



Evaluation of the refractive indices of pure organic dyes using binary mixture models

Ouafa Sijilmassi^{a,*}, Pilar García-Parejo^b, Alberto Álvarez-Herrero^b

^a Complutense University of Madrid, Av. Séneca, 2, 28040, Madrid, Spain

^b Instituto Nacional de Técnica Aeroespacial (INTA), Carretera de Ajalvir, Km. 4, Torrejón de Ardoz, 28850, Madrid, Spain

ARTICLE INFO

Keywords:

Organic dye
Binary mixtures
Mixing rule
Refractometer
Refractive index

ABSTRACT

The refractive index (RI) of organic dyes is highly important due to their applications in many optical and optoelectronic fields. Because the refractive indices of various organic dyes are unknown, in the present work, we have developed an easy and simple method to estimate the refractive indices of pure organic dyes using binary mixing rules. The refractive indices were measured at a temperature of 20 °C for a wavelength $\lambda = 589.6$ nm with an Abbe refractometer. The method was previously checked for two compounds with known refractive indices, Xylene and Fluorescein, both solved in ethanol. According to the acquired results, it can be stated that Arago-Biot and Gladstone-Dale mixing rules best check the RI. Afterward, this method was applied to the Phloxine B, diluted in ethanol, to determine its unknown RI. The obtained experimental refractive index data of Phloxine B + ethanol solutions at higher ethanol mole fractions were correlated satisfactorily with both models.

1. Introduction

The Refractive Index (RI) is one of the most important optical properties of substances because it provides fundamental insights into the electronic configuration of the different ions and molecules forming materials. It is basically a measure of the change in velocity of a light wave as it travels from one medium to another, and is directly related to the molecular structure of the material it traverses [1]. This parameter is highly important because of its uses in different fields of science such as biology [2,3], pharmacology [4], mineralogy [5], and chemistry [6], where the RI value can give interesting information. In biology, for example, RI is one of the most important properties in the characterization of biological tissues [7]. Basic research with the aim to determine the RI of biological tissues is highly important in biomedical optics because of its numerous applications [8].

Organic dyes are usually used in biology and medicine to highlight structures in biological tissues. However, they have also long been known for their multi-functional applications in photonics and biophotonic applications [9,10]. All-photon devices, which are materials where photons are used instead of electrons as the information carrier, play an essential role in all-optical communications and information processing. However, photon-photon interactions are only possible within optical materials. Organic dyes have linear optical

properties and are considered optical materials [11,12]. The linear and nonlinear response of an optical material is characterized by the measurement of the RI [13]. Numerous methods for measuring the RI of liquid solutions are well documented [14,15]. However, the RI data for several organic dyes cannot be found in reference books, bibliographies, or reference sources and must be measured if needed. To the best of our knowledge, a reliable method for measuring the RIs of organic dyes is not currently available.

The RIs of pure liquids and their binary mixtures can readily be measured directly using refractometers. There are two ways of obtaining information on RI values in binary liquid mixtures: experimental measurement and calculation based on the known values of RI of the pure components of mixtures [14]. However, in the available literature, we could not find any reports on how to obtain or measure the RIs of pure organic dyes. In order to evaluate the RI of organic dyes, this work was carried out to find the best method, which is easier to perform and interpret. The method described here requires only an Abbe refractometer. This instrument is simple in principle, sufficiently precise, and easy to use.

To verify the effectiveness of the proposed method, we check, firstly, the known RI of two pure components, each compound was adequately diluted with ethanol. The first one is a liquid, a mixture of pure isomeric xylenes (*ortho*-xylene, *meta*-xylene, and *para*-xylene), and the second

* Corresponding author.

E-mail address: o.sijilmassi@ucm.es (O. Sijilmassi).

one is a biological dye (fluorescein), whose RIs are already known in the literature [16,17]. Finally, we apply this method to evaluate the RI of a dye, Phloxine B, that we do not know its RI. The chemical structures of all components are shown in Fig. 1.

The use of mixing rules for the theoretical estimation of RIs of binary liquid mixtures is well documented [18–20]. The most commonly used mixing rule is the Lorentz – Lorenz equation which relates the RI of a liquid to the scalar average molecular electronic polarizability. This model is the most suited to account for specific refractivity and effective polarizability, and therefore to define molar refraction [21,22]. Generally, the Lorentz-Lorenz equation can be applied to large composition domains, the others mixing rules are recommended for more diluted solutions. Bruggeman formalism is widely used to estimate the effective permittivity of a particulate composite medium comprising two component mediums [23]. Finally, the Arago-Biot model has the same advantages and disadvantages as the Gladstone-Dale equation [24].

In the current manuscript, several common mixing rules were used to correlate the experimental data: Arago-Biot (A–B) [25], Lorentz-Lorenz (L–L) [26], Gladstone-Dale (G–D) [27], Eyring-John (E–J) [28], and Bruggeman [23] (Eqs.1–5, respectively):

$$n = n_1 \cdot \varphi_1 + n_2 \cdot \varphi_2 \quad (1)$$

$$\frac{n^2 - 1}{n^2 + 2} = \frac{n_1^2 - 1}{n_1^2 + 2} \cdot \varphi_1 + \frac{n_2^2 - 1}{n_2^2 + 2} \cdot \varphi_2 \quad (2)$$

$$n - 1 = (n_1 - 1) \cdot \varphi_1 + (n_2 - 1) \cdot \varphi_2 \quad (3)$$

$$n = n_1 \cdot \varphi_1^2 + 2(n_1 \cdot n_2)^{1/2} \cdot \varphi_1 \cdot \varphi_2 + n_2 \cdot \varphi_2^2 \quad (4)$$

$$n = n_2 \cdot \frac{1 + \varphi_1 \cdot \left(\sqrt{\frac{n_1}{n_2}} - 1 \right)}{1 + \varphi_1 \cdot \left(\sqrt{\frac{n_2}{n_1}} - 1 \right)} \quad (5)$$

where n represents the RI of the mixture, n_1 is RI of pure component-1 and n_2 is RI of pure component-2, φ_1 is the volume fraction of pure component-1, and φ_2 is the volume fraction of pure component-2.

Equations (1) and (3) are identical if, in both cases, volume additivity is assumed. However, if non-additivity is not ignored in the mixture the Gladstone-Dale equation differs therefore from the Arago-Biot equation [19,29].

2. Materials and methods

2.1. Dye dilution protocol

The volume fraction, φ_i , of component i in binary mixtures at a given temperature and pressure is defined by:

$$\varphi_i = \frac{\chi_i \cdot V_{m,i}}{\sum \chi_j \cdot V_{m,j}} \quad (6)$$

where χ_i and χ_j are the mole fraction of the components in the mixture, $V_{m,i}$ and $V_{m,j}$ are their molar volumes. The relation between mole fractions and volumetric fractions is approximated by Amagat's law [30], i.e., assuming the ideal behavior of mixtures.

The mole fraction, χ_i , can be calculated using the following formula:

$$\chi_i = \frac{n_i}{\sum n_j} \quad (7)$$

Where n_i is the number of moles of the solute, and n_j is the total number of moles in the given solution.

In the present research, three samples were prepared at different mole fractions of solute (χ_1) as follows: From 0 to 1, in steps of 0.1, for the binary mixture formed by (xylene-ethanol). From 0 to 0.0011, in steps of 0.0001, for the binary mixture formed by (fluorescein + ethanol). Finally, from 0 to 0.0002, in steps of 0.00001, for the binary mixture formed by (Phloxine B + ethanol). In this work, mole fractions of dyes were very small. In this manner, the final solution is clear and slightly transparent. On the contrary, with higher mole fractions, the solution becomes opaque. The Abbe refractometer does not work satisfactorily with dark opaque solutions, as the light does not pass through the liquid.

It should be noted that the dye dilution process in the binary mixture (liquid-dye) is a very important step to obtain the RI of the organic dye

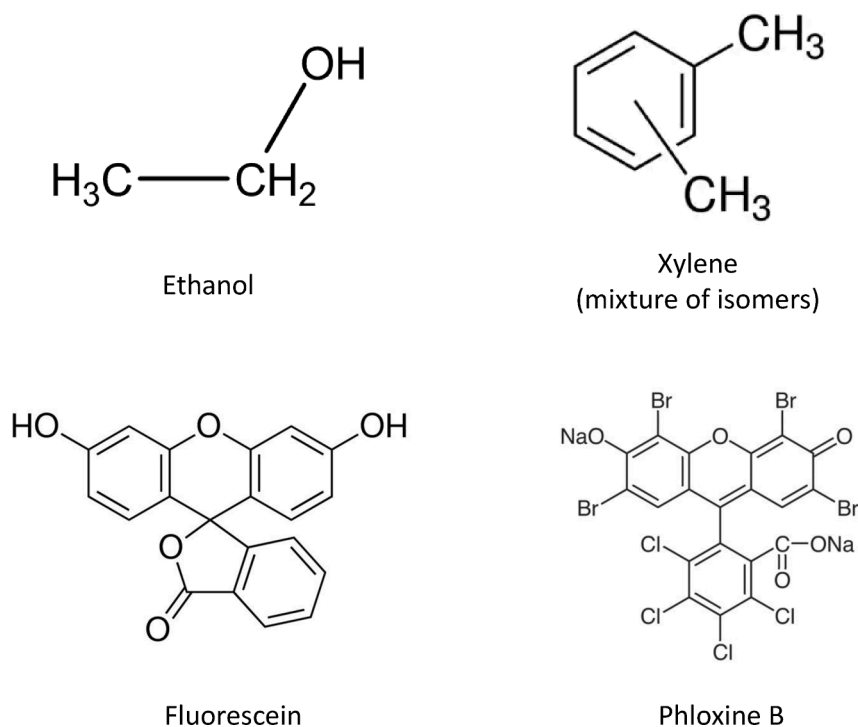


Fig. 1. Chemical structure of the components used in this study.

by using a refractometer. Further, it is important to note that dye solubility must always be considered during dilution.

For the preparation of our mixtures, both dyes were diluted in the solvent as follows: First, the mass of the dye was fixed. Then, the number of moles of the dye, n_{Dye} , was calculated as $n_{Dye} = \frac{m}{M}$, where m , is the weight of the dye, and M is the molar mass or the molecular weight of the dye. So, for a fixed number of moles of the dye we can estimate the number of moles of the solvent (ethanol, in our case), n_{Eth} , necessary for a given dye mole fraction χ_{Dye} :

$$\chi_{Dye} = \frac{n_{Dye}}{n_{Dye} + n_{Eth}} \Rightarrow n_{Eth} = \frac{n_{Dye} - \chi_{Dye} \cdot n_{Dye}}{\chi_{Dye}} \quad (8)$$

On this way, we can calculate the volume of the solvent (ethanol), V_{Eth} , needed to prepare several dilution solutions for different concentrations using the formula:

$$V_{Eth} = n_{Eth} \cdot V_{M_{Eth}} \quad (9)$$

where $V_{M_{Eth}}$ is the molar volume of the solvent (ethanol, in our case).

Therefore, the solutions were diluted according to the formula shown in Eq. (9). That is, we can know the appropriate volume of the solvent liquid for the desired dye mole fraction.

2.2. Chemicals and materials

Ethanol was purchased from Uvasol® Merck Ltd., 99.9%. Xylene, isomers mixture, was of quality 'purissimum', obtained from Panreac (Barcelona, Spain). Fluorescein dye was purchased from Sigma-Aldrich, Germany, and Phloxine B dye from Aldrich Chemical Company, Inc. USA (Dye content 93%). Table 1 shows some properties of these components.

2.3. Sample preparation

The solutions used in this experiment were prepared by diluting different volumes of pure ethanol with known masses of pure xylene (0.862 g), fluorescein (0.01 g), or Phloxine B (0.002 g) in glass vials with plastic snap-cap in order to minimize the evaporation losses. All measurements of mass were performed in a four decimal place balance (AAA 100LE, AE Adam) with an accuracy of ± 0.0001 g. The RIs were measured with a high-accuracy Abbe refractometer model 60/HR (Bellingham and Stanley Ltd, Tunbridge Wells, UK) with a standard uncertainty of ± 0.0001 and measuring range from 1.36 to 1.86. The values of RI were obtained using sodium D light (589.6 nm). The refractometer was calibrated by using a test sample (a glass test piece) with a known RI supplied with the instrument. A circulating water bath with a constant temperature (293.15 K) was used. The temperature was controlled by a thermostatic water bath (Grant GD120, Grant Instruments Ltd., Cambridge, Great Britain) with temperature stability ± 0.02 K.

Binary mixture solutions were prepared at different mole fractions (see, Tables 2, 4, and 8). The RI of each sample was measured five times. The mean value of these 5 RI measurements, n_E , was considered the final result.

Table 1

Some properties of the components used in the experiment: Molecular Weight (M.W.), density (ρ), and molar volume (V_M).

| Compound | CAS # | M.W. (g/mol) | ρ (g.cm ⁻³) | V_M (cm ³ .mol ⁻¹) |
|-------------|------------|--------------|------------------------------|---|
| Ethanol | 64-17-5 | 46.07 | 0.79 | 58.3 |
| Xylene | 1330-20-7 | 106.17 | 0.862 | 123.4 |
| Fluorescein | 2321-07-5 | 332.31 | 1.5 | 221.5 |
| Phloxine B | 18472-87-2 | 829.66 | 0.65 | 1276.4 |

3. Results and discussion

Calculated data using Arago-Biot (A-B), Lorentz-Lorenz (L-L), Gladstone-Dale (G-D), Eyring-John (E-J), and Bruggeman equations for different volume fractions of the two binary mixtures, (xylene + ethanol) and (fluorescein + ethanol), are presented in Table 2 and Table 4, respectively. Tables 3 and 5 show the uncertainty calculation for all parameters. The measured RIs are plotted in Fig. 2A and 2B.

First, the effectiveness of the proposed method has been verified using two components whose RIs are already known, xylene ($n_X = 1.4971$) and fluorescein ($n_F = 1.792$). From Tables 2 and 4, it can be observed that all estimated RIs using the mixing rules were reasonably close to the measured values. As shown in Figure 2A, there is an excellent agreement between the experimentally measured RIs, and the theoretical values calculated by mixing rules equations described above. Furthermore, the measured RIs show good linearity with the volume fractions. On the other hand, we also find good accord between the measured RI results related to the binary mixture composed of a solvent and an organic dye (liquid-dye), i.e., (fluorescein + ethanol) (Fig. 2B). Nevertheless, the A-B and G-D models fit the data reasonably well and slightly better than the other models. Both models exhibit very good linearity with the experimentally measured values. As shown in Fig. 2B, a linear relationship between the RI and the volume fraction is clearly established. In summary, at all volume fractions, A-B, L-L, G-D, E-J, and Bruggeman relations give fairly good results. However, A-B and G-D equations are found to be nearer to the experimental results. Hence, both models, A-B and G-D are slightly more suitable.

The uncertainties for each of these parameters were calculated and are listed in Table 3.

The suitability of these rules was also evaluated by means of the absolute average deviation (AAD). The percent AAD (AAD %) was calculated as:

$$AAD(\%) = \frac{100}{N_m} \cdot \sum_{i=1}^{N_m} \left| \frac{P_i^{exp} - P_i^{calc}}{P_i^{exp}} \right| \quad (10)$$

where P^{exp} and P^{calc} are the experimental and calculated values of the RI, respectively. N_m is the number of experimental points considered. So, the AAD (%) between the experimental data and the calculated values are presented in Table 6.

The percent AAD was calculated for all fractions using Eq. (10), and the results obtained were low, demonstrating the suitability of the used mixing rules. On the other hand, a comparison of all AAD values for different mixing rules indicates that A-B and G-D models give very low deviations for both binary mixtures studied. It should be noted that the calculated average deviation values between the A-B and G-D relations are exactly the same for both binary mixtures. According to the literature, this result is expected because of similarities in the functional form of both mixture rules Eq. (1) and Eq. (3) [31]. Finally, the AAD values obtained for the binary mixture (fluorescein + ethanol) show better agreement than for (xylene + ethanol). Moreover, as mentioned above, the results shown in Fig. 2B revealed that both A-B and G-D correlations fitted the data very well, since the application of the A-B and G-D models results in a linear dependence of RI on volume fraction, for both higher and lower volume fraction values; while L-L, E-J, and Bruggeman models lead to a deviation from linearity at high volume fraction values. At all volume fractions, the values obtained from A-B and G-D relations are found to be nearer. For this reason, we propose the evaluation of the RI of the mixtures (liquid-dye) at varying volume fractions using A-B or G-D models.

3.1. Estimation of the refractive index from A-B and G-D mixing rules and evaluation of the goodness of the method.

The parameters φ_1 and φ_2 are the volume fractions of the solute and solvent in the solution, respectively. Since $\varphi_1 + \varphi_2 = 1 \Rightarrow \varphi_1 = 1 - \varphi_2$,

Table 2

Comparison of experimental values of RI (n_E) for (Xylene + ethanol) mixture at 293.15 K with various models. φ_1 and φ_2 are the fraction volumes of xylene and ethanol, respectively.

| χ_1 | χ_2 | V_{Eth} | φ_1 | φ_2 | n_E | A-B | L-L | G-D | E-J | Bruggeman |
|----------|----------|-----------|-------------|-------------|--------|--------|--------|--------|--------|-----------|
| 0 | 1.0 | pure | 0 | 1.0000 | 1.3614 | 1.3614 | 1.3614 | 1.3614 | 1.3614 | 1.3614 |
| 0.1000 | 0.9000 | 4.2645 | 0.1900 | 0.8100 | 1.3876 | 1.3872 | 1.3862 | 1.3872 | 1.3867 | 1.3865 |
| 0.200 | 0.800 | 1.8953 | 0.345 | 0.655 | 1.4084 | 1.4083 | 1.4068 | 1.4083 | 1.4075 | 1.4073 |
| 0.300 | 0.700 | 1.1056 | 0.475 | 0.525 | 1.4259 | 1.4258 | 1.4242 | 1.4258 | 1.4250 | 1.4248 |
| 0.400 | 0.600 | 0.7107 | 0.585 | 0.415 | 1.4413 | 1.4407 | 1.4391 | 1.4407 | 1.4399 | 1.4397 |
| 0.500 | 0.500 | 0.4738 | 0.679 | 0.321 | 1.4535 | 1.4535 | 1.4520 | 1.4535 | 1.4528 | 1.4525 |
| 0.600 | 0.400 | 0.3159 | 0.760 | 0.240 | 1.4645 | 1.465 | 1.463 | 1.465 | 1.464 | 1.464 |
| 0.70 | 0.30 | 0.2031 | 0.831 | 0.169 | 1.4742 | 1.474 | 1.473 | 1.474 | 1.474 | 1.474 |
| 0.80 | 0.20 | 0.1185 | 0.89 | 0.11 | 1.4827 | 1.483 | 1.482 | 1.483 | 1.482 | 1.482 |
| 0.90 | 0.10 | 0.0526 | 0.95 | 0.05 | 1.4906 | 1.490 | 1.490 | 1.490 | 1.490 | 1.490 |
| 1.00 | 0.00 | 0 | 1.00 | 0.00 | 1.4971 | 1.497 | 1.497 | 1.497 | 1.497 | 1.497 |

Table 3

Uncertainty calculation results for all parameters given in Table 2.

| χ | φ | n_E | A-B | L-L | G-D | E-J | Bruggeman |
|-------------|-------------|-----------|-------------|-------------|-------------|-------------|-------------|
| - | - | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} |
| 2.10^{-4} | 3.10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} |
| 10^{-3} | 10^{-3} | 10^{-4} | 2.10^{-4} | 2.10^{-4} | 2.10^{-4} | 2.10^{-4} | 2.10^{-4} |
| 2.10^{-3} | 2.10^{-3} | 10^{-4} | 3.10^{-4} | 3.10^{-4} | 3.10^{-4} | 3.10^{-4} | 3.10^{-4} |
| 4.10^{-3} | 4.10^{-3} | 10^{-4} | 5.10^{-4} | 6.10^{-4} | 5.10^{-4} | 5.10^{-4} | 6.10^{-4} |
| 6.10^{-3} | 5.10^{-3} | 10^{-4} | 7.10^{-4} | 7.10^{-4} | 7.10^{-4} | 7.10^{-4} | 7.10^{-4} |
| 9.10^{-3} | 7.10^{-3} | 10^{-4} | 10^{-3} | 10^{-3} | 10^{-3} | 10^{-3} | 10^{-3} |
| 0.01 | 7.10^{-3} | 10^{-4} | 10^{-3} | 10^{-3} | 10^{-3} | 10^{-3} | 10^{-3} |
| 0.02 | 0.01 | 10^{-4} | 10^{-3} | 10^{-3} | 10^{-3} | 10^{-3} | 10^{-3} |
| 0.02 | 0.01 | 10^{-4} | 10^{-3} | 10^{-3} | 10^{-3} | 10^{-3} | 10^{-3} |
| 0.03 | 0.01 | 10^{-4} | 10^{-3} | 10^{-3} | 10^{-3} | 10^{-3} | 10^{-3} |

substituting this formula into Eq.(1) and expanding the resulting expression to linear order in φ_2 , in the linear approximation, Eq.(1) may be written as follow:

$$n = n_1(1 - \varphi_2) + n_2\varphi_2 = (n_2 - n_1)\varphi_2 + n_1 \quad (11)$$

On the other hand, substituting $\varphi_1 = 1 - \varphi_2$ into Eq. (3):

$$\begin{aligned} n - 1 &= (n_1 - 1)(1 - \varphi_2) + (n_2 - 1)\varphi_2 \\ n - 1 &= n_1 - 1 - (n_1 - 1)\varphi_2 + (n_2 - 1)\varphi_2 \\ n &= 1 + n_1 - 1 - n_1\varphi_2 + \varphi_2 + n_2\varphi_2 - \varphi_2 \end{aligned} \quad (12)$$

Hence, we can also express the G-D equation (Eq.(3)) as:

$$n = (n_2 - n_1)\varphi_2 + n_1 \quad (13)$$

Therefore, A-B and G-D equations can be expressed as a linear function where the slope m is given by $m = n_2 - n_1$ and the y-intercept (b) of the regression line is the unknown RI of the pure component-1: $b = n_1$.

Using the measured experimental data, the effective RIs, n_E , of the binary mixtures investigated in this study at 293.15 K can be related to volume fraction by the equation:

Table 4

Comparison of experimental values of RI (n_E) for (Fluorescein + ethanol) mixture at 293.15 K with various models. φ_1 and φ_2 are the fraction volumes of fluorescein and ethanol, respectively.

| χ_1 | χ_2 | V_{Eth} | φ_1 | φ_2 | n_E | A-B | L-L | G-D | E-J | Bruggeman |
|---------------|----------|-----------|---------------|-------------|--------|--------|--------|--------|--------|-----------|
| 0 | 1 | pure | 0 | 1 | 1.3614 | 1.3614 | 1.3614 | 1.3614 | 1.3614 | 1.3614 |
| 10^{-4} | 0.999900 | 17.5602 | 4.10^{-4} | 0.999600 | 1.3616 | 1.3616 | 1.3615 | 1.3616 | 1.3616 | 1.3615 |
| 2.10^{-4} | 0.999800 | 8.7792 | 8.10^{-4} | 0.999200 | 1.3617 | 1.3617 | 1.3617 | 1.3617 | 1.3617 | 1.3617 |
| 3.10^{-4} | 0.999700 | 5.8522 | $1.1.10^{-4}$ | 0.99890 | 1.3619 | 1.3619 | 1.3618 | 1.3619 | 1.3619 | 1.3618 |
| 4.10^{-4} | 0.999600 | 4.3887 | $1.5.10^{-4}$ | 0.99850 | 1.3621 | 1.3621 | 1.3620 | 1.3621 | 1.3620 | 1.3620 |
| 5.10^{-4} | 0.999500 | 3.5106 | $1.9.10^{-4}$ | 0.99810 | 1.3622 | 1.3622 | 1.3621 | 1.3622 | 1.3622 | 1.3621 |
| 6.10^{-4} | 0.999400 | 2.9252 | $2.3.10^{-4}$ | 0.99770 | 1.3624 | 1.3624 | 1.3622 | 1.3624 | 1.3623 | 1.3623 |
| 7.10^{-4} | 0.999300 | 2.5071 | $2.7.10^{-4}$ | 0.99730 | 1.3625 | 1.3625 | 1.3624 | 1.3625 | 1.3625 | 1.3624 |
| 8.10^{-4} | 0.999200 | 2.1935 | 3.10^{-4} | 0.99700 | 1.3627 | 1.3627 | 1.3625 | 1.3627 | 1.3626 | 1.3626 |
| 9.10^{-4} | 0.99910 | 1.9496 | $3.4.10^{-4}$ | 0.99660 | 1.3629 | 1.3629 | 1.3627 | 1.3629 | 1.3628 | 1.3627 |
| 10^{-3} | 0.99900 | 1.7544 | $3.8.10^{-4}$ | 0.99620 | 1.3630 | 1.3630 | 1.3628 | 1.3630 | 1.3629 | 1.3629 |
| $1.1.10^{-3}$ | 0.99890 | 1.5948 | $4.2.10^{-4}$ | 0.99580 | 1.3632 | 1.3632 | 1.3629 | 1.3632 | 1.3631 | 1.3630 |

$$n_E = m \cdot \varphi_2 + b \quad (14)$$

where φ_2 is the volume fraction of ethanol, m is the slope or gradient, and b is the y-intercept.

The uncertainties can be determined by taking the difference between the high and low values of the slope and dividing by 2. These calculations are shown below:

Uncertainty in the Slope:

$$\Delta_{Slope} = \frac{m_{max} - m_{min}}{2} \quad (15)$$

Uncertainty in the Y-Intercept:

$$\Delta_{y-intercept} = \frac{b_{max} - b_{min}}{2} \quad (16)$$

The linear relationships of the effective RI with the volume fraction of ethanol were linearly fitted by Matlab® software (MathWorks Inc.). We used Curve Fitting Tool in Matlab to fit the effective RI with variable parameters m and b (95% Confidence Interval (CI)). In the case of the mixture of (xylene + ethanol), for example, the fitting curve can be expressed as: $n_x = -0.1356 \cdot \varphi_2 + 1.4971$, n_x is the effective RI of the binary mixture (xylene + ethanol) and φ_2 is the volume fraction of the ethanol.

As can be seen from Table 7, by using A-B model or G-D, we can estimate the RIs of the pure components with good accuracy: xylene ($n_x = 1.4971 \pm 0.0003$) and fluorescein ($x_f = 1.79 \pm 0.01$). If we compare the value of the results obtained in this experiment with those reported in the literature $n_x = 1.4971$ and $n_f = 1.792$, respectively, these results corroborate existing literature findings [16,17].

Eq. (14) shows that the RI of a pure component can be calculated directly using the measured value for the RI of the binary mixture. Hence, we used the A-B and G-D models to determine the unknown RI of an organic dye (Phloxine B). Table 8 summarizes the effective RI of the binary mixture (Phloxine B + ethanol). Uncertainty calculations are given in Table 9. So, we can determine that the RI of Phloxine B, n_B , is

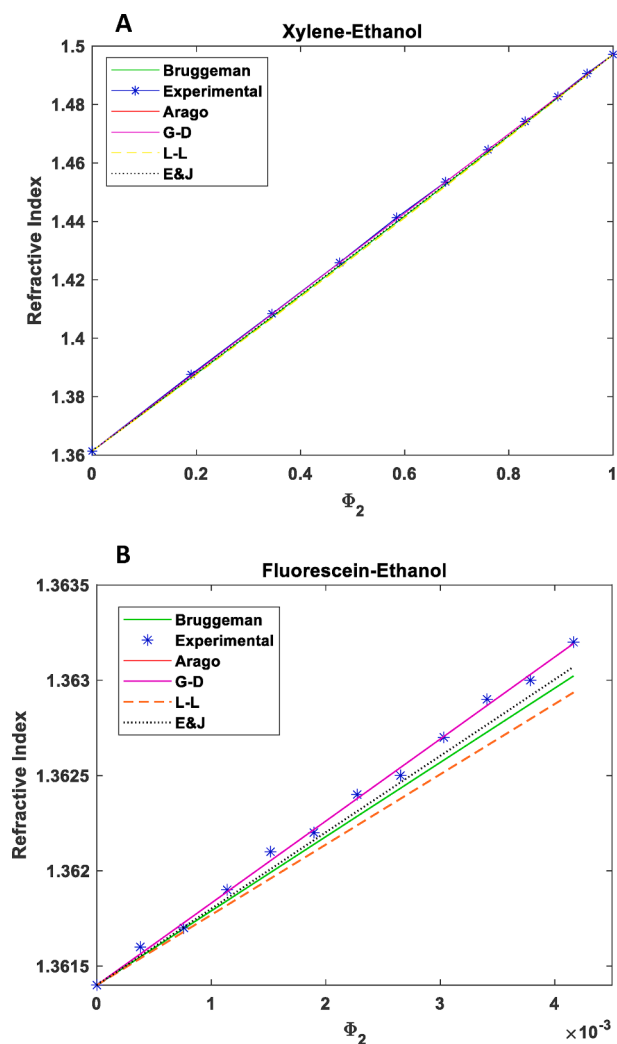


Fig. 2. Effective refractive index as a function of volume fraction for (xylene + ethanol) mixture (A) and (fluorescein + ethanol) (B) at various mole fractions. The curves represent the experimental data and values calculated from Eq. (1.5).

Table 5
Uncertainty calculation results for all parameters given in Table 4.

| χ | φ | n_E | A-B | L-L | G-D | E-J | Bruggeman |
|-------------|-------------|-----------|-----------|-----------|-----------|-----------|-----------|
| – | – | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} |
| 10^{-6} | 4.10^{-6} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} |
| 2.10^{-6} | 8.10^{-6} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} |
| 3.10^{-6} | 10^{-5} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} |
| 4.10^{-6} | 2.10^{-5} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} |
| 5.10^{-6} | 2.10^{-5} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} |
| 6.10^{-6} | 2.10^{-5} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} |
| 8.10^{-6} | 3.10^{-5} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} |
| 9.10^{-6} | 3.10^{-5} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} |
| 10^{-5} | 4.10^{-5} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} |
| 10^{-5} | 4.10^{-5} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} |
| 10^{-5} | 4.10^{-5} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} | 10^{-4} |

($n_B = 1.8205 \pm 0.0005$), calculated from the experimental data using A-B model.

Based on the results in the current study, we suggest that the A-B and G-D mixing rules offer the best experimental data fit of binary mixture systems formed by a solid (dye) and liquid compound. Altogether A-B and G-D models perform the best of all methods and show good agreement with experimental values. It is important to note that these

Table 6

The percent absolute average deviation (AAD %) for various mixing rules at 293.15 K.

| AAD (%) | A-B | L-L | G-D | E-J | Bruggeman |
|-----------------------|-------|------|-------|-------|-----------|
| Xylene + Ethanol | 0.01 | 0.07 | 0.01 | 0.04 | 0.05 |
| Fluorescein + Ethanol | 0.002 | 0.01 | 0.002 | 0.005 | 0.007 |

Table 7

RI correlation at varying volume fractions.

| Binary mixture | m | b |
|-----------------------|------------------------------------|---------------------------------|
| Xylene + Ethanol | $-0.1356; (CI = -0.1360, -0.1351)$ | $1.4971; (CI = 1.4969, 1.4974)$ |
| Fluorescein + Ethanol | $-0.4269; (CI = -0.4412, -0.4125)$ | $1.7883; (CI = 1.7740, 1.8026)$ |

Table 8

Experimental values of RI (n_E) for (Phloxine B + ethanol) mixture at 293.15 K. φ_1 and φ_2 are the fraction volumes of Phloxine B and ethanol, respectively.

| χ_1 | χ_2 | V_{Eth} | φ_1 | φ_2 | n_E |
|-------------|-----------|-----------|-------------|-------------|--------|
| 0 | 1 | pure | 0 | 1 | 1.3614 |
| 10^{-5} | 0.9999900 | 14.0683 | 0.000200 | 0.999800 | 1.3615 |
| 2.10^{-5} | 0.9999800 | 7.0341 | 0.00040 | 0.99960 | 1.3616 |
| 3.10^{-5} | 0.999970 | 4.6893 | 0.00070 | 0.99930 | 1.3617 |
| 4.10^{-5} | 0.999960 | 3.5170 | 0.00090 | 0.99910 | 1.3618 |
| 5.10^{-5} | 0.999950 | 2.8135 | 0.00110 | 0.99890 | 1.3619 |
| 6.10^{-5} | 0.999940 | 2.3446 | 0.00130 | 0.99870 | 1.3620 |
| 7.10^{-5} | 0.999930 | 2.0096 | 0.00150 | 0.99850 | 1.3621 |
| 8.10^{-5} | 0.999920 | 1.7584 | 0.00170 | 0.99830 | 1.3622 |
| 9.10^{-5} | 0.999910 | 1.5630 | 0.00200 | 0.99800 | 1.3623 |
| 10^{-4} | 0.999900 | 1.4067 | 0.00220 | 0.99780 | 1.3624 |
| 2.10^{-4} | 0.999800 | 0.7033 | 0.0044 | 0.9956 | 1.3634 |

Table 9

Uncertainty Calculation Result for all parameters given in Table 8.

| χ | φ | n_E |
|-------------|-------------|-----------|
| – | – | 10^{-4} |
| 4.10^{-7} | 9.10^{-6} | 10^{-4} |
| 8.10^{-7} | 2.10^{-5} | 10^{-4} |
| 10^{-6} | 2.10^{-5} | 10^{-4} |
| 2.10^{-6} | 4.10^{-5} | 10^{-4} |
| 2.10^{-6} | 4.10^{-5} | 10^{-4} |
| 3.10^{-6} | 7.10^{-5} | 10^{-4} |
| 3.10^{-6} | 7.10^{-5} | 10^{-4} |
| 3.10^{-6} | 7.10^{-5} | 10^{-4} |
| 4.10^{-6} | 9.10^{-5} | 10^{-4} |
| 4.10^{-6} | 9.10^{-5} | 10^{-4} |
| 9.10^{-6} | 2.10^{-4} | 10^{-4} |

equations can only be applied if there are no chemical reactions in the mixture and if there are no changes in volume during mixing [32].

4. Conclusions

Nowadays, the interest in organic dyes is growing and has attracted wide research interest from academia and industry owing to the unique characteristics offered by these materials such as the optoelectronic tuneability, cost-effectiveness, architectural flexibility, and photo-physical feature. The most important parameters of the dyes are the optical energy gap, RI, dielectric constant, and optical conductivity. The RI of natural dyes, however, is useful to estimate their purity, viscosity, and other thermodynamic properties. In the present work, we give a very simple method to obtain the refractive indices of organic dyes using

the knowledge of the RI of the pure solvent used to dilute the dye. To measure an unknown RI of a pure organic dye, experimental data of a binary mixture composed of an organic dye and ethanol were considered to evaluate the suitability of some mixture models.

Our results show that all estimated refractive indices using the mixing rules were reasonably close to the measured values, being the best of them the Arago–Biot and Gladstone–Dale relations, both models show good agreement with theoretical values. We find that we can estimate the pure refractive indices in the range of (1.4969–1.4974) and (1.7740–1.8026) for xylene and fluorescein, respectively, which lie close to the values reported in the literature (1.4971 for the xylene and 1.792 for the fluorescein). On the other hand, the RI of the Phloxine B dye was not available in the literature, for this reason, mixture rules were also used to evaluate the RI of Phloxine B dye. Our results show that the RI of Phloxine B dye, measured at a temperature of 20 °C and a wavelength of 589.6 nm, was given to be between 1.820 and 1.821. In conclusion, this method is a simple way of obtaining the RI of organic dyes. Further experiments are clearly called for in order to test the applicability of the method to other organic dyes.

CRedit authorship contribution statement

Ouafa Sijilmassi: Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Pilar García Parejo:** Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Supervision. **Alberto Álvarez Herrero:** Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

First of all, the author Ouafa Sijilmassi would like to express her sincere gratitude to the Space Optics Department at the National Institute for Aerospace Technology (Instituto Nacional de Técnica Aeroespacial - INTA), for granting her the privilege to carry out this research at their laboratory and providing facilities for the study. This research was funded by a postdoctoral fellowship awarded by Complutense University of Madrid (CT31/21) and financed by the Ministry of Universities with Next Generation funds from the European Union “European UnionNextGenerationEU”.

References

- [1] S. Singh, Refractive index measurement and its applications, *Phys. Scr.* 65 (2002) 167.
- [2] R. Khan, B. Gul, S. Khan, H. Nisar, I. Ahmad, Refractive index of biological tissues: review, measurement techniques, and applications, *Photodiagnosis Photodyn Ther.* 33 (2021), 102192.
- [3] H. Ding, J.Q. Lu, W.A. Wooden, P.J. Kragel, X.-H. Hu, Refractive indices of human skin tissues at eight wavelengths and estimated dispersion relations between 300 and 1600 nm, *Phys. Med. Biol.* 51 (2006) 1479.
- [4] S. Mohan, E. Kato, J.K. Drennen III, C.A. Anderson, Refractive index measurement of pharmaceutical solids: a review of measurement methods and pharmaceutical applications, *J. Pharm. Sci.* 108 (2019) 3478–3495.
- [5] M. Rieder, Variation of physical properties across the mineralogical system, *Phys. Chem. Miner.* 47 (2020) 1–6.
- [6] J.-g. Liu, M. Ueda, High refractive index polymers: fundamental research and practical applications, *J. Mater. Chem.* 19 (2009) 8907–8919.
- [7] V.V. Tuchin, L. Wang, D.A. Zimnyakov, *Optical polarization in biomedical applications*, Springer Science & Business Media, 2006.
- [8] I. Ahmad, M. Ahmad, K. Khan, M. Ikram, Polarimetry based partial least square classification of ex vivo healthy and basal cell carcinoma human skin tissues, *Photodiagnosis. Photodyn. Ther.* 14 (2016) 134–141.
- [9] M. Rashidian, D. Dorrani, S.A. Darani, S. Saghafi, M. Ghorannevis, Nonlinear responses and optical limiting behavior of Basic Violet 16 dye under CW laser illumination, *Optik* 120 (2009) 1000–1006.
- [10] S.R. Nersisyan, N.V. Tabiryan, D.M. Steeves, B.R. Kimball, V.G. Chigrinov, H. S. Kwok, Study of azo dye surface command photoalignment material for photonics applications, *Appl. Opt.* 49 (2010) 1720–1727.
- [11] O.S. Khudhair, A.O. Mousa, S.R. Rassol, The effect of mixing two organic dyes on the optical linear properties, *Nveo-Nat. Volatiles & Essential Oils J.* | NVEO. (2021) 8128–8138.
- [12] Q.M.A. Hassan, Nonlinear optical and optical limiting properties of chicao sky blue 6B doped PVA film at 633 nm and 532 nm studied using a continuous wave laser, *Mod. Phys. Lett. B* 22 (2008) 1589–1597.
- [13] J.-L. Meyzonnette, J. Mangin, M. Cathelinaud, Refractive index of optical materials, Springer, Springer Handbook of Glass, 2019, pp. 997–1045.
- [14] V.V. Sechenyh, J.-C. Legros, V. Shevtsova, Experimental and predicted refractive index properties in ternary mixtures of associated liquids, *J. Chem. Thermodyn.* 43 (2011) 1700–1707.
- [15] M.A. Rahman, Q. Galand, M. Soliman, S. Van Vaerenbergh, M. Saghir, Measurement of refractive indices of binary mixtures using digital interferometry and multi-wavelength Abbemat refractometer, *Opt. Lasers Eng.* 51 (2013) 503–513.
- [16] ChemSpider. Xylene. <https://itwreagents.com/italy/en/product/xylene-mixture-of-isomers%20pure/141769>.
- [17] ChemSpider. Fluorescein. http://www.chemspider.com/Chemical-Structure.15968.html?rid=29799443-c4d8-427f-a751-bf4817a669ea&page_num=0.
- [18] S. Isehunwa, E. Olanisebe, O. Ajiboye, S. Akintola, Estimation of the refractive indices of some binary mixtures, *Afr. J. Pure Appl. Chem.* 10 (2015) 58–64.
- [19] Bhatia SC, Tripathi N, Dubey GP. Refractive indices of binary liquid mixtures of squalene with benzene, cyclohexane and hexane at 298.15 to 313.15 K. 2001.
- [20] F. Aliaj, N. Syla, A. Kurtishaj, N. Elezaj, Z. Tolaj, T. Arbneshi, et al., Densities, refractive indices, and derived properties of binary mixtures of ethanol with benzene and pyridine at various temperatures under atmospheric pressure, *Int. J. Thermophys.* 41 (2020) 1–17.
- [21] Lorentz H. The Theory of Electrons and Its Application to the Phenomena of Light and Radiant Heat, II edition (Leipzig, 1916). A course of lectures delivered at Columbia University, New York, March and April. 1906:132.
- [22] H. Kragh, The lorentz-lorentz formula: origin and early history, *Substantia* 2 (2018) 7–18.
- [23] V.D. Bruggeman, Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen, *Ann. Phys.* 416 (1935) 636–664.
- [24] O. Iulian, A. Stefanu, O. Ciocirlan, A. Fedeleş, Refractive index in binary and ternary mixtures with diethylene glycol, 1, 4-dioxane and water between 293.15–313.15 K, *UPB Sci. Bull. Ser. B Chem. Mater. Sci.* 72 (2010) 37–44.
- [25] D. Arago, J. Biot, Refractive properties of binary mixtures, *Mem. Acad. Fr.* 15 (1806) 7–11.
- [26] H. Lorentz, On the lorentz-lorentz formula and model of dielectric, *Annalen. Der. Physik.* 9 (1880) 641–665.
- [27] T.P. Dale, J.H. Gladstone, On the influence of temperature on the refraction of light, *Philos. Trans. R. Soc. Lond.* 148 (1858) 887–894.
- [28] Eyring H, Jhon MS. Significant liquid structures. 1969.
- [29] W. Heller, Remarks on refractive index mixture rules, *J. Phys. Chem.* 69 (1965) 1123–1129.
- [30] E.H. Amagat, Mémoire sur la compressibilité des gaz à des pressions élevées, *Ann. Chim. Phys.* 19 (1880) 345.
- [31] T.M. Aminabhavi, H.T. Phayde, R.S. Khinnavar, B. Gopalakrishna, H.K.C. Densities, refractive indices, speeds of sound, and shear viscosities of diethylene glycol dimethyl ether with ethyl acetate, methyl benzoate, ethyl benzoate, and diethyl succinate in the temperature range from 298.15 to 318.15 K, *J. Chem. Eng. Data.* 39 (1994) 251–260.
- [32] M. Yahya, M.Z. Saghir, Prediction and experimental measurement of refractive index in ternary hydrocarbon mixtures, *J. Chem. Eng. Data.* 60 (2015) 2329–2342.