

# Application of the One-Third Rule in Hydrocarbon and Crude Oil Systems

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## Abstract

Thermodynamic and transport properties of hydrocarbon systems are determined, in part, by the van der Waals attractions between molecules. These van der Waals attractions (or London dispersion interactions) are related to the electronic polarizability and molar refractivity of the molecules. Molar refractivity is related to refractive index and molar volume through the Lorentz-Lorenz equation. In this work we present a method that relates the refractive index of a hydrocarbon substance with its mass density. This is based on the observation that the molar refractivity is approximately proportional to the molecular weight of a hydrocarbon molecule. The proportionality constant is approximately equal to one-third for hydrocarbons and crude oil systems. Although both the refractive index and the mass density are functions of temperature, it has been found that the proportionality constant of this model is nearly invariable over a wide range of pressures and temperatures. Therefore, given the temperature dependence of one of the variables, it is possible, by applying the “One-Third” rule, to estimate the temperature dependence of the other variable. This correlation has been validated with over 200 crude oil samples, in a wide range of densities (10-55°API) and temperatures (10-70°C), and

the results obtained are remarkable. The applications of the One-Third rule in the calculation of properties such as solubility parameter, viscosity, thermal conductivity, diffusivity and heat capacity of hydrocarbons and crude oil systems, as a function of the mass density, are presented and discussed. This approach also provides an alternative to calculate the refractive index based on densities obtained from an equation of state. The method presented in this work is promising in offering a new, simple and reliable method for estimating hydrocarbon and crude oil properties as a function of their mass density.

**Keywords:**

Refractive index; mass density; solubility parameter; physical property estimation; crude oil

## 1. Introduction

Both density and refractive index are important properties of crude oils that are routinely monitored, most of the time independently. Mass density (typically reported as American Petroleum Institute gravity -API gravity-) not only determines if a crude oil is light or heavy, but also is an important input parameter for experimental determination of interfacial tension, viscosity and other transport properties. Additionally, mass density is an input parameter in reservoir and wellbore simulators. Thus, an accurate determination of the mass density of crude oils is essential. Refractive index,  $n$ , is another property of great importance, which can give information about the intermolecular interactions in a system. 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 directly related to the refractive index through the Lorentz-Lorenz equation.

$$\alpha = \left( \frac{3}{4\pi N_A} \right) R_m \quad (1)$$

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

where:  $\alpha$  is the electronic polarizability,  $R_m$  is the molar refractivity,  $N_A$  is the Avogadro's number,  $n$  is refractive index at the frequency of the sodium-D line, and  $V$  is the molar volume.

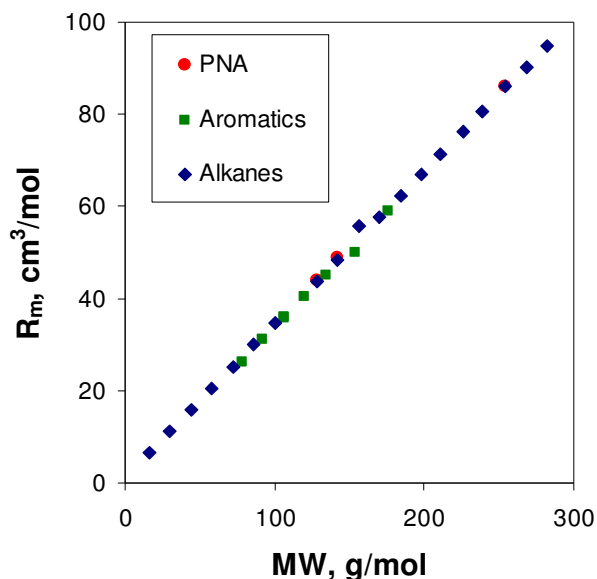
Buckley et al. [1] have reported that for the case of asphaltenes in crude oil systems, it is polarizability and not polar interactions, which determines the asphaltene phase behavior. These observations are in good agreement with our simulation results [2-7]. A method based on refractive index measurements to determine asphaltene stability has been proposed and successfully implemented by Wang and Buckley [8].

There are several correlations that have been reported in the literature that relate the solubility parameter as well as transport properties, such as viscosity, diffusivity, thermal conductivity and heat capacity with the refractive index [8-10].

Therefore, refractive index and density measurements, can give important information about the phase behavior and transport properties of petroleum systems. Furthermore, as it has been recognized in previous independent works, density and refractive index are strongly correlated [11-15]. The objective of this work is to provide a practical method for taking advantage of this correlation in the analysis of data and prediction of properties of hydrocarbon and crude oil systems.

## 2. Definition of the One-Third Rule

We have previously reported that the molar refractivity of different families of pure hydrocarbons can be correlated to their molecular weight [15], according to Figure 1.



**Figure 1.** Molar refractivity as a function of the molecular weight for different pure hydrocarbons. A common slope equal to about one-third is obtained. Reprinted in part with permission from [15]. Copyright 2009 American Chemical Society.

The relationship between molar refractivity and molecular weight is obtained from the Lorentz-Lorenz model, where the molar refractivity is a function of the refractive index,  $n$ , the molecular weight,  $MW$ , and the mass density,  $\rho$ , according to equation (3).

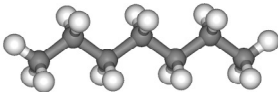
$$R_m = \left( \frac{n^2 - 1}{n^2 + 2} \right) \frac{MW}{\rho} = F_{RI} \frac{MW}{\rho} \quad (3)$$

From Figure 1 we can readily conclude that molar refractivity is approximately proportional to molecular weight for a wide range of hydrocarbons, with a proportionality constant equal to about one-third. This result implies that the function of the refractive index,  $F_{RI}$ , divided by the mass density,  $\rho$ , is a constant approximately equal to one-third for all the different tested substances. The name “One-Third” rule is used as an easy way to remember an approximate value for this relationship. This ratio does not necessarily hold for all the substances. However, in many cases, in the absence of more accurate data, the value of one-third can be used with very good results.

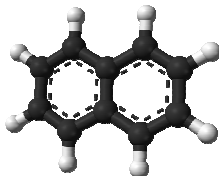
To exemplify the broad coverage of this relationship, consider the comparison between two substances: *n*-heptane and naphthalene. The former is a transparent liquid at ambient conditions, possesses a linear molecular structure, and its mass density and refractive index are 0.6837 g/cm<sup>3</sup> and 1.3878, respectively, at 20°C [16]; the latter is a crystalline white solid with the structure of two fused benzene rings; at 20°C its mass density is 1.0253 g/cm<sup>3</sup> and its refractive index is 1.6230 [16]. Despite the very different appearance, structure and physical properties, as illustrated in Table 1, both substances have almost the same value of the ratio  $F_{RI}/\rho$ . Note that this ratio is not exactly equal to one-third but it is close to this value.

**Table 1.** Comparison of physical properties of n-heptane and naphthalene. Despite the difference of appearance, and physical properties, the ratio  $F_{RI} / \rho$  is about the same for both substances.

**n-heptane**



**naphthalene**

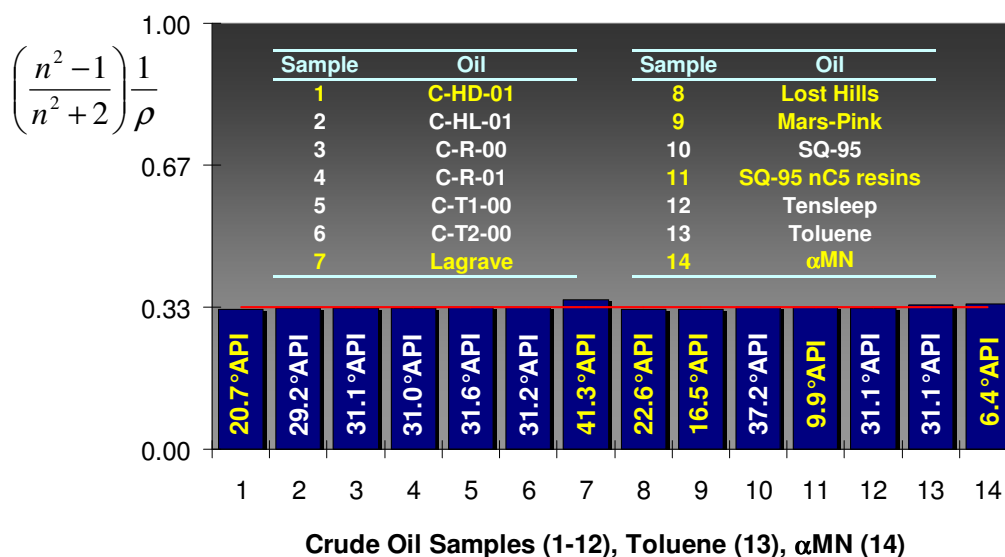


T = 20°C

$\rho, \text{g/cm}^3$	0.6837	1.0253
n	1.3878	1.6230
$\left(\frac{n^2 - 1}{n^2 + 2}\right) \frac{1}{\rho}$	0.345	0.344

Data from: CRC Handbook of Chemistry and Physics [16].

Good agreement is also obtained when we apply the One-Third rule to petroleum systems. Wang and Buckley [17] reported information of refractive indices and mass densities for 12 different crude oils. The ratios of  $F_{RI} / \rho$  for the different oils, pure toluene and pure  $\alpha$ -methyl naphthalene are presented in Figure 2.



**Figure 2.** Validation of the One-Third rule for 12 crude oil samples, pure toluene, and  $\alpha$ -methyl naphthalene. Experimental data were from Wang and Buckley [17]. Reprinted in part with permission from [15]. Copyright 2009 American Chemical Society.

The wide range of API gravities, ranging from 9.9 to 41.3, assures the broad application of the One-Third rule in crude oil systems. Note that for the lightest crude oil (Lagrove), the ratio  $F_{RI}/\rho$  is slightly over the value of one-third. For the rest of the studied samples, the agreement is remarkable.

To offer a physical interpretation of the One-Third rule, the following analysis is proposed. In equation (3), the ratio  $MW/\rho$  represents the apparent molar volume of the fluid, whereas  $R_m$  the actual volume occupied by molecules per unit mol. Therefore, the function of refractive index,  $F_{RI}$ , constitutes the fraction of fluid occupied by the molecules.

A different way of writing equation (3) is by explicitly defining a molecular mass density,  $\rho^\circ$ , that turns out to be approximately equal to 3 g/cm<sup>3</sup> for hydrocarbons and crude oil systems, according to equation (4).

$$\left(\frac{n^2-1}{n^2+2}\right)\frac{1}{\rho} = \frac{R_m}{MW} = \frac{1}{\rho^\circ} \approx \frac{1}{3} \quad (4)$$

where  $\rho^\circ$  is the mass density of a molecule in units of g/cm<sup>3</sup>.

In other words, the value of one-third represents the inverse of the density of a hydrocarbon molecule. This value is common for many pure hydrocarbons and mixtures. However, as we pointed out previously the one-third value does not necessary apply to all the components. For light and very heavy hydrocarbons there is a deviation from the one-third value. Table 2 shows the values of  $F_{RI}/\rho$  for several pure hydrocarbons.

According to Table 2, the ratio  $F_{RI}/\rho$  is, strictly speaking, a function of the mass density. For low densities the value  $F_{RI}/\rho$  increases, as the density decreases. This explains why in Figure 2, the lighter crude oils are underestimated using a constant value of one-third.

**Table 2.** FRI /  $\rho$  values for aliphatic, aromatic and polyaromatic hydrocarbons at 20°C.

Substance	$MW$ g/mol	$n$	$\rho$ g/cm <sup>3</sup>	$\frac{F_{RI}}{\rho} = \frac{1}{\rho^{\circ}}$
<i>Aliphatic Hydrocarbons</i>				
Methane	16.04	1.1926 <sup>a</sup>	0.3026 <sup>b</sup>	0.408
Ethane	30.07	1.2594 <sup>a</sup>	0.4358 <sup>b</sup>	0.375
Propane	44.10	1.3016 <sup>a</sup>	0.5188 <sup>b</sup>	0.362
Butane	58.12	1.3308	0.5788	0.353
n-Pentane	72.15	1.3575	0.6262	0.350
n-Hexane	86.18	1.3749	0.6548	0.350
n-Heptane	100.20	1.3878	0.6837	0.345
n-Nonane	128.26	1.4054	0.7176	0.342
n-Decane	142.28	1.4102	0.7300	0.340
n-Dodecane	170.34	1.4216	0.7487	0.339
n-Tridecane	184.37	1.4256	0.7564	0.338
n-Tetradecane	198.39	1.4290	0.7628	0.338
n-Pentadecane	210.40	1.4389	0.7764	0.339
n-Hexadecane	226.45	1.4345	0.7733	0.337
n-Heptadecane	238.46	1.4432	0.7852	0.338
n-Octadecane	254.50	1.4390	0.7768	0.339
n-Nonadecane	268.53	1.4409	0.7855	0.336
n-Eicosane	282.50	1.4425	0.7886	0.336
<i>Aromatic Hydrocarbons</i>				
Benzene	78.11	1.5011	0.8765	0.336
Toluene	92.14	1.4961	0.8669	0.337
Ethylbenzene	106.17	1.4959	0.8670	0.337
Propylbenzene	120.19	1.4920	0.8620	0.337
Butylbenzene	134.22	1.4898	0.8601	0.336
m-Xylene	106.17	1.4972	0.8642	0.339
Heptylbenzene	176.30	1.4865	0.8567	0.335
<i>Poly-nuclear Aromatic Hydrocarbons</i>				
Naphthalene	128.17	1.6230	1.0253	0.344
1-Methylnaphthalene	142.20	1.6170	1.0202	0.343
Nonylnaphthalene	254.41	1.5477	0.9371	0.339

Data from CRC Handbook of Chemistry and Physics [16].

<sup>a</sup> Estimated using equation (2), with molecular polarizabilities [16] and molar volumes from Barton [18]. <sup>b</sup> Estimated with values of molar volume from Barton [18].



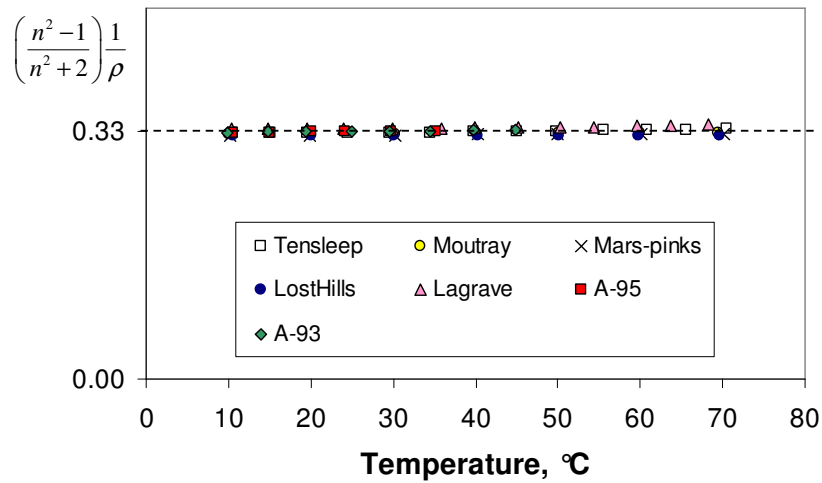
Data for  $F_{RI}/\rho$  and mass densities reported in Table 2 were correlated and equation (5) was obtained:

$$\frac{F_{RI}}{\rho} = \frac{1}{\rho^0} = 0.5054 - 0.3951\rho + 0.2314\rho^2 \quad (5)$$

Equation (5) is known as the Lorentz-Lorenz expansion [11], and the parameters 0.5054, -0.3951 and 0.2314 are the first three refractivity virial coefficients at 20°C. Mass densities for condensed gases in Table 2 were calculated from molar volumes reported in the literature [18].

Note that equation (5) was fit to data of pure hydrocarbons at 20°C and, thus, this correlation is valid at temperatures near to ambient conditions, at which most of the data are reported. However, because  $R_m$  is nearly independent of the temperature and pressure, the value  $F_{RI}/\rho$ , obtained from experimental data, from equation (5) or just by assuming the one-third value, can also be used with confidence over a wide range of temperatures and pressures. As an example consider the information reported in Figure 3 that shows notable agreement of the One-Third rule (assuming  $F_{RI}/\rho = 1/3$ ) compared to experimental data reported by Wang [19] for seven crude oils in a temperature range of 10 to 70°C. Thus, although both mass density and refractive index are functions of temperature, the ratio  $F_{RI}/\rho$  is nearly constant in this temperature range.

With this result we can be confident that the One-Third rule can be successfully applied in correlating density and refractive index, for pure substances and mixtures, over a wide range of operating conditions.



**Figure 3.** Validation of the One-Third rule in a wide range of temperatures for different crude oils. Experimental data was provided by Wang [19]. Reprinted with permission from [15]. Copyright 2009 American Chemical Society.

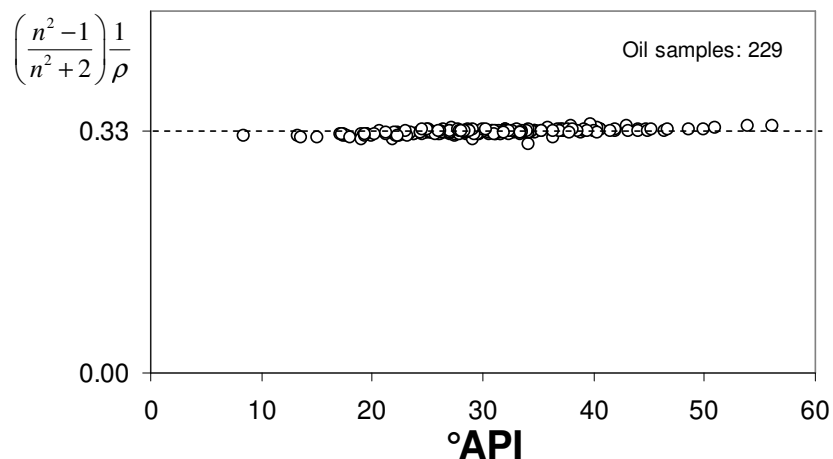
The rediscovery and extension of this relationship, proposed originally for pure substances by Bykov [20], offers the possibility of its practical application to real crude oil systems.

### 3. Applications of the One-Third Rule

#### 3.1. Data Consistency Test

A clear application of the One-Third rule is a consistency test for experimental measurements of refractive index and mass density, when both values are obtained independently. Even in its simplest form, assuming that  $F_{RI}/\rho = 1/3$ , it can be easily recognized when an experimental measurement is not consistent.

Figure 4 shows the results of a consistency test applied to over two hundred crude oil samples. For most of the cases the ratio  $F_{RI}/\rho$  is about 1/3.



**Figure 4.** Consistency test for refractive index and mass density measurements of over 200 crude oil samples. The ratio  $F_{RI}/\rho$  is about 1/3 for most of the tested samples. Reprinted with permission from [15]. Copyright 2009 American Chemical Society.

Another example of how the One-Third rule can be useful in determining data consistency is when we analyze data from the CRC handbook of Chemistry and Physics [16]. It reports for *n*-undecane a refractive index of 1.4398 and a mass density of 0.7402 g/cm<sup>3</sup>, which gives an experimental value of  $F_{RI}/\rho = 0.356$ . According to equation (5) the expected value would be  $F_{RI}/\rho = 0.3395$ . It turns out that the reported refractive index is incorrect.

A refractive index of  $n = 1.4167$  is estimated using  $F_{RI}/\rho = 0.3395$ . An experimental value of  $n = 1.4171$  is reported in the literature [21]. Thus, by using the above procedure it is not only possible to identify data inconsistency, but we can also estimate the correct data values.

### 3.2. Interpolation/Extrapolation of data

Refractive index data are most of the times reported at ambient conditions. However, for practical applications sometimes it is desirable to know the refractive index at other temperatures. This is possible if we have information of mass density at ambient temperature and at the desired temperature. Because, as we previously stated,  $F_{RI} / \rho$  can be assumed independent of temperature, we can readily obtain equation (6):

$$F_{RI}(T) = F_{RI}(T_0) \frac{\rho(T)}{\rho(T_0)} \quad (6)$$

where:  $T$  and  $T_0$  represent the desired temperature and the reference temperature, respectively.

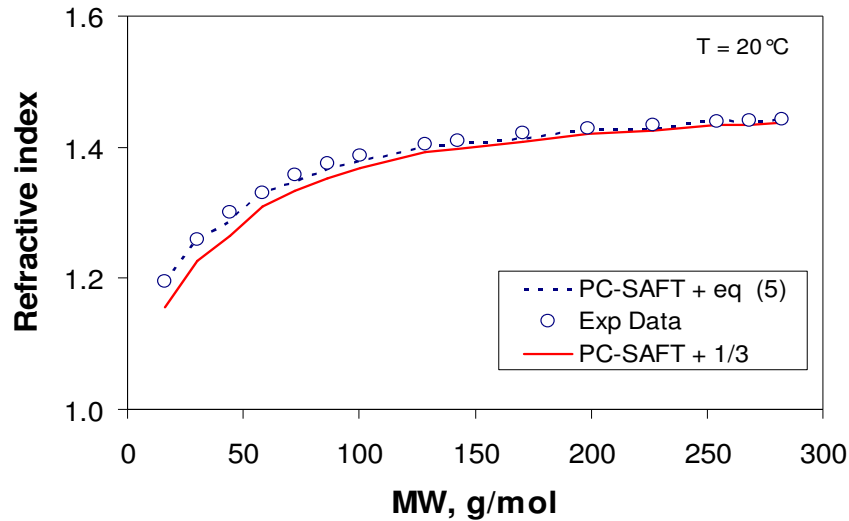
As an example consider the case of *n*-nonadecane, for which information about mass density and refractive index are reported at 35°C. At this temperature,  $n = 1.4356$  and  $\rho = 0.7752 \text{ g/cm}^3$  [22]. The refractive index at 70°C is 1.4210 [22]. With this information, by applying equation (6) we readily obtain that the density at 70°C should be  $0.7524 \text{ g/cm}^3$ . The reported value is  $0.7521 \text{ g/cm}^3$  [22].

Now let us assume that we only know information about the mass density at ambient temperature and the desired temperature. From Table 2, density of *n*-nonadecane at 20°C is  $0.7855 \text{ g/cm}^3$ . Using equation (5) we obtain  $F_{RI} / \rho = 0.3376$ . Using density at 70°C ( $0.7521 \text{ g/cm}^3$ ) we get the refractive index,  $n = 1.4216$  (absolute error = +0.0006). Agreement is remarkable considering that no information about refractive index at any temperature was used. Note that if the density value at 35°C was used, instead of the value at 20°C, a refractive index of  $n = 1.4220$  would be obtained. As we previously

pointed out the reason of the increase in error is due to the fact that equation (5) was fit to experimental data at 20°C.

### 3.3. Refractive Index from an Equation of State

The One-Third rule can also be applied for estimating the refractive index from values of mass density obtained from an equation of state. For this calculation it is necessary to use an equation of state capable of reproducing accurate values of liquid mass density. We have previously reported the successful application of the Perturbed Chain version of the Statistical Associating Fluid Theory (PC-SAFT) equation of state in predicting liquid properties, including mass density, and the phase behavior of crude oil systems [7]. Figure 5 shows the comparison between the experimental values of refractive indices reported in Table 2 and the results obtained from simulations using the PC-SAFT equation of state combined with the One-Third rule.



**Figure 5.** Estimation of refractive index using a combination of PC-SAFT and the One-Third rule. The continuous line was obtained with  $F_{RI}/\rho = 1/3$  and the dashed line with equation (5). Experimental data is reported in Table 2.

The solid line is assuming  $F_{RI}/\rho = 1/3$  whereas the dashed line is obtained with equation (5). Note that for heavy hydrocarbons the approximation of  $F_{RI}/\rho = 1/3$  is good enough. However, this approximation is not as good for lighter hydrocarbons. In such cases, equation (5) should be employed.

### 3.4. Solubility Parameter Calculation

Accurate calculation of solubility parameters is of great importance in modeling complex systems such as those composed by polymers or asphaltenic crude oils, using a regular solution theory based models. Examples of application to crude oil systems are numerous [1, 23-25]. Wang and Buckley [8] reported a correlation between the solubility parameter and the function of refractive index,  $F_{RI}$ , at ambient conditions:

$$\delta = 52.042F_{RI} + 2.904 \quad (7)$$

where  $\delta$  is units of  $\text{MPa}^{0.5}$ .

The One-Third rule can now be applied to estimate solubility parameters of liquid hydrocarbons or crude oil systems as a function of their mass densities at ambient temperature. Note that although  $F_{RI}/\rho = 1/3$  can be used as a rough approximation, for light hydrocarbons it may be preferable to use equation (5). Incorporating equation (5) into equation (7) we obtain:

$$\delta = 2.904 + 26.302\rho - 20.5618\rho^2 + 12.0425\rho^3 \quad (8)$$

where  $\delta$  is units of  $\text{MPa}^{0.5}$  and  $\rho$  is in units of  $\text{g/cm}^3$ .

Note that equation (8) is intended to be valid only at ambient conditions.

As an example consider the cases of *n*-hexane and toluene, which, according to Table 2, have mass densities of 0.6548 and 0.8669  $\text{g/cm}^3$ , respectively. Using equation (8), the

solubility parameter for *n*-hexane is 14.7 MPa<sup>0.5</sup> and for toluene is 18.1 MPa<sup>0.5</sup> at ambient conditions, which are in good agreement with values reported in the literature [18].

Prediction of solubility parameters at ambient conditions is useful. However, it is also necessary to extend the calculation of solubility parameters to other conditions of pressure and temperature. The corresponding equations can be derived from thermodynamic relationships.

We have previously derived the expression that describes the pressure dependence of the solubility parameter at constant temperature, T, [15]:

$$\delta^2(P, T) = P + \frac{\rho(P, T)}{\rho_0(P_0, T)} [\delta_0^2(P_0, T) - P_0] + \left( \frac{1 - T\alpha_P}{\kappa_T} \right) \left( 1 - \frac{\rho(P, T)}{\rho_0(P_0, T)} \right) \quad (9)$$

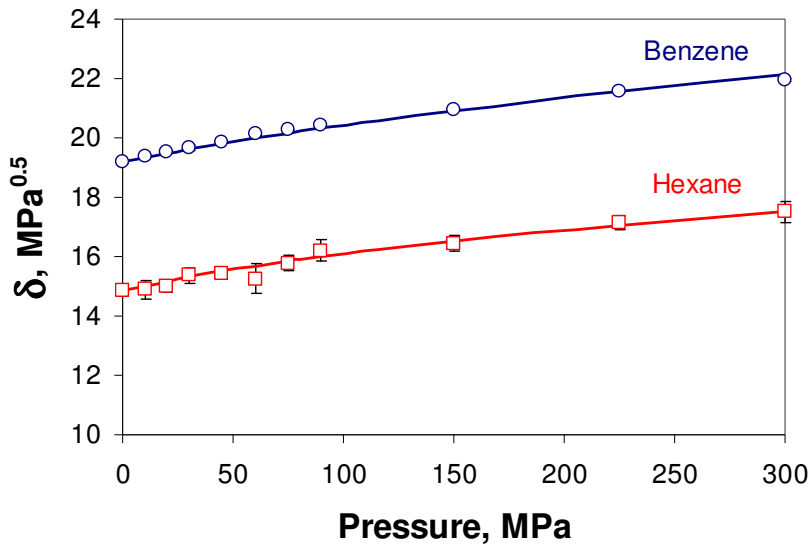
Where  $\rho$  and  $\rho_0$  are the mass densities evaluated at actual conditions ( $P$ ,  $T$ ) and reference conditions ( $P_0$ ,  $T$ ), respectively;  $\alpha_P$  is the thermal expansion coefficient and  $\kappa_T$  is the isothermal compressibility coefficient, which are defined according to equations (10) and (11), respectively.

$$\alpha_P = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_P \quad (10)$$

$$\kappa_T = +\frac{1}{\rho} \left( \frac{\partial \rho}{\partial P} \right)_T \quad (11)$$

Using equation (9), the solubility parameter of a liquid can be calculated at a given  $P$ , starting from a known solubility parameter value at reference pressure,  $P_0$ . If the pressure range is wide, it can be split into several small intervals, and use successive calculations. At every interval, the corresponding values of  $\alpha_P$  and  $\kappa_T$  are calculated. Solubility parameters at reference condition,  $\delta_0$ , can be obtained from the literature [18] or, alternatively, they can be estimated using equation (8) at ambient pressure,  $P_0 = 1$  bar.

The procedure described above was implemented for the calculation of the solubility parameter of *n*-hexane and benzene as a function of pressure. Solubility parameters at ambient pressure were obtained from Barton [18]. Density data were obtained from the National Institute of Standards and Technology (NIST) database [26]. Figure 6 shows the excellent agreement between successive calculations using equation (9) and molecular simulation data reported by Rai et al [27].



**Figure 6.** Comparison between proposed model (continuous lines) and data [27] (open markers) for the solubility parameters of benzene and hexane, as a function of the pressure. Reprinted with permission from [15]. Copyright 2009 American Chemical Society.

The temperature dependence of solubility parameter can also be derived from thermodynamic relationships, and the final result is reported in equation (12):

$$\delta^2(P, T) = \delta_0^2(P, T_0) \exp[-\alpha_p(T - T_0)] + \frac{C_V \cdot \rho_0(P, T_0)}{MW \cdot \alpha_p} (\exp[-\alpha_p(T - T_0)] - 1) \quad (12)$$

where  $\rho_0$  is the mass densities evaluated at reference conditions ( $P, T_0$ );  $\alpha_p$  is the thermal expansion coefficient and it is defined according to equation (10);  $C_V$  is the heat capacity at constant volume; and  $MW$  is the molecular weight.



Equation (12) can be simplified as we identify that the first term has a much greater value than the second term. We can drop the second term and obtain equation (13):

$$\delta^2(P, T) = \delta_0^2(P, T_0) \exp[-\alpha_p(T - T_0)] \quad (13)$$

Note that equation (13), is equivalent to the expression reported by Hildebrand and Scott [24] for the calculation of the temperature dependence of the solubility parameter.

In equation (13), once again, the value of solubility parameter at the reference condition, e.g.  $T = 20^\circ\text{C}$ , can be obtained from the literature [18] or calculated using equation (8). Values of mass density to estimate the thermal expansion,  $\alpha_p$ , can be obtained from the NIST database [26]. When the temperature range is wide, it can be split into several small intervals, and use successive calculations. At every interval, the corresponding value of  $\alpha_p$  is calculated.

With these analyses we conclude that the solubility parameter at any pressure and temperature can be estimated based solely on data of mass density at the pressures and temperatures of interest, using equations (8), (9) and (13).

### 3.5. Transport Properties Prediction

Riazi [9, 10, 28] has reported that a general model for calculating transport properties, such as viscosity ( $\mu$ ), diffusivity ( $D$ ), and thermal conductivity ( $k$ ), has the form presented in equation (14):

$$\theta_{ir} = A \left( \frac{1}{F_{RI}} - 1 \right) + B \quad (14)$$

Where  $\theta_{ir}$  is a transport property in the form of  $1/\mu$ ,  $1/k$  or  $D$ , at the same temperature as  $F_{RI}$ . Constants A and B for various hydrocarbons are given by Riazi et al. [9].

Combining equations (6) and (14) we obtain:

$$\theta_{ir}(T) = A \left( \frac{1}{F_{RI}(T_0)/\rho(T_0)} \cdot \frac{1}{\rho(T)} - 1 \right) + B \quad (15)$$

where the term  $F_{RI}(T_0)/\rho(T_0) = 0.5054 - 0.3951\rho(T_0) + 0.2314[\rho(T_0)]^2$ , according to equation (5).

For the heat capacity, Razi [10] proposed equation (16):

$$C_p = A_1 \left( \frac{F_{RI}}{1 - F_{RI}} \right) + B_1 \quad (16)$$

where  $A_1$  and  $B_1$  have been determined for pure hydrocarbons from various groups, and they are independent of temperature. Riazi also presented correlations for these constants as a function of molecular weight for different homologous series [10].

Similarly to equation (15), equation (16) can also be expressed in terms of mass densities, by using equations (5) and (6).

#### 4. Conclusions

In this work we present a method that relates the refractive index of a substance with its mass density. Although it is not the first time that the relationship between these two variables is described, we extend this approach to the analysis and estimation of properties in hydrocarbons and petroleum systems. An interesting characteristic of this model is that the Lorentz-Lorenz expression leads to a value of  $F_{RI}/\rho$  approximately equal to one-third for several pure hydrocarbons and its mixtures. This is particularly the case for crude oils. From this fact, this model receives the name of One-Third Rule. This

value, which is nearly independent of pressure and temperature, has a physical meaning because it can be regarded as the inverse of the mass density of a molecule.

Practical applications of the One-Third Rule are numerous, ranging from data consistency tests to estimation of thermodynamic and transport properties. The calculation of the solubility parameter is particularly interesting. As it was shown in this work, to estimate the solubility parameter of a substance it is only necessary to know information about its mass density in the range of temperature and pressure of interest.

Our model also allows the remarkably accurate calculation of the refractive index from liquid density values obtained from the PC-SAFT equation of state. This result enables the incorporation of this property calculation into commercial simulators.

The method presented in this work is promising in offering a new, simple and reliable method for analyzing and estimating hydrocarbon and crude oil properties as a function of their mass density.

#### *List of Symbols*

$A, B$	empirical constants, eqs (14) & (15), units of $\theta_r$ .
$A_1, B_1$	empirical constants, eq (16)
$C_P$	heat capacity at constant pressure [kJ/kg-K]
$C_V$	heat capacity at constant volume [J/mol-K]
$D$	diffusion coefficient [cm <sup>2</sup> /s]
$F_{RI}$	Lorentz-Lorenz function of refractive index, $=(n^2-1)/(n^2+2)$
$k$	thermal conductivity [W/m-K]
$MW$	molecular weight [g/mol]
$n$	refractive index at frequency of sodium-D line
$N_A$	Avogadro's number [ $\approx 6.022 \times 10^{23} \text{ mol}^{-1}$ ]
$P$	pressure [MPa]

*List of Symbols (Continued)*

$R_m$	molar refractivity [ $\text{cm}^3/\text{mol}$ ]
$T$	temperature [K]
$V$	apparent molar volume [ $\text{cm}^3/\text{mol}$ ]

*Greek Symbols*

$\alpha$	electronic polarizability [ $\text{cm}^3$ ]
$\alpha_p$	thermal expansion coefficient [ $\text{K}^{-1}$ ]
$\delta$	solubility parameter [ $\text{MPa}^{0.5}$ ]
$\kappa_T$	isothermal compressibility coefficient [ $\text{MPa}^{-1}$ ]
$\mu$	viscosity [cP = mPa-s]
$\rho$	mass density of bulk [ $\text{g}/\text{cm}^3$ ]
$\rho^\circ$	mass density of a molecule [ $\text{g}/\text{cm}^3$ ]
$\theta_r$	transport property in the form of $1/\mu$ , $1/k$ or $D$ , equations (14) and (15)

Subscripts

$0$	reference condition
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## References

- [1] J.S. Buckley, G.J. Hirasaki, Y. Liu, S. Von Drasek, J.X. Wang, B.S. Gill, Asphaltene precipitation and solvent properties of crude oils, *Pet. Sci. Technol.*, 16 (1998) 251-285.
- [2] D.L. Gonzalez, G.J. Hirasaki, J. Creek, W.G. Chapman, Modeling of Asphaltene Precipitation Due to Changes in Composition Using the Perturbed Chain Statistical Associating Fluid Theory Equation of State, *Energy Fuels*, 21 (2007) 1231-1242.
- [3] D.L. Gonzalez, P.D. Ting, G.J. Hirasaki, W.G. Chapman, Prediction of Asphaltene Instability under Gas Injection with the PC-SAFT Equation of State, *Energy Fuels*, 19 (2005) 1230-1234.
- [4] D.L. Gonzalez, F.M. Vargas, G.J. Hirasaki, W.G. Chapman, Modeling Study of CO<sub>2</sub>-Induced Asphaltene Precipitation, *Energy Fuels*, 22 (2008) 757-762.
- [5] P.D. Ting, D.L. Gonzalez, G.J. Hirasaki, W.G. Chapman, Application of the PC-SAFT EoS to Asphaltene Phase Behavior, in: O.C. Mullins, E.Y. Sheu, A. Hammami, A.G. Marshall (Eds.) *Asphaltenes, Heavy Oils, and Petroleomics*, Springer, New York, 2007, pp. 301-327.
- [6] P.D. Ting, G.J. Hirasaki, W.G. Chapman, Modeling of Asphaltene Phase Behavior with the SAFT Equation of State, *Pet. Sci. & Tech.*, 21 (2003) 647 - 661.
- [7] F.M. Vargas, D.L. Gonzalez, G.J. Hirasaki, W.G. Chapman, Modeling Asphaltene Phase Behavior in Crude Oil Systems Using the Perturbed Chain Form of the Statistical Associating Fluid Theory (PC-SAFT) Equation of State, *Energy Fuels*, 23 (2009) 1140-1146.
- [8] J.X. Wang, J.S. Buckley, A Two-Component Solubility Model of the Onset of Asphaltene Flocculation in Crude Oils, *Energy Fuels*, 15 (2001) 1004-1012.
- [9] M.R. Riazi, G.A. Enezi, S. Soleimani, Estimation of transport properties of liquids, *Chem. Eng. Commun.*, 176 (1999) 175-193.
- [10] M.R. Riazi, Y.A. Roomi, Use of the refractive index in the estimation of thermophysical properties of hydrocarbons and petroleum mixtures, *Ind. Eng. Chem. Res.*, 40 (2001) 1975-1984.
- [11] H.J. Achtermann, J. Hong, W. Wagner, A. Pruss, Refractive index and density isotherms for methane from 273 to 373 K and at pressures up to 34 MPa, *J. Chem. Eng. Data*, 37 (1992) 414-418.
- [12] J. Hadrich, The Lorentz-Lorentz function of five gaseous and liquid saturated hydrocarbons, *Appl. Phys.*, 7 (1975) 209-213.
- [13] M.A. Iglesias-Otero, J. Troncoso, E. Carballo, L. Romaní, Density and refractive index in mixtures of ionic liquids and organic solvents: Correlations and predictions, *J. Chem. Thermodyn.*, 40 (2008) 949-956.
- [14] R.K. Krishnaswamy, J. Janzen, Exploiting refractometry to estimate the density of polyethylene: The Lorentz-Lorentz approach re-visited, *Polym. Test.*, 24 (2005) 762-765.
- [15] F.M. Vargas, D.L. Gonzalez, J.L. Creek, J. Wang, J. Buckley, G.J. Hirasaki, W.G. Chapman, Development of a General Method for Modeling Asphaltene Stability, *Energy Fuels*, 23 (2009) 1147-1154.
- [16] D. Lide, *CRC Handbook of Chemistry and Physics*, 81st ed., CRC, 2000.
- [17] J. Wang, J.S. Buckley, Asphaltene Stability in Crude Oil and Aromatic Solvents-The Influence of Oil Composition, *Energy Fuels*, 17 (2003) 1445-1451.

- [18] A.F.M. Barton, CRC Handbook of Solubility Parameters and Other Cohesion Parameters, CRC Press, USA, 1991.
- [19] J.X. Wang, Personal Communication, 2008.
- [20] M.I. Bykov, Calculation of specific and molar refraction of hydrocarbons, Chem. Technol. Fuels Oils, 20 (1984) 310.
- [21] C. Wohlfarth, Refractive index of undecane, in: Refractive Indices of Pure Liquids and Binary Liquid Mixtures (Supplement to III/38), 2008, pp. 521-522.
- [22] L.T. Chu, C. Sindilariu, A. Freilich, V. Fried, Some Physical Properties of Long Chain Hydrocarbons, Can. J. Chem, 64 (1986) 481-483.
- [23] C.M. Hansen, Hansen solubility parameters : a user's handbook, second ed., Taylor & Francis, Boca Raton, 2007.
- [24] J.H. Hildebrand, R.L. Scott, The Solubility of Nonelectrolytes, 1st Dover Edition ed., Dover, 1964.
- [25] A. Hirschberg, L.N.J. De Jong, B.A. Schipper, J.G. Meyers, Influence of Temperature and Pressure on Asphaltene Flocculation, SPE Paper No. 11202 (1982).
- [26] P.J. Linstrom, W.G. Mallard, National Institute of Standards and Technology, NIST Chemistry WebBook, NIST Standard Reference Database, 2005.
- [27] N. Rai, J.I. Siepmann, N.E. Schultz, R.B. Ross, Pressure Dependence of the Hildebrand Solubility Parameter and the Internal Pressure: Monte Carlo Simulations for External Pressures up to 300 MPa, J. Phys. Chem. C, 111 (2007) 15634-15641.
- [28] M.R. Riazi, G.N. Al-Otaibi, Estimation of viscosity of liquid hydrocarbon systems, Fuel, 80 (2001) 27-32.