

Electronic polarizability of light crude oil from optical and dielectric studies

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Abstract. In the present paper we report the temperature dependence of density, refractive indices and dielectric constant of three samples of crude oils. The API gravity number estimated from the temperature dependent density studies revealed that the three samples fall in the category of light oil. The measured data of refractive index and the density are used to evaluate the polarizability of these fluids. Molar refractive index and the molar volume are evaluated through Lorentz-Lorentz equation. The function of the refractive index, F_{RI} , divided by the mass density ρ , is a constant approximately equal to *one-third* and is invariant with temperature for all the samples. The measured values of the dielectric constant decrease linearly with increasing temperature for all the samples. The dielectric constant estimated from the refractive index measurements using Lorentz-Lorentz equation agrees well with the measured values. The results are promising since all the three measured properties complement each other and offer a simple and reliable method for estimating crude oil properties, in the absence of sufficient data.

1. Introduction

Crude oil is a complex combination of hydrocarbons consisting predominantly of aliphatic, alicyclic and aromatic hydrocarbons covering carbon numbers, which may vary from C1 to C60. The determination of the physical and thermodynamic properties of a particular crude oil is important to provide a basis for further investigations related to exploration and transportation. Both density and refractive index are important properties of crude oils that are routinely monitored, most of the time independently. Specific gravity (typically reported as American Petroleum Institute gravity – API gravity) [1] as determined by the density, not only determines if a crude oil is light or heavy but also is an important parameter for the experimental determination of the interfacial tension and other transport properties.

Along with density (ρ), refractive index (n) and electronic polarizability (α) are important physical properties of crude oil and are intimately connected to density [2-6]. Refractive index is easily measurable and because it correlates to density, it has been used as proxy measurement for density in some processes [7]. Measurements for both parameters are not always available, and it is desirable to find an accurate correlation between the two properties for crude oils. Electronic polarizability tells us how much the crude oil can respond to applied external electric fields. In a particular case of hydrocarbon and crude oil systems, where polar interactions are weak, intermolecular attractions are determined by the polarizability that can be directly related to the refractive index through the Lorentz-Lorentz equation [8]. The dielectric property has been widely used [9-15] to characterize crude oil for its reformation under thermal changes, the precipitation of asphaltenes with the addition of hexane, dielectric properties based on infrared spectroscopy, etc. The dielectric constant is closely related to the refractive index through Lorentz-Lorentz equations. In this paper we are making a comparison of the theoretical value of the dielectric constant computed using the refractive index data to the directly measured values.



2. Experimental measurements

The density of the samples was measured as a function of temperature using an *Anton Paar* precision density meter. The details of the measurements are given in an earlier [9] publication. An *Abbé* refractometer was used to measure the refractive index of the samples as a function of temperature ranging from 20 to 50°C. The liquid sample is sandwiched between the illuminating prism and the refracting prism. Dielectric investigations were performed using a *Wayne Kerr* (WK6500B) Impedance Analyser along with a Test Fixture. The temperature variation of capacitance and dielectric loss ($\tan \Delta$) are studied using 1Vp-p oscillating level of 100 kHz frequency. The variation of dielectric constant with temperature was estimated from observed capacitance.

3. Results and discussion

All three samples of oil studied (*Sayyala*, *Mabrook* and *Daleel*) are procured from the oil fields which are located in the different regions of the Sultanate of Oman. Hereafter we term them as, Sample 1 (*Sayyala*), Sample 2 (*Mabrook*) and Sample 3 (*Daleel*).

3.1. Density and API gravity

The density of the three crude oil samples decreases linearly with temperature as can be seen in Fig 1. The API gravity was measured using the equation $API = 141.5 / \rho - 131.5$, where ρ is the density at 15.6°C, is found by extrapolation. The API gravity of the oils are: 44.3°, 42.0° and 37.9° for samples 1, 2 & 3 respectively. According the API classification [1], all three samples are termed as *light oil*.

3.2. Refractive index as a function of temperature

We used an *Abbe* Refractometer to measure refractive index as a function of temperature from 20°C to 50°C in steps of 5° C. The refractive index is found to decrease linearly with increasing temperature for all samples (Fig 2). Samples with higher API have lower refractive index.

3.3. Correlation between refractive index and electronic polarizability.

Polarizability is the ability for a molecule to be polarized. Polarizabilities determine the dynamical response of a bound system to external fields, and provide insight into a molecule's internal structure. Large molecules, as in hydrocarbon liquids, get grossly affected by applied electric field.

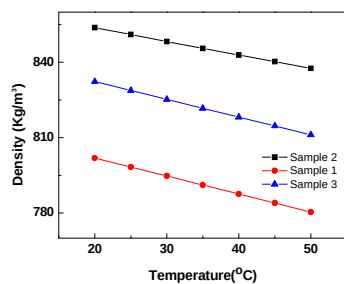


Fig. 1: Density as a function of temperature.

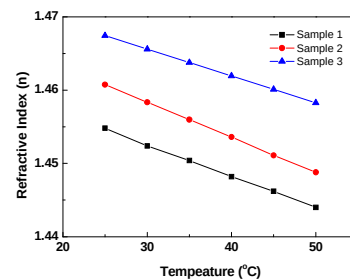


Fig. 2: Refractive index as a function of temperature.

The polarization (P) is defined as the dipole moment per unit volume, averaged over the volume of a cell. The dielectric constant (ϵ) is related to electronic polarizability (α) through the famous Clausius - Mossotti relation [8],

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \sum_j N_j \alpha_j \quad (1)$$

where N_j is the concentration and α_j is the polarizability of atom j . For $\epsilon = n^2$ one gets,

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \sum_j N_j \alpha_j \quad (2)$$

In the particular case of hydrocarbon and crude oil systems, where polar interactions are weak, intermolecular attractions are determined by the polarizability that can be related to the refractive index through Lorentz-Lorentz equation [16,17],

$$\alpha = \left(\frac{3}{4\pi N_A} \right) R_m \text{ with } R_m = \left(\frac{n^2 - 1}{n^2 + 2} \right) V_m \quad (3)$$

Here, R_m is the molar refractivity, N_A is the Avogadro's number, n is the refractive index and V_m is the molar volume. The values of the electronic polarizability (α) are presented in Table 1.

Table 1: Electronic polarizability as a function of temperature and the ratio F_{RI}/ρ

Temperature (°C)	Electronic Polarizability, $\alpha \times 10^{-24}$ (cm ³ /mol)			F_{RI}/ρ		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
25	2.4958	2.4826	2.4493	0.3375	0.3372	0.3368
30	2.4909	2.4907	2.4526	0.3376	0.3372	0.3369
35	2.4859	2.4988	2.4558	0.3376	0.3374	0.3369
40	2.4808	2.5071	2.4590	0.3378	0.3375	0.3372
45	2.4756	2.5153	2.4622	0.3379	0.3375	0.3370
50	2.4703	2.5237	2.4654	0.3380	0.3377	0.3371

3.4: Testing of the One-third rule

Equation (3) of molar refractivity can further be expanded in terms of the molecular weight (M) and the density (ρ), i.e.,

$$R_m = \left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{M}{\rho}, \text{ or } R_m = \left(\frac{F_{RI}}{\rho} \right) M \text{ where } F_{RI} = \left(\frac{n^2 - 1}{n^2 + 2} \right) \quad (4)$$

a fraction of refractive index. The computed values of (F_{RI}/ρ) for liquid hydrocarbons are tabulated in table 1.

The results suggest that (F_{RI}/ρ) is constant over a wide range of temperature of investigations. This often called in the literature [18] as *one-third rule* and is widely used for correlating the density and refractive index of crude oil. The average value of (F_{RI}/ρ) for light crude oil is around 0.337 which is very close to 1/3.

In addition to the above, the density data was used to calculate the refractive index as a function of temperature using the Lorentz-Lorentz expansion [3]:

$$\frac{F_{RI}(T)}{\rho(T)} = \left(\frac{n^2(T) - 1}{n^2(T) + 2} \right) \frac{1}{\rho(T)} = \frac{1}{\rho_o(T)} = 0.5054 - 0.3951\rho(T) - 0.2314\rho^2(T) \quad (5)$$

where $F_{RI}(T)$ is the fraction of the refractive index, $\rho_o(T)$ is the mass density of a molecule and $\rho(T)$ is the density. Refractive index (n) computed from measured density via equation (5) is close to the experimentally determined values of n . Near the room temperature it is found to differ by about 1.6%, 0.26% and 0.20% for samples 1,2 and 3 respectively. Similar variations are found at other temperatures.

3.5: Dielectric studies

The variation of the dielectric constant (ϵ') estimated from the observed capacitance with temperature is plotted in Fig 3. It has been observed that all three samples, the dielectric constant decreases with increasing temperature. The variation of the dielectric loss ϵ'' studied as a function of temperature is plotted in Fig 4. It has been observed that ϵ'' increases linearly with temperature. The gradient

$d\varepsilon''/dT \approx 4.85 \times 10^{-3}$ is the same for all three samples of light oils where the API varies in the range of 37.9° to 44.3°

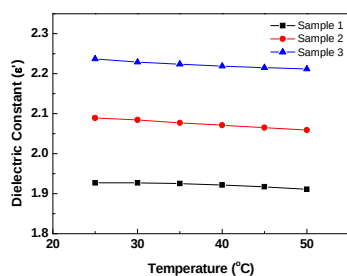


Fig. 3: Experimental values of the dielectric constant

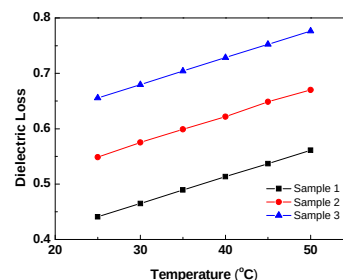


Fig. 4: Variation of the dielectric loss with temperature

For the sake of comparison, we also used the Lorentz-Lorentz equation:

$$\frac{\varepsilon'(T) - 1}{\varepsilon'(T) + 2} = \frac{n^2(T) - 1}{n^2(T) + 2}, \quad (6)$$

to compute the dielectric constant from the refractive index. We found that ε' determined from equation (6) agree reasonably well with the directly measured value; the largest variation is in the case of Sample 1 (around 8%) at higher temperature. In the case of Sample 2 and 3, it differs by about 2.8% and 4.2% respectively.

4. Conclusions

The present study suggests that the density, refractive index and dielectric constant can readily be used to characterize crude oil samples. Since the three measured parameters complement each other, our results are promising as it offers a simple and reliable method for estimating crude oil properties, even when sufficient data is not available.

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