs as plotted on the figure. Knowing that the amplitude of NMR signal is proportional to the number of protons, it is possible to evaluate the number of protons belonging either to the liquid phase or to the solid one, as explained in the following (Fig. 2). Signal amplitude at $t = 0$ is proportional to the total number of protons in the sample. Extrapolation of the second part of the curve (i.e. between 40 and 100 µs) at $t = 0$ is representative of the number of protons in the liquid phase. This extrapolation avoids calibration sequences which were presented by Pedersen (1991). Nevertheless, it (the extrapolation) has to deal with the 11 µs “dead time” of the spectrometer, which prevents to sample the signal before this delay. Another issue was the sampling rate, which has to be as fast as possible to have a sufficient number of points on the curve. We could achieve a sampling rate of 2 µs. So it was possible to have 44 signal values between 11 and 100 µs. In this way, the amount of protons in the solid phase can be calculated with the Equation (1):

$$H_{\text{solid}} = \frac{S_{t=0}^{L+S} - S_{t=0}^L}{S_{t=0}^{L+S} - S_{t=0}^L + S_{t=0}^L}$$

where $H_{\text{solid}}$ is the number of protons in the solid phase, $H_{\text{total}}$ is the total number of protons in the mixture, $S_{t=0}^{L+S}$ is the amplitude of the signal for the sample containing a solid (S) and a liquid (L) phases and $S_{t=0}^L$ is the amplitude of the signal for the sole liquid phase of the sample, extrapolated at $t = 0$.

![Figure 1](image1.png)

**Figure 1**
Relaxation of protons in a liquid and in a solid sample.

![Figure 2](image2.png)

**Figure 2**
Relaxation curve of a mixture of liquid and solid phases.
1.1 Experimental parameters

The relaxation delay was 2 s after a 90° pulse width of 2 µs. The signal was measured between 11 µs (“dead time” of the spectrometer) and 100 µs at 2 µs time interval. The same acquisition was repeated 100 times. Samples were contained in a capillary tube, the volume of which was 1 cm³. It has been checked that all the volume of the sample was irradiated. In this condition, the NMR signal is proportional to the amount of protons.

2 MEASUREMENTS ON PURE COMPONENT MIXTURES

In order to evaluate the sensibility of the method, we performed some experiments with pure component mixtures. We prepared various mixtures of hexatriacontane in n-heptane and for each of these mixtures we measured the amount of protons in the solid phase. The spectrometer was regulated at 40°C. At this temperature, hexatriacontane is considered insoluble in n-heptane. Results obtained are presented on Figure 3. Concentrations of hexatriacontane in mixtures varied between 6 and 48% in weight. The difference between weighted and measured concentrations of hexatriacontane was about 5%. In order to evaluate the accuracy of the method two mixtures with the same concentration were prepared and concentration of protons in the solid phase were measured. The difference between the two determinations was 5%. We considered that this value was representative of the accuracy of the method.

3 MEASUREMENTS ON CRUDE OILS

The purpose of this study was to measure the amount of solid fraction versus temperature in crude oils. So the probehead of the spectrometer was regulated at various temperatures (between 40 and 0°C) and for every temperature the NMR spectrum was measured in the same experimental conditions as for the pure component mixtures. Three crude oils were studied. For one of them results were compared to those obtained with DSC and those of the thermodynamic model CRYSPAR (Calange, 1996).

3.1 Determination of the amount of solid knowing the number of proton in the liquid and solid phases

As we saw it here above, for pure component mixtures calculation of the amount of solid knowing the number of protons is simple because and the compositions of the liquid and solid phases are easily available. Considering crude oils it is more difficult because compositions of the liquid and solid phases are not available and moreover are different at each temperature. For this purpose, crude oils had to be analysed in order to evaluate the number of proton in the solid and in the liquid phases. Analyses are described hereafter.

In a first time, the crude oil was split by distillation into two fractions, i.e.: a light fraction C_{200–} and a heavy fraction C_{200+}. After that, the heavy fraction was split by crystallisation in methyl ethyl ketone at low temperature (~−20°C) into two fractions: the dewaxed C_{200+} and the “wax” fraction. Then the dewaxed C_{200+} and the C_{200} were recombined in order to obtain the “matrix”. On each fraction (matrix and wax), elemental analysis was performed in order to measure the ratio between the number of carbon and of hydrogen atoms. Then the amount of solid can be calculated using Equation (2):

\[
\% H_{\text{solid}} = \frac{(S_{L}^{x} - S_{L}^{y}) MM_{\text{solid}}}{nb \cdot H_{\text{solid}}} + \frac{S_{L}^{x} MM_{\text{solid}}}{nb \cdot H_{\text{liquid}}} - \frac{(S_{L}^{y} - S_{L}^{x}) MM_{\text{liquid}}}{nb \cdot H_{\text{liquid}}} - \frac{S_{L}^{y} MM_{\text{liquid}}}{nb \cdot H_{\text{solid}}}
\]

where \(MM\) are the molecular weights of the solid phase or the liquid one and \(nb \cdot H\) are the numbers of hydrogen atoms per molecule in the solid or in the liquid phases.

In order to determine the ratio \(\frac{MM}{nb \cdot H}\) assumptions were made, as given in the following. A representative molecule for each phase (liquid and solid) can be expressed as: \(n(C\_b H)\), where \(b\) is the ratio between the numbers of carbon (C) atoms and hydrogen (H) atoms. It can be calculated

![Figure 3](image-url)
using the elemental analysis results (Eq. 3). The ratio \( \frac{MM}{nb \cdot H} \) is then obtained with Equation (4):

\[
b = \frac{\%C/12}{\%H}
\]

\[
\frac{MM}{nb \cdot H} = \frac{\%C}{\%H} + 1
\]

Near the WAT, the composition of the liquid phase was considered to be the same as the crude oil one and the composition of the solid phase was considered to be the same as the “wax” one. At low temperature, the liquid phase was represented by the “matrix” and the solid phase by the “wax”.

### 3.2 Results

Results obtained are presented on Figures 4 and 5. It can be seen on Figure 4 that the three crude oils do not show the same behaviour. For the first crude oil (crude oil V) the amount of solid is quite low, even at low temperature. On the contrary, the crude oil D shows a high amount of solid between 0 and 30°C. It appears that amount of solid below 1% could not be measured and so the WAT (amount = 0) was not detected. The NMR spectroscopy is not sensitive enough to evaluate the WAT. It is in agreement with results on pure component mixtures, where the concentration of solid fraction has to be above 5% to be properly measured.

On Figure 5 NMR results are compared to DSC and modeling one. There is a good agreement between the two experimental techniques and the modeling. Discrepancies are acceptable knowing the accuracy of each method.

Field data were not available to compare with our results. However considering Figure 4 it appears that it will be more difficult to produce the crude oil D than the crude oil V. These qualitative evaluation is in agreement with observations made by the companies who are in charge of the exploitation of these crude oils.

### CONCLUSION

It has been possible to measure the amount of solid versus temperature for three crude oils, using pulsed NMR technique. An experimental procedure was developed in order to evaluate the NMR value of the signal at \( t = 0 \) for the liquid and for the solid phases. The method has been evaluated with pure component mixtures. It has been shown that it was possible to measure the amount of solid with an accuracy of about 5%.

Three measurement have been done with crude oils. In order to transform the NMR signal (which represent a ratio in term of number of hydrogen atoms) in a ratio (in weight)
between the amount of solid and liquid phases assumptions were made to estimate the composition of solid and liquid phases at the different temperatures. Results have been compared to the DSC one and a good agreement was obtained. Unfortunately field data were not available for comparison but the qualitative information is correct regarding the difficulty of exploitation.

The technique could be improved with higher sampling rate of the signal and using the mathematical treatment of the signal as proposed by Le Botlan (1997). For a more reliable interpretation of the results, a precise knowledge of the composition of liquid and solid phases of the tested sample would be required.

Nevertheless, the NMR method is a powerful technique to obtain the amount of solid versus temperature in crude oils. Data can be used to fit or validate thermodynamic model calculations. The later are then used to predict the amount of solid at various conditions (temperature and pressure) of exploitation.

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REFERENCES


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