Correlation of Refractive Index and Density of Crude Oil and Liquid Hydrocarbon

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***Abstract*—**Density and refractive index of light crude oil (API = 46.2), heavy crude oil (API = 16.4) and hydrocarbon liquids, Propanol and Butanol were measured as a function of temperature. A high precision density meter was used for density measurements and the refractive index was measured using an Abbe Refractometer. 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-Lorenz equation. Molar refractivity is found to be proportional to the molecular weight of the hydrocarbon molecules; the proportionality constant is found to obey the *one-third* rule. Though the density and the refractive index are temperature dependent, the proportionality constant is found to be independent of temperature. The results are promising since it offers a simple and reliable method for estimating crude oil and hydrocarbon properties as a function of density and refractive index, when no other data is available

***Keywords*—**density, electronic polarizability, molar refractive index, one-third rule.

I. Introduction

THE thermo-physical and optical properties of crude oil is important to provide a basis for further investigations related to exploration and transportation. Two important parameters which are routinely monitored in crude oils are the mass density and the refractive index. Mass density not only determines if a crude oil is heavy or light, but also is an input parameter for the experimental determination of viscosity and other transport properties. Another important property of crude oil is the refractive index which can give information about the intermolecular interaction of the system. It has been established that the density and refractive index are strongly correlated [1-5]. The molar refractivity is approximately proportional to the molecular weight of the hydrocarbon molecule. The proportionality constant is found to be equal to one-third for hydrocarbon liquids and crude oil [6].

In the present work, we have experimentally determined the temperature dependence of density and refractive index for light and heavy crude oils. For the sake of comparison, we have also determined these values for liquid hydrocarbons like Propanol and Butanol. These directly measured data are further used to compute the electronic polarizability and molar refractive index. Our results imply that molar refractivity is proportional to molecular weight for a wide range of liquid hydrocarbons, with a proportionality constant equal to one-third over a wide range of temperature.

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II. Experimental Measurements and Data

A. Density as a function of temperature

The temperature dependence of the density of the various specimens of hydrocarbon liquids was measured using *Anton Paar* Density Meter. The density meter consists of a system for electronic excitation, frequency counting and display. The density is calculated based on the measurement of sample oscillation period and temperature. The temperature was controlled to ±0.01°C during the measurement using a built-in thermostat. By measuring the damping of the U-tube's oscillations caused by the viscosity of the filled-in sample, the instrument automatically corrects the viscosity related errors. Measurement accuracy is up to ± 0.005 g/cm^3

The light and heavy crude oil samples were procured from the oil fields of Zhair and Sayala located in Oman. To make a comparative study, we have also used other hydrocarbon liquids, such as 1-Propanol and 1-Butanol. We have varied the temperature from 20°C to 60°C in increment of 5°C for crude oil samples and from 20°C to 32°C in increment of 2°C for 1-Propanoal and 1-Butanoal samples. Propanol and Butanol are comparatively very volatile and hence higher temperature investigation is not possible. The temperature was controlled to ±0.01°C during measurement. The data obtained is listed in table 1.

TABLE 1
MEASURED DENSITY AT DIFFERENT TEMPERATURES OF HYDROCARBON SAMPLES

(t) ± 0.01 (°C)	Density ±5×10^{-3} (g/cm^3)		(t) ± 0.01 (°C)	Density ±5×10^{-3} (g/cm^3)	
	Heavy	Light		Propa-nol	Buta-nol
20	0.9541	0.7929	20	0.8104	0.8104
25	0.9508	0.7894	22	0.8088	0.8089
30	0.9476	0.7857	24	0.8072	0.8074
35	0.9444	0.7821	26	0.8055	0.8058
40	0.9411	0.7784	28	0.8039	0.8043
45	0.9377	0.7747	30	0.8022	0.8027
50	0.9345	0.7711	32	0.8006	0.8012
55	0.9314	0.7674			
60	0.9282	0.7637			

The density decreases linearly with the increase of temperature for all samples. These values are fitted in to the equation,

$$\rho(t) = \rho_o + t(\partial\rho / \partial T) \quad (1)$$

where, $\rho(t)$ is the density at any temperature (t), ρ_o is density at room temperature, t is the temperature in °C. Equations of density as a function of temperature of hydrocarbon liquid samples are obtained from graphs,

$$\text{Sayala (light)}: \rho(t) = 0.80771 - 7.32\times10^{-4}\,t$$
$$\text{Zahir (heavy)}: \rho(t) = 0.96705 - 6.49\times10^{-4}\,t \quad (2)$$

$$\text{1-Propanol}: \rho(t) = 0.82692 - 8.12\times10^{-4}\,t$$
$$\text{1-Butanol}: \rho(t) = 0.82585 - 7.67\times10^{-4}\,t \quad (3)$$

where, ρ is in (g/cm^3) and t in (^{o}C).

The American Petroleum Institute (API) gravity is commonly used to measure how heavy or light a petroleum liquid is compared to water. API is computed [7] from the equation,

$$API = \frac{141.5}{\rho(\text{at } 15.6^o\text{C})} \quad . \quad (4)$$

Equations (2) and (3) are used to extrapolate ρ at 15.6^{o}C. The computed values of API for Sayala (light), Zahir (heavy), Propanol and Butanol are 46.2^o, 16.4^o, 42.3^o and 42.4^o, respectively. Temperature dependent density is very useful [8, 9] to determine thermo-physical properties.

B. Refractive index as a function of temperature

Refractive index of crude oils is measured as a function of temperature from 20^{o}C to 60^{o}C in steps of 5^{o}C. Also, refractive index of 1-Propanoal and 1-Butanol as a function of temperature is measured from 20^{o}C to 32^{o}C in steps of 2^{o}C. The measurements have done using an *Abbe* Refractometer. The data are tabulated in table 2.

TABLE II
MESURED REFRACTIVE INDEX DATA AT DIFFERENT TEMPERATURES

(t) ± 0.01 (^{o}C)	Refractive index, $\pm$ 1×10^{-5}		(t) ± 0.01 (^{o}C)	Refractive index, $\pm$ 1×10^{-5}	
	Heavy oil	Light oil		Propa-nol	Buta-nol
20	1.6668	1.4530	20	1.3861	1.3990
25	1.6639	1.4525	22	1.3856	1.3986
30	1.6597	1.4492	24	1.3852	1.3981
35	1.6565	1.4478	26	1.3849	1.3977
40	1.6535	1.4454	28	1.3844	1.3972
45	1.6498	1.4436	30	1.3840	1.3969
50	1.6459	1.4429	32	1.3837	1.3965
55	1.6434	1.4398			
60	1.6402	1.4379			

The refractive index is found to decrease linearly with increasing temperature for all the liquids. We have fitted n as a function of t as,

$$n_{heavy} = 1.68029 - 6.736\times10^{-4}\,t$$
$$n_{light} = 1.46118 - 3.83967\times10^{-4}\,t \quad (5)$$

$$n_{Butanol} = 1.40319 - 2.09107\times10^{-4}\,t$$
$$n_{Propanol} = 1.39009 - 1.99643\times10^{-4}\,t \quad (6)$$

As t increase from 20^{o}C to 60^{o}C, n_{heavy} falls by about 3% and n_{light} decreases by about 1.5%. On the other hand, n of Propanol and Butanol decrease only by 0.24% when t is increased from 20^{o}C to 32^{o}C.

III. ELECTRONIC POLARIZIBILITY AND REFRACTIVE INDEX

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. 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 [10],

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3}\sum_j N_j \alpha_j \quad (7)$$

where N_j is the concentration and α_j is the polarizability of atom j. The dielectric constant at optical frequencies arises from the electronic polarizability. The dipolar and ionic contributions are small at higher frequencies. For $\epsilon = n^2$ (n is the refractive index) one gets,

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3}\sum_j N_j \alpha_j \quad (8)$$

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 [11,12],

$$\alpha = \left(\frac{3}{4\pi N_A}\right) R_m \quad (9)$$

$$\alpha = \left(\frac{3}{4\pi N_A}\right)\left(\frac{n^2 - 1}{n^2 + 2}\right) V_m \quad (10)$$

with

$$R_m = \left(\frac{n^2 - 1}{n^2 + 2}\right) V_m \quad . \quad (11)$$

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 computed values of the electronic polarizability α and the molar refractivity R_m are tabulated in table 3 (a) & 3(b).

TABLE III(A)
MOLAR REFRACTIVITY (R_M) AS A FUNCTION OF TEMPERATURE

(t) ± 0.01 (^{o}C)	R_m (cm^3/mole)		(t) ± 0.01 (^{o}C)	R_m (cm^3/mole)	
	Heavy	Light		Propa-noal	Buta-nol
20	0.372	0.270	20	0.234	0.241
25	0.370	0.270	22	0.234	0.241
30	0.369	0.268	24	0.234	0.241
35	0.367	0.267	26	0.234	0.241
40	0.366	0.266	28	0.234	0.240
45	0.364	0.265	30	0.233	0.240
50	0.362	0.265	32	0.233	0.240
55	0.361	0.263			
60	0.360	0.262			

TABLE III(b)
ELECTRONIC POLARIZABILITY (α) AS A FUNCTION OF TEMPERATURE

(t) ± 0.01 (°C)	$\alpha\times10^{-24}$ (cm^3/mole)		(t) ± 0.01 (°C)	$\alpha\times10^{-24}$ (cm^3/mole)	
	Heavy	Light		Propa-noal	Buta-nol
20	2.171	1.897	20	6.927	8.795
25	2.171	1.904	22	6.932	8.805
30	2.167	1.900	24	6.940	8.811
35	2.166	1.904	26	6.950	8.821
40	2.166	1.904	28	6.956	8.828
45	2.164	1.906	30	6.964	8.838
50	2.161	1.913	32	6.973	8.849
55	2.162	1.910			
60	2.161	1.912			

It can be seen that the electronic polarizability (α) of heavy oil is approximately 14% higher than that of the light oil. α of heavy oil slowly decreases with increasing temperature. However, light oil exhibits opposite trend where α is found to increase with increasing temperature. Similar trend is also exhibited for the light hydrocarbon liquids, Propanol and Butanol. The magnitude of α of pure hydrocarbon liquids is almost 3 to 4.6 times higher than crude oil. However, R_m of heavy oil is about 48% higher than light oil near the room temperature. For Propanol and Butanol R_m are close to each other, but slightly lower than that of light oil.

IV. TESTING OF ONE-THIRD RULE

Equation (11) of molar refractivity can further be expanded in terms of the molecular weight (M) and the density (ρ), i.e.,

$$R_m = \left(\frac{n^2-1}{n^2+2}\right)\frac{M}{\rho} \tag{12}$$

Or,

$$R_m = \left(\frac{F_{RI}}{\rho}\right) M \tag{13}$$

where,

$$F_{RI} = \left(\frac{n^2-1}{n^2+2}\right) \tag{14}$$

a fraction of refractive index. The computed values of (F_{RI}/ρ) for liquid hydrocarbons are tabulated in table 4.

TABLE IV
(F_{RI}/ρ) FOR CRUDE OIL AND HYDROCARBON FLUIDS

(t) ± 0.01 (°C)	(F_{RI}/ρ)		(t) ± 0.01 (°C)	(F_{RI}/ρ)	
	Light oil	Heavy oil		Propanol	Butanol
20	0.340	0.390	20	0.289	0.298
25	0.342	0.390	22	0.290	0.298
30	0.341	0.389	24	0.290	0.299
35	0.342	0.389	26	0.290	0.299
40	0.342	0.389	28	0.291	0.299
45	0.342	0.388	30	0.291	0.299
50	0.343	0.388	32	0.291	0.300
55	0.343	0.388			
60	0.343	0.388			

The results suggest that (F_{RI}/ρ) is constant over a wide range of temperature of investigations. This often called in the literature 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 0.34 which is very close to 1/3. Similarly for liquid hydrocarbons, the average value is around 0.29. (F_{RI}/ρ) for heavy oil is slightly higher, in the range of 0.39.

V. SUMMARY AND CONCLUSION

The temperature dependence of density (ρ) and refractive index (n) for light and heavy crude oil, Propanol and Butanol were measured as a function of temperature. These properties are essential for the evaluation of thermo-physical, thermodynamic, and other optical properties of liquid hydrocarbons. Both density and refractive index are found to decrease linearly with increasing temperature. At room temperature, n of heavy oil is higher than heavy oil, Propanol and Butanol. n is further used to estimate the electronic polarizability which indicates the strength of intermolecular interactions. The computed values of the molar refractivity are found to be proportional to the molecular weight of the hydrocarbon liquids. The proportionality constant is found to be closer to 1/3 values for light oil, but a bit higher for heavy oil.

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