Energy & Fuels | 3b2 | ver.9 | 7/11/09 | 0:33 | Msc: ef-2009-00861d | TEID: nlr00 | BATID: 00000 | Pages: 3.64

*Energy Fuels* **XXXX**, *XXX*, 000–000 · DOI:10.1021/ef900861d

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# Measurement of the Refractive Index of Crude Oil and Asphaltene Solutions: Onset Flocculation Determination

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*Received August 7, 2009. Revised Manuscript Received October 27, 2009*

In this work, we measure the refractive index of crude oils and asphaltene in toluene solutions using a fiber optic refractometer designed to work with high-viscosity and high optical density samples. The data of the samples were analyzed using the Lorentz–Lorenz theory and simple mixing rules. The refractive index for crude oils without dilution for three crude oils with different American Petroleum Institute (API) degree, asphaltene quantity, and stability were measured. Flocculation onset for crude oils and asphaltene solutions were measured using *n*-heptane as the precipitant agent. Results showed that medium crude oils and maltenes from medium, heavy, and extra-heavy crude oils follow the Lorentz–Lorenz mixing rule. In the case of Boscan crude oil, a sample without any significant asphaltene precipitation problems, the refractive index is lower than that obtained for toluene. In contrast, Furrial crude oil, a sample with severe asphaltene precipitation problems, gave a refractive index higher than toluene. Finally, asphaltene flocculation onset was clearly followed by refractive index measurement in crude oils and asphaltene in toluene solutions after *n*-heptane addition.

## Introduction

Heavy crude oils are a complex mixture of hydrocarbons traditionally divided for convenience into several fractions of different solubility. These include saturates, aromatics, resins, and asphaltenes (SARA) and insolubles. The group of fractions composed by saturates, aromatics, and resins are known as maltenes. When the insoluble part is discarded, crude oil components can be dissolved by aromatic solvents, such as toluene. An aliphatic solvent, such as heptane, can be used to precipitate asphaltenes from crude oil samples. The asphaltene defined as the insoluble fraction in low-molecular-weight saturates and soluble in toluene is responsible for severe problems during production transport and refining. This fraction consists of polyaromatic hydrocarbon molecules that vary in molecular weight. *n*-Heptane addition to asphaltene in toluene solution is used to study the tendency of asphaltene to form aggregates.[1–3] At the flocculation onset, only the heaviest portion of the asphaltene fraction is expected to precipitate. The lighter portions of the asphaltene fraction will precipitate, with an excess in heptane added being the last to come out of solution.

Physical and thermodynamics properties of crude oils can be obtained from the literature or can be readily measured using well-established laboratory methods. The refractive index (RI) has been shown to represent various important properties of multicomponent native petroleum, processed fuels as well their respective components.[4–7] The RI can be accurately measured and used to correlate other parameters, such as density, and other properties of hydrocarbons with high reliability.[7–9] Information obtained from RI measurements is usually applied to various reservoir engineering calculations. This property in light and some medium crude oils can be directly measured using conventional refractometers. However, direct measurements of the RI of some heavy crude oils are unattainable because the high optical density of the medium (or too black) and do not permit light transmission and clear refraction. In these cases, it is usually assumed that a solution of a crude oil behaves as an ideal binary mixture of the components,[10] RI is determined for a series of oil–solvent mixtures, and the results are extrapolated (in an assumption of mixing rule theory) to determine the value for the crude oil. The theoretical basis of the relationship between macroscopic optical/electrical properties (dielectric constant and RI) to the corresponding microscopic molecular properties (e.g., molecular polarizability) was established in the late 19th and early 20th century. Also, the theory has been largely developed for pure materials of the same chemical species, and its extension to multicomponent mixtures has not been well-investigated.

The Lorentz–Lorenz relation relates the RI to the polarizability of the molecules in the following way:

$$\mathrm{RI} = \left(\frac{n^2 - 1}{n^2 + 2}\right) = \frac{N_a \alpha \rho_m}{3M} \qquad (1)$$

where $N_a$ is the universal Avogadro's number, $\rho_m$ is the density, $\alpha$ is the polarizability, $n$ is the refractive index, and $M$ is the molecular weight of the material.

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Equation 1 reveals the dependence of the RI on the molecular polarizability of the molecule for simple systems; for homogeneous multicomponent systems, there are some mixture rules useful to calculate different physical parameters in the system. The so-called volume-mixing rule, whereby the effective mass density is given by

$$\rho_{\mathrm{me}} = \sum_i f_i \rho_{\mathrm{m}i} \qquad (2)$$

where the sum is over all of the constituents of the mixture and $f_i$ and $\rho_{\mathrm{m}i}$ are the volume fraction and the partial mass density of the $i$th component of the mixture, respectively. The effective molecular weight $M_{\mathrm{e}}$ in this equation is the apparent molecular weight of a mixture given by

$$\frac{1}{M_{\mathrm{e}}} = \sum \frac{\phi_i}{M_i} = \left(\sum_i f_i \rho_{\mathrm{m}} i\right)^{-1} \sum_i \frac{f_i \rho_{\mathrm{m}} i}{M_i} \qquad (3)$$

where $\phi_i$ and $M_i$ are the mass fraction and the partial molecular weight of the $i$th constitutes, respectively. The effective refractive index is simply the volume mean refractive index given by eq 4

$$n_{\mathrm{e}} = \sum_i f_i n_i \qquad (4)$$

where $n_{\mathrm{e}}$ and $n_i$ are the effective refractive index and the partial refractive index of the $i$ components, respectively. From these mixing rules, it is easy to obtain a Lorentz–Lorenz relation based in effective magnitudes[11–13] according to eq 5

$$\mathrm{RI} = \left(\frac{{n_{\mathrm{e}}}^2 - 1}{{n_{\mathrm{e}}}^2 + 2}\right) = \frac{N_{\mathrm{a}} \alpha_{\mathrm{e}} \rho_{\mathrm{m}} e}{3 M_{\mathrm{e}}} \qquad (5)$$

where $e$ is the effective medium.

Because of the difficulty in measuring the RI of crude oils, it is common practice to consider that a mixture of crude oil and a nonprecipitant solvent behaves as an ideal binary mixture,[14] where the crude oil is treated as a single component and the solvents are treated like the second in the mixture. In this way, a simple mixing rule can be applied to crude oil in toluene solutions, and by extrapolation, the RI of crude oils is achieved.[4] However, from our experience, heavy and extra-heavy crude oils change most of these properties when they are diluted with polar solvents and the mixing rule is unusable in these cases. For this, a system was develop to measure the RI in dense and dark samples, such as heavy and extra-heavy crude oils, and, with this system, follow the changes in RI in an onset titration experiment to detect the flocculation point and the changes in the RI as a result of the phase change on the mixture.

## Experimental Section

**Materials and Methods.** Samples of Venezuelan crude oils (CLD48, Boscan, and Furrial crude oils from Monagas State in eastern Venezuela) having different American Petroleum Institute (API) gravities (5, 11, and 21, respectively), flocculation tendencies, and SARA compositions were used in this work. CLD48 crude oil has a very low quantity of asphaltene (less than 1%) and does not show flocculation problems. Boscan and Furrial have a different content of asphaltenes, 12 and 7%, respectively, and Boscan crude oil has medium flocculation problems in contrast to Furrial, which has severe asphaltene precipitation problems. Toluene (HPLC-grade Riedel-Han) was used to reduce the viscosity and diminish the optical density of the sample in flocculation experiments. The asphaltenes flocculation was induced by the addition of $n$-heptane (HPLC-grade Riedel-Han).

Asphaltenes were obtained by extraction from the correspondent crude oil from a 1:1 crude oil/toluene solution by the addition of 40 volumes of $n$-heptane, as described earlier.[15,16] Direct measurement of asphaltene samples is very difficult, and the results have great variability. The asphaltene precipitated is composed of small particles of amorphous solids, which produce random reflectivity, and for that, very variable RIs are obtained.

The studies of flocculation were carried out by the addition of $n$-heptane to the crude oil in toluene. To induce the asphaltene flocculation, different volumes of $n$-heptane are added to 10 mL of the selected crude oil in toluene solution. All of the experiments were conducted at a controlled temperature of 25 °C.

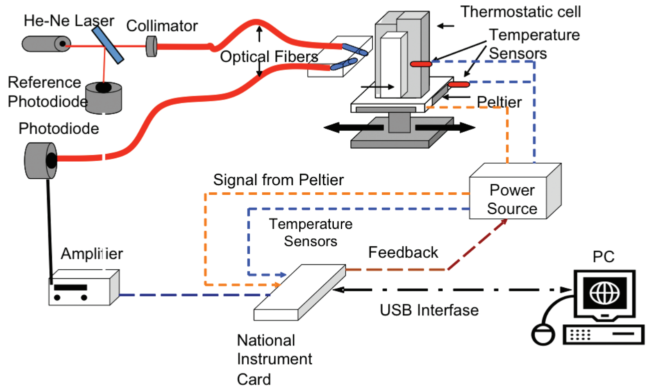


**Figure 1.** Homemade fiber optics refractometer to measure the RI in opaque samples.

**Techniques.** RI measurements were made with a homemade fiber optics refractometer. Figure 1 present the setup of the refractometer. The light from a He–Ne laser is spliced by a 90:10 beam splitter. A fraction of the light goes to a photodiode detector used to correct the laser intensity fluctuations. The straight light is guided by a optical fiber to the sample container. This container is a glass cell in a temperature control system to maintain all of the system in thermal equilibrium. The light reflected at the interface sample cell is guided by a second optical fiber to the photodiode detector. The detector outputs are connected to a National Instrument acquisition card, and the readout and control of the system are connected to Labview software. The fundamentals of the system were clearly described in ref 15.

## Results and Discussion

**Crude Oils RI.** The calibration of the system was accomplished by measuring the interface reflection for pure compounds of different RIs. Figure 2 presents a calibration curve showing the variation in the signal as a function of the RI of the sample. The fitting data shown are possible to achieve a RI change on the order of $10^{-5}$. With this setup optimized, it was possible to measure the RI in crude oil and crude oil in toluene solutions. Figure 3 shows the variation in RI for CLD48, Furrial, and Boscan crude oils as a function of the crude oil fraction. The plot for CLD48 crude oil, showing a

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