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

Jimmy Castillo,* Hector Gutierrez, Maria Ranaudo, and Otsmar Villarroel

Facultad de Ciencias, Escuela de Química, Universidad Central de Venezuela (UCV), Caracas 47102, Venezuela

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:

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

where N_a is the universal Avogadro's number, ρ_m is the density, α is the polarizability, n is the refractive index, and M is the molecular weight of the material.

*To whom correspondence should be addressed. E-mail: jimmy.castillo@ciens.ucv.ve.

(1) Branco, V. A. M.; Mansoori, G. A.; Xavier, L. C. D. A.; Park, S. J.; Manafi, H. *J. Pet. Sci. Eng.* **2001**, *32*, 217–230.
(2) Aüstlund, J. A.; Läüfroth, J. E.; Holmberg, K.; Nyden, M. *J. Colloid Interface Sci.* **2002**, *253*, 150–158.
(3) Mousavi-Dehghania, S. A.; Riazib, M. R.; Vafaie-Seftic, M.; Mansoori, G. A. *J. Pet. Sci. Eng.* **2004**, *42*, 145–156.
(4) Buckley, J.; Hirasaki, G. J.; Liu, Y.; Drasek, S. V.; Wang, J. X.; Gill, B. S. *Pet. Sci. Technol.* **1998**, *16*, 251–285.
(5) Buckley, J. S.; Wang, J. *J. Pet. Sci. Eng.* **2002**, *33*, 195–202.
(6) Wang, J.; Buckley, J. S. *Energy Fuels* **2003**, *17*, 1445–1451.

(7) Riazi, R.; Mansoori, G. A. *Oil Gas J.* **1993**, 108–111.
(8) Sing, S. *Phys. Scr.* **2002**, *65*, 167–180.
(9) Raty, J.; Keraneny, E.; Peiponenz, K. E. *Meas. Sci. Technol.* **1998**, *9*, 95–99.
(10) Taylor, S. D.; Czarnecki, J.; Masliyah, J. *Fuel* **2001**, *80*, 2013–2018.

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

$$\rho_{\text{me}} = \sum_i f_i \rho_{\text{m}i} \tag{2}$$

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

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

where ϕ_i and M_i are the mass fraction and the partial molecular weight of the ith constitutes, respectively. The effective refractive index is simply the volume mean refractive index given by eq 4

$$n_{\text{e}} = \sum_i f_i n_i \tag{4}$$

where n_{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

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

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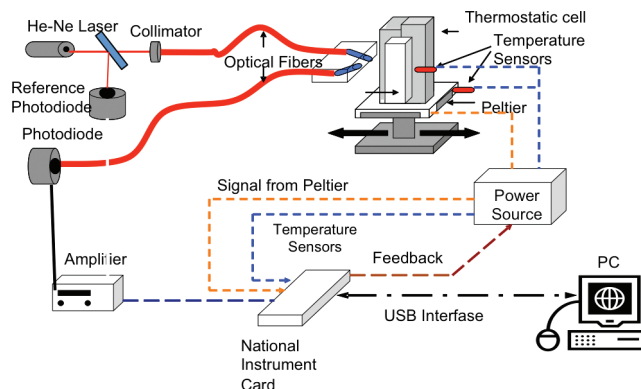
Figure 1. Homemade fiber optics refractometer to measure the RI in opaque samples.

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.

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

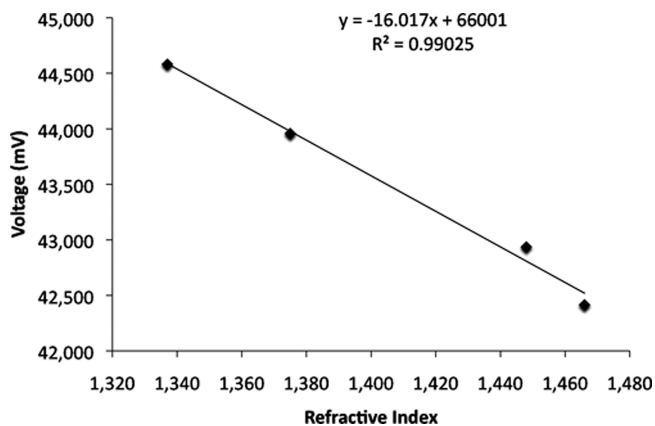(11) Francesconi, R.; Ottani, S. *J. Mol. Liq.* **2007,** *133,* 125–133.
(12) Liu, Y.; Daum, P. H. *J. Aerosol Sci.* **2008,** *39,* 974–986.
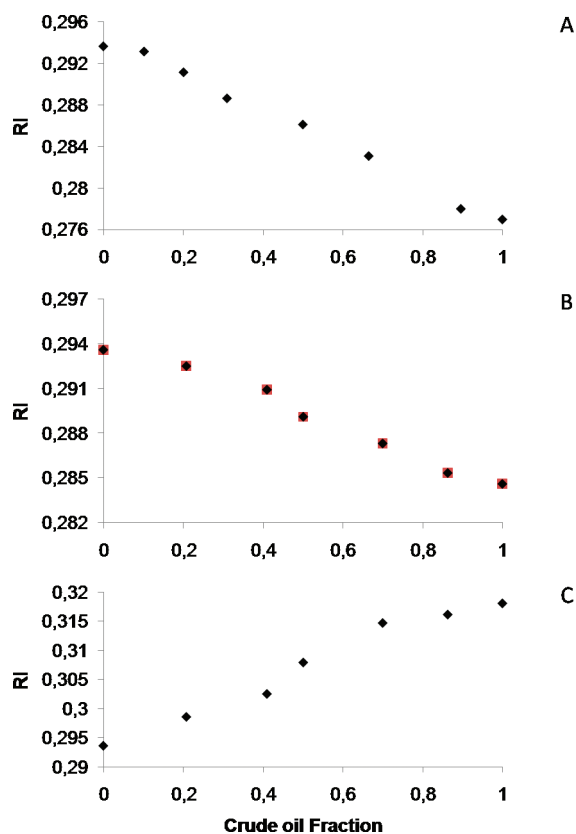(13) Toumi, A.; Bouanz, M. *J. Mol. Liq.* **2008,** *139,* 55–60.
(14) Evdokimov, I. N.; Losev, A. P. *Fuel* **2007,** *86,* 2439–2445.

(15) Castillo, J.; Canelon, C.; Acevedo, S.; Carrier, H.; Daridon, J.-L. *Fuel* **2006,** *85,* 2220–2228.
(16) Rizzo, A.; Carrier, H.; Castillo, J.; Acevedo, S.; Pauly, J. *Fuel* **2007,** *86,* 1758–1764.
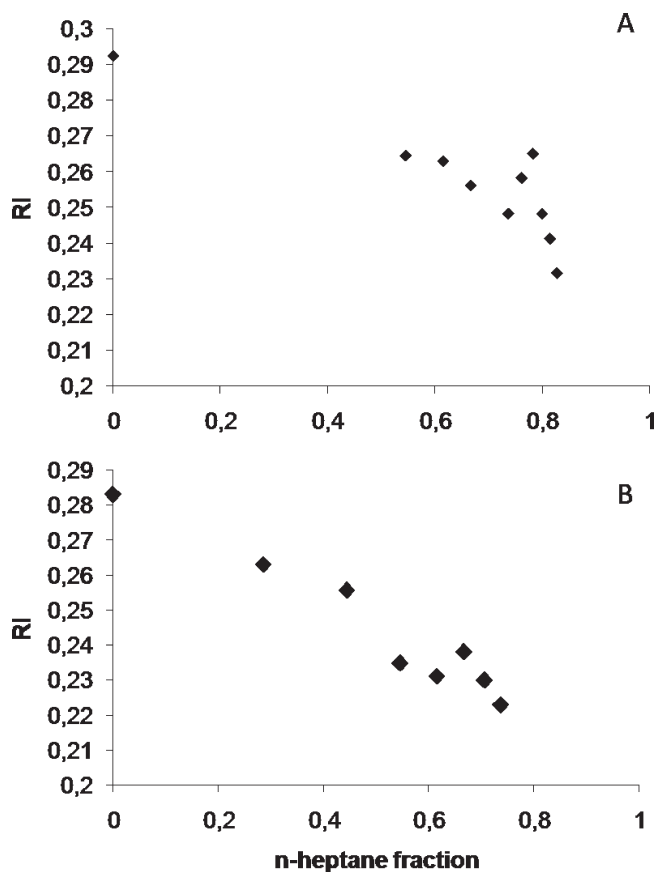
Figure 2. Calibration curve, with the parameters for the best fit line in the inset.

Figure 3. Variation in RI for (A) CLD48, (B) Furrial, and (C) Boscan crude oils as a function of the crude oil fraction in toluene solutions.

Figure 4. RI plots for (A) Boscan crude oil (12 000 mg/g) and (B) Boscan asphaltenes (2000 mg/g) in the toluene−heptane mixture.

linear behavior of the RI, means that the sample is in agreement with the mixing rule and that there are not changes in the molecular interaction behavior in the sample, when the ratio of the solvent decreased. For this crude oil, the approximation to measure the RI is useful. For Boscan and Furrial crude oils, there were a variation from the ideal behavior, more pronounced in the case of Furrial. In Boscan crude oils, the linear decreasing behavior shown at high dilution is lost when the ratio of crude oil is over 40%, achieving values lower than expected. Furrial crude oil, with a RI higher than 1.5, presents an increasing RI as a function of the crude oil ratio. This curve presents two changes: one at 40% of the crude oil and a second at 70%. As in the previous

case, the RI achieved by extrapolation at higher dilution is higher than the real value. These variations in the RI with the dilution of the sample show the changes in the interactions of the crude oil with the solvent when the ratio is increased. The variations can be associated with the tendency of the crude oils to form an unstable system that tends to form an aggregate with posterior flocculation when suffering variations in the media. All of the components in the crude oils form a complex mixture, and the addition of a solvent-like toluene promotes changes in the interaction of asphaltenes and maltenes, which can promote desorption and increments in the effective polarizability of the global mixture,[17,18] showing these variations in the RI.

Crude Oil and Asphaltene Flocculation. Changes of RI with asphaltenes flocculation for Boscan crude oil and Boscan asphaltene were presented in Figure 4. Solutions of 12 000 mg/g of crude oil were dissolved in toluene, and then different quantities of *n*-heptane were added. Figure 4A shows a nonlinear behavior of the RI as a function of the *n*-heptane added. At low *n*-heptane ratios, the decrease in the RI is linear with the *n*-heptane volume added. When the precipitation onset is reached, an abrupt change in the plot is observed and the RI increases. This change in the RI is due to the growing of the asphaltene colloids forming flocculations. After 75% of heptane is added, the flocculation sediments and the signal return to the predicted value for a ideal mixture. In Figure 4B, the data was plotted for a 2000 mg/g solution of asphaltenes. The same behavior was observed as

(17) Fotland, P.; Askvik, K. M. *Colloids Surf., A* **2008**, *324*, 22–27.
(18) Sheu, E. Y.; Acevedo, S. *Fuel* **2006**, *85*, 1953–1959.
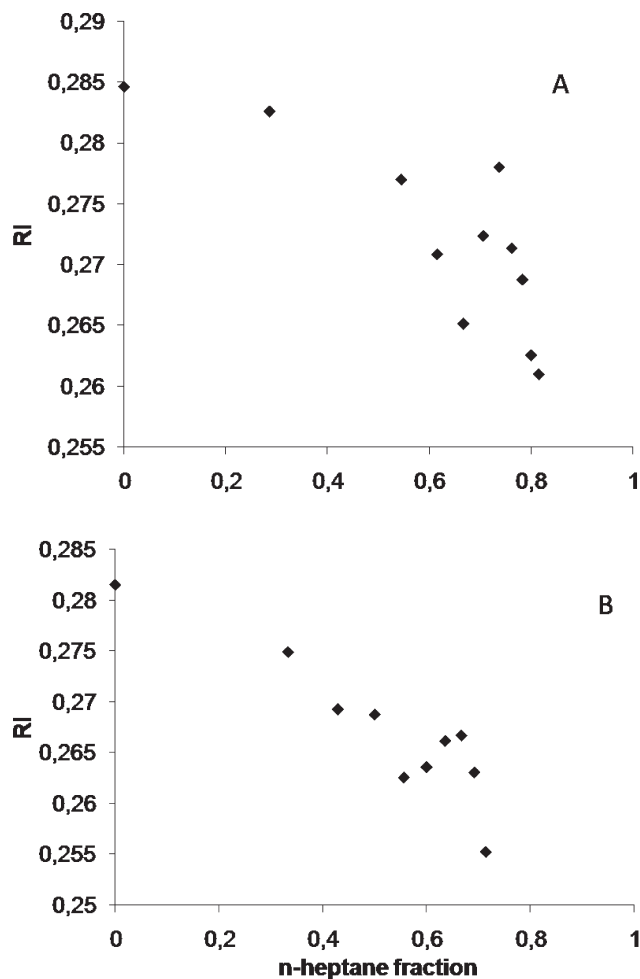
Figure 5. RI plots for (A) Furrial crude oil (50 000 mg/g) and (B) Furrial asphaltenes (2000 mg/g) in the toluene−heptane mixture.

the correspondent for the crude oil. A sharp variation in the RI at 60% of *n*-heptane added was observed, and it corresponded to asphaltene aggregation in the toluene−heptane mixture. In a 12 000 mg/g sample of Boscan crude oil, the asphaltene content is approximately 2000 mg/g

and the flocculation point is reached at higher *n*-heptane/toluene ratios. This fact is indicative of the stabilizing effect of the maltenes in the asphaltenes. Panels A and B of Figure 5 show the data for 50 000 mg/g of Furrial crude oil in toluene and 2000 mg/g of Furrial asphaltene in toluene, respectively, as a function of the *n*-heptane fraction. As in the previous sample, a sharp variation of the linear behavior was observed at 65% of *n*-heptane for the crude oil solution and 55% of *n*-heptane for the asphaltene solution. These results show the remarkable effect of the maltenes in the asphaltene stabilization. In fact, Furrial crude oil behavior, unlike Boscan crude oil behavior, is far from linearity at low *n*-heptane/toluene ratios, and this is a reflection of the different nature of the asphaltenes present in the crude oil and, consequently, the variation differences in the interaction of the asphaltene with the rest of the components of the crude oil. In all of the cases, the asphaltene aggregation is reflected as increments in the RI of the sample, and this behavior is due to the increasing local effective polarizability of the sample addressed by the change in the solubility parameter of the media, which promote the asphaltene aggregation.

Conclusions

From this work, it can be concluded that the developed system based on a simple reflection theory permits us to measure the RI in dense and dark samples with a precision of 10^{-5} RI units. With this system, RIs for crude oils and their toluene solutions were measured, obtaining real values without approximations. The flocculation onset was followed at very high concentrated samples of crude oil in toluene and asphaltene solutions. The microscopy changes in the system were followed by the RI measurement, detecting early aggregate formation. Observed changes for variations in toluene−heptane mixtures can be extrapolated to changes in variables as pressure and temperature.