

Studies on crude oil-water biphasic mixtures by low field NMR

Renzo C. Silva^{a,*}, Giovanna F. Carneiro^a, Lúcio L. Barbosa^a, Valdemar Lacerda Jr.^a,
Jair C. C. Freitas^{a,b}, Eustáquio V. R. de Castro^a

Research and Methodology Development Laboratory for Crude Oil Analysis – LabPetro, ^a Department of Chemistry, ^b Department of Physics, Federal University of Espírito Santo, Vitória, 29075-910, Brazil.
(* corresponding author: renzocsilva@gmail.com)

The presence of water in the petroleum production chain is of great economical and technological relevance. During the transportation of fluids, it is often necessary to know in real time how much of crude oil or water is being transported – for example, in the transport of crude oil to a refinery or after a biphasic or triphasic separator facility. Low field ¹H NMR has found a huge number of applications in recent years, including *in situ* evaluations of petroleum formations (NMR logging), benchtop analyses of rocks and fluids, use in the food and pharmaceutical industry, etc. Because of the intrinsic characteristics of low-field NMR, such as good ¹H sensitivity, non-destructiveness and easy-to-do measurements, there is a trend in both the academic community and the industry to develop on-line low-field NMR-based tools [1,2]. Then, this work is concerned with the quantification of the fluids present in mixtures of crude oil and water by low field NMR.

A Maran-2 Ultra NMR spectrometer from Oxford Instruments, operating at 52mT (2.2MHz for ¹H), was used in all reported CPMG experiments, which were conducted in a 51mm diameter probe. Initially, 22 biphasic mixtures were prepared (named Series I), starting from crude oil (with kinematic viscosity of 60.8mm².s and specific gravity 0.8823g.cm⁻³, both values at 27.5°C) and deionized water (electrical conductivity of 0.05μS.cm⁻¹). Later, a Mn²⁺ 360ppm aqueous solution, prepared using MnCl₂.4H₂O and deionized water, was used to prepare 17 biphasic mixtures (about 40g) of the previous crude oil and this Mn²⁺ solution (named Series II). The T₂ distribution curves were computed by the inverse Laplace transform (ILT) of the echo decay data, using the WinDXP[®] software.

The peaks associated with each component of the Series I mixtures are clearly distinct in the recorded T₂ distribution curves, given the large difference between the mean T₂ values of pure water (±2s) and of crude oil (typically below 100ms). To calculate the water content in these samples, the relative area of water peak (corrected by RHI) on the T₂ distribution curve was used. For the crude oil used in this work, an RHI value of 1.13 was found (value also confirmed by elemental analysis of the oil). A good linear correlation is observed (R²=0.999), and also a standard deviation of 0.9%.

T₂ distribution for the Series II mixtures shows superimposed contributions from both phases (Figure

1). The use of PLS regression [3] becomes then a promising approach to deal with this kind of situation. To avoid the uncertainties introduced by the ILT when starting from the somewhat noisy original CPMG data in Series II samples (with S/N≅100-150), a PLS regression was performed using the first 1000 even echoes in the CPMG data. This method resulted in a two latent variable model with RMSECV=1.6%, which is a significant result since this difficult scenario.

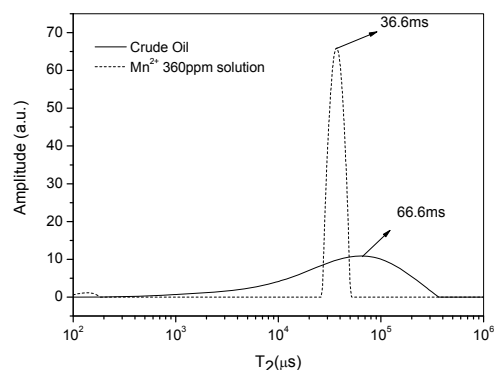


Fig. 1. T₂ distribution curves for the Mn²⁺-doped aqueous solution and for the crude oil used to prepare the Series II samples.

This study shows that quantification of crude oil and water in biphasic mixtures is a relatively simple task when the relaxation behaviors of the fluids are very distinct. Estimated errors below 1% are found for data with S/N≅250, using the T₂ distribution curves in these cases. For complex mixtures containing superimposed NMR signals with similar relaxation rates, PLS regression seems to be an interesting way to process and analyze the data. For CPMG data with S/N≅125, the water content was predicted with RMSECV=1.6%. The robustness of multivariate methods is once again demonstrated, showing the importance of a judicious choice of the mathematical procedures used to analyze the low-field NMR data, which is especially promising aiming on-line applications.

References

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