

Published as: Pretorius, F., Focke, W. W., Androsch, R. & Du Toit, E. 2021. Estimating binary liquid composition from density and refractive index measurements: A comprehensive review of mixing rules. *Journal of Molecular Liquids*, 332, 115893.

Estimating binary liquid composition from density and refractive index measurements: A comprehensive review of mixing rules

Franco Pretorius ^a, Walter W Focke ^a, René Androsch ^b, Elizabeth du Toit ^a

^a UP Institute for Sustainable Malaria Control & MRC Collaborating Centre for Malaria Research, University of Pretoria, Private Bag X20, Hatfield 0028, Pretoria, South Africa, Pretoria, South Africa

^b Interdisciplinary Center for Transfer-oriented Research in Natural Sciences, Martin Luther University Halle-Wittenberg, D-06099 Halle/Saale, Germany

Correspondence to: Walter Focke, walter.focke@up.ac.za

Highlights

- Most refractive index mixture models are linear in either mole- or volume fraction
- Models linear in volume fraction fail to predict mixture composition data accurately
- Excellent predictions with Lorentz-Lorenz molar refraction model linear in mole fraction
- Real binary mixtures considered behave ideally with respect to molar refraction

Abstract

A comprehensive review of refractive index mixing rules of binary solutions is presented. All published mixing rules, with the exception of the Wiener mixing rule, can be reformulated into expressions with a linear dependence in either mole- or volume-fractions. Comparison of the predictive performance of both types of linear mixture models show that mixture models which are linear in volume fractions fail to represent real data trends. Mixture refractive index data reveal that both positive and negative deviations from linear behaviour in this property with volume fraction can occur, explaining the inability of linear models in volume fraction to be generally applicable. Improved data fits are possible with the modified Eykman and the power mean mixing rules, provided that in both cases the adjustable constant can be tuned for each binary system of interest. Only the Lorentz-Lorenz molar refraction mixing rule that is linear in mole fraction provides excellent data fits for all the systems investigated, allowing for prediction of

composition of solutions from combined density and refractive index measurements. The aforementioned conclusions are derived from extensive experimental data of binary systems consisting of *n*-alkanes (C12 to C32) and different organic solvents, ultimately providing a tool to determine liquid composition from refractive index measurements.

Keywords: refractive index; molar refraction; mixing rules; composition estimates; liquid mixtures

1. INTRODUCTION

Standardised procedures, based on refractive index (RI) and/or density, are well established techniques for characterising liquids [1]. For example, they are widely used to determine the sugar content of soft drinks, the alcohol concentration in beer, wine and spirits, and even hand sanitiser formulations, etc. [2] The importance of such RI measurements is bound to increase considering recent advances in instrumentation, particularly in the utilisation of lasers and fibre-based sensor systems [3-6]. This holds promise for real-time, in-line RI data acquisition in refineries and other chemical plants for improved process- and product-quality control. This implies a need for algorithms that will allow RI data interpretation to an accuracy level that is acceptable for engineering applications (errors within 1 – 2 mol%). For that purpose, it is important to assess whether existing RI-mixture rules can be exploited to develop predictive equations for composition determination from RI measurement data that conform to this requirement.

Depending on the equipment used, RI measurements can be supplemented by various combinations of other mixture property data. Depending on these mixture property measurements and the availability of information for the pure components, different ways of estimating the mixture composition should be considered when the applicability of RI mixture rules are assessed. The different measurement possibilities are as follows:

- Case A: Temperature and density of the solution are measured
- Case B: Temperature, mixture-density and -refractive index are measured
- Case C: Mixture-density and -refractive index are measured but the temperature is unknown
- Case D: Temperature and the mixture refractive index are measured

The aim of this work is therefore to derive workable equations for composition prediction for each of the above cases by considering existing RI mixing rules.

Towards this goal, available, mainly predictive, mixing rules for the refractive index of mixtures are thoroughly reviewed. Methods for calculating mixture composition, subject to the availability of data

according to the four scenarios listed above, are subsequently developed. Here it is assumed that correlations are available for the variation of the pure component properties, i.e., density and refractive index, with temperature. In order to assess the predictive capability of the respective equations, literature RI data of binary mixtures of *n*-alkanes with other, mainly polar, organic components with known composition are considered. In addition, some of the underlying assumptions regarding the temperature dependent RI - behaviour of pure *n*-alkanes are confirmed by experimental measurements. These are applied during model development. The ultimate hope is that one or more predictive correlations can be found that will yield acceptable composition estimates from knowledge of refractive index information.

2. THEORY: MOLAR VOLUME AND REFRACTIVE INDEX OF IDEAL SOLUTIONS

The molar refraction (R) for nonpolar, nonmagnetic materials is defined [7] as

$$R = \alpha N_A / (3\epsilon_0) \quad (1)$$

where α is the mean molecular polarizability; N_A is Avogadro's number; and ϵ_0 is the permittivity of free space. For a fluid of hard-core spheres of uniform size, the polarizability is given by:

$$\alpha = 4\pi\epsilon_0 a^3 \quad (2)$$

where a represents the sphere radius. Substitution of equation (2) into equation (1) results in:

$$R = \frac{4\pi}{3} N_A a^3 \quad (3)$$

For such a hypothetical fluid, the molar refraction can be interpreted as the hard core volume of one mole of spherical molecules of radius a [7]. These expressions have found utility for real organic liquids and their mixtures despite the fact that they were derived on the basis of extremely simple models.

2.1. Pure compounds

The Lorentz–Lorenz relationship links the molar refraction with the refractive index (n) and the molar volume (V) [8]:

$$R = V \frac{n^2 - 1}{n^2 + 2} \quad (4)$$

where the molar volume V is defined by the ratio of the molar mass (M) to the density (ρ) of the compound, i.e., M/ρ . Experimental evidence indicates that the molar refraction of a pure compound is approximately temperature invariant [9]. Furthermore, for hydrocarbons, including alkanes, the so-called “one third rule” applies which states [9]:

$$\frac{R}{M} = \frac{1}{\rho} \left(\frac{n^2 - 1}{n^2 + 2} \right) \approx \frac{1}{3} \quad (5)$$

2.2. Mixtures

The molar volume of an ideal binary solution follows the linear mixing rule:

$$V = V_1 x_1 + V_2 x_2 \quad (6)$$

where $V_i = M_i/\rho_i$, M_i is the molar mass, ρ_i the density and x_i is the mole fraction of component i . When the mixture density data are known, the molar volume behaves as for an ideal solution, and since $x_1 + x_2 = 1$, equation (6) allows the composition to be calculated from:

$$\frac{1}{x_1} = 1 - \frac{\rho_2 M_1 (\rho_1 - \rho)}{\rho_1 M_2 (\rho_2 - \rho)} \quad (7)$$

Theoretical considerations [10] suggest that the molar refraction of an ideal binary liquid mixture is also additive on a mole fraction basis:

$$R = R_1 x_1 + R_2 x_2 \quad (8)$$

Substitution of R from equation (4) in equation (8) yields the Lorentz-Lorenz R -mixing ($L-L-R$) rule:

$$V \frac{n_{mix}^2 - 1}{n_{mix}^2 + 2} = V_1 x_1 \frac{n_1^2 - 1}{n_1^2 + 2} + V_2 x_2 \frac{n_2^2 - 1}{n_2^2 + 2} \quad (9a)$$

or, expressed in a more general, compact and more legible form:

$$R = VN = x_1 V_1 N_1 + x_2 V_2 N_2 \quad (9b)$$

where the following definitions were applied

$$N = (n_{mix}^2 - 1)/(n_{mix}^2 + 2) \quad \text{and} \quad N_i = (n_i^2 - 1)/(n_i^2 + 2) \quad (10)$$

The calculation of the molar refraction R of a mixture requires information about the density and the refractive index. When both are available, the composition of the mixture can be established directly in terms of the mole fraction of component 1:

$$\frac{1}{x_1} = 1 - \frac{\rho_2 M_1 (\rho N_1 - \rho_1 N)}{\rho_1 M_2 (\rho N_2 - \rho_2 N)} \quad (11)$$

Density data for the pure components, at the mixture temperature, are required when applying equation (11). However, this is not essential. If the molar refractions R_1 and R_2 are known and temperature-invariant, then $R_i = M_i N_i / \rho_i$. Thus, the composition can also be estimated with a different expression:

$$\frac{1}{x_1} = 1 - \frac{NM_1 - \rho R_1}{NM_2 - \rho R_2} \quad (12)$$

Its application allows direct calculation of the component mole fractions from measurements of just the density and the refractive index of the mixture. In other words, it is not necessary to know the temperature.

When there is no information available for the mixture density, another approach must be followed. The required relationship is labelled the Lorentz-Lorenz N -mixing rule ($L-L-N$) which is established by combining equation (6) and equation (9). This gives

$$\frac{n_{mix}^2 - 1}{n_{mix}^2 + 2} = \varphi_1 \frac{n_1^2 - 1}{n_1^2 + 2} + \varphi_2 \frac{n_2^2 - 1}{n_2^2 + 2} \quad (13a)$$

or

$$N = \varphi_1 N_1 + \varphi_2 N_2 \quad (13b)$$

The volume fraction, at the mixture temperature, is defined in terms of the pure component molar volumes (V_i) as follows:

$$\varphi_i \equiv V_i x_i / (V_1 x_1 + V_2 x_2) \quad (14)$$

Numerous studies found that, for many real mixtures, predictions of mixture refractive indices according to the modified Lorentz-Lorenz relationship, i.e. the $L-L-N$ mixing rule of equation (13), agree reasonably well with experimental results [8] [11] [12] [13]. Equation (13) allows direct estimation of the volume fraction of an equilibrium phase from refractive index measurements, expressed in terms of N -values as follows:

$$\varphi_1 = (N - N_2) / (N_1 - N_2) \quad (15)$$

The n_i values must be known at the mixture temperature in order to calculate the N_i . The mole fraction and mass fraction can then be established from the following relationships:

$$\frac{1}{x_1} = 1 - \frac{N_2 R_1 (N - N_1)}{N_1 R_2 (N - N_2)} \quad (16)$$

and

$$w_1 = M_1 x_1 / (M_1 x_1 + M_2 x_2) \quad (17)$$

Equation (16) shows that the mole fraction of component 1 can be calculated directly using the measured value for the refractive index of the mixture. However, knowledge of the pure component values at the system temperature are required.

It is worth recalling the basic assumptions that underlie the key expressions developed for estimating the composition of binary mixtures. Both equation (11), equation (12) and equation (16) assume that the molar refraction corresponds to the expectations for an ideal solution as expressed by equation (8). Use of equation (11) also requires knowledge of the mixture and component densities in addition to refractive index data. In contrast, equation (16) does not require density data for the mixture for its application. However, it relies on the additional assumption that the molar volume follows the expression applicable to an ideal solution as stated in equation (6). Furthermore, if both properties conform to the expectations for an ideal solution, the following expression holds:

$$N = \frac{\rho_2 M_1 N_1 x_1 + \rho_1 M_2 N_2 x_2}{\rho_2 M_1 x_1 + \rho_1 M_2 x_2} \quad (18)$$

Equation (18) represents the simplest mixing rule for ideal solutions. It indicates that the mixture refractive index is fully defined by knowledge of the densities, molar masses and refractive indices of the pure individual components.

Table 1 summarises the relationships derived for the different measurement cases. Note that in some cases it is assumed that the system temperature is also known and that correlations exist for calculating the required pure component properties.

Table 1. Different measurement combinations for temperature (T), density (ρ) and refractive index (n)

Case	T	ρ	n	Assumptions	Known	Measured	Expression for x_1
A	✓	✓		$V = V_1 x_1 + V_2 x_2$	M_1, M_2, ρ_1, ρ_2	ρ	$\left[1 - \frac{\rho_2 M_1}{\rho_1 M_2} \left(\frac{\rho_1 - \rho}{\rho_2 - \rho} \right) \right]^{-1}$
B	✓	✓	✓	$R = R_1 x_1 + R_2 x_2$	$M_1, M_2, \rho_1, \rho_2, n_1, n_2$	ρ, n	$\left[1 - \frac{\rho_2 M_1 (\rho N_1 - \rho_1 N)}{\rho_1 M_2 (\rho N_2 - \rho_2 N)} \right]^{-1}$
C		✓	✓	$R = R_1 x_1 + R_2 x_2$ $R_i \neq f(T)$	M_1, M_2, R_1, R_2	ρ, n	$\left[1 - \frac{NM_1 - \rho R_1}{NM_2 - \rho R_2} \right]^{-1}$
D	✓		✓	$V = V_1 x_1 + V_2 x_2$ $R = R_1 x_1 + R_2 x_2$	R_1, R_2, n_1, n_2	n	$\left[1 - \frac{N_2 R_1 (N - N_1)}{N_1 R_2 (N - N_2)} \right]^{-1}$

2.3. Alternative mixing rules

Numerous other mixing rules have been proposed with the hope to improve the Lorentz-Lorenz approach detailed above. Eyring and John [14] and Lichtenecker [15] proposed nonlinear mixing rules for the refractive index (n). However, as shown below, their proposals can be recast in linear forms:

$$\text{Eyring and John:} \quad n = \left(\varphi_1 \sqrt{n_1} + \varphi_2 \sqrt{n_2} \right)^2 \quad (19a)$$

$$\sqrt{n} = \varphi_1 \sqrt{n_1} + \varphi_2 \sqrt{n_2} \quad (19b)$$

$$\text{Lichtenecker:} \quad n = n_1^{\varphi_1} n_2^{\varphi_2} \quad (20a)$$

$$\ell n(n) = \varphi_1 \ell n(n_1) + \varphi_2 \ell n(n_2) \quad (20b)$$

Table 2. Summary of the mixing rules proposed in the literature including possible definitions for the variable N in equation (9) or in equation (13b)

Model type	Model	Expression	Reference
$VN = V_1 N_1 x_1 + V_2 N_2 x_2$	Lorentz-Lorenz Eykman	$d = 2$	[16]
with	Modified Eykman	$d = 0.4$	[17]
$N = (n^2 - 1)/(n^2 + d)$		variable d	
$VN = V_1 N_1 x_1 + V_2 N_2 x_2$	Oster	$N = (n^2 - 1)(2n^2 + 1)/n^2$	[18]
with revised	Looyenga	$N = n^{2/3} - 1$	[19]
expressions	Arago-Biot	$N = n$	[20]
for N	Dale-Gladstone	$N = n - 1$	[21]
	Newton	$N = n^2 - 1$	[22]
Volume fraction	Lichtenecker	$p = 0$	[15]
weighted	Eyring	$p = 1/2$	[14]
power mean	Looyenga	$p = 2/3$	[19]
of order p :	Arago-Biot &	$p = 1$	[20]
$n = \left(\varphi_1 n_1^p + \varphi_2 n_2^p \right)^{1/p}$	Dale-Glastone		[21]
	Newton	$p = 2$	[22]
		p variable	This study
Complex models	Heller (valid for low values of φ_2)	$\varphi_2 = \frac{2(n - n_1) \left[n_2^2 + 2n_1^2 \right]}{3n_1 (n_2^2 - n_1^2)}$	[15]
	Wiener	$\varphi_2 = \left(\frac{n^2 - n_1^2}{n_2^2 - n_1^2} \right) \left(\frac{n_2^2 + 2n_1^2}{n^2 + 2n_1^2} \right)$	[15, 23]

This means that most proposals introduced changes to the expression used for N but retained the linear composition dependence on the volume fraction as defined by equation (13b). Comparison of the linear forms of the Eyring and John [14] and Lichtenecker, as well as numerous other mixture rule proposals, reveals that they correspond to the same family of volume-fraction-weighted power means of order p defined by:

$$n_p = \left(\varphi_1 n_1^p + \varphi_2 n_2^p \right)^{1/p} \quad (21)$$

This expression includes the geometric mixing rule defined by Lichtenecker, as it corresponds to the limiting case where the power index approaches zero from above ($p \rightarrow 0^+$). Table 2 summarizes the mixing rules reported in the literature for the refractive index of binary mixtures. Note that most investigators retain the “1” found in the expressions for N in the Looyenga, Arago-Biot, Dale-Gladstone and Newton expressions, even when they use it in the volume fraction mixing rule. This is superfluous, as the volume fractions add up to unity, i.e. $\varphi_1 + \varphi_2 = 1$.

More complex models include the proposals by Heller [15] and Wiener [23]. The Heller model is limited to low concentrations of the dispersed phase, i.e., φ_2 , while the Wiener [23] equation is valid over the full composition range. It can be shown that Wiener’s proposal is equivalent to the following Padé-type mixing rule:

$$n^2 = \frac{n_1^4 \varphi_1 + 2n_1^2 n_2^2 + n_2^4 \varphi_2}{n_1^2 (2 - \varphi_1) + n_2^2 (2 - \varphi_2)} \quad (22)$$

Several studies compared the relative performance of some of the mixture models listed in Table 2 [24-27]. It was mentioned that the Arago–Biot mixing rule offered the worst experimental data fit [26, 28]. Most studies concluded that the Lorentz-Lorenz relations gave the best correlation for all systems investigated [8, 24, 29]. However, none of them considered the Looyenga [19] proposal.

3. MATERIALS AND METHODS

Table 3 lists details of the compounds used, including the suppliers. The n -alkanes were all obtained from Merck. All samples were used as received without further purification.

Table 3. Details and properties of chemicals used

Alkane/compound	CAS #	Product code	Code	Purity, %
Dodecane	112-40-3	101987112	297879	> 99
Hexadecane	544-76-3	101444299	296317	> 99
Eicosane	112-95-8	1002515748	219274	99
Tetracosane	641-31-1	1002801750	T8752	99
Octacosane	630-02-4	102200614	O504	99
Dotriacontane	544-85-4	102181345	D223107	97

Refractive index values of the pure components listed in Table 3 were measured as a function of temperature using a Mettler Toledo R4 instrument. The calibration of the instrument was checked using double distilled and deionised water. The instrument precision was ± 0.0001 and repeatability was ± 0.0002 refractive index units. Sample amounts were weighed out and directly placed into the instrument cell where they were allowed to equilibrate before measurement proceeded.

Published refractive index data on other alkanes and binary mixtures of these components with polar organic compounds were sourced from literature to supplement the experimental data. Table 4 lists the different systems considered together with the relevant literature sources for the density and refractive index of pure components and binary mixtures. In a few cases, when the density of pure components was not available, it was calculated using the correlations reported by Yaws and Pike [30].

Table 4. List of data sources for density and refractive index for pure components and binary mixtures

Pure compounds	Temperature range, °C	References
Dodecane	20–100	[31-34]
Hexadecane	20–60	[27, 35]
Eicosane	40–100	[35, 36]
Tetracosane	60–100	[30, 35]
Octacosane	50–100	[30]
Dotriacontane		[30]
Systems		
Acetone-alkanes	15–35	[33, 37-39]
Anisole-alkanes	20–30	[40-42]
Benzene-alkanes	10–40	[40, 43-49]
Chlorobenzene-alkanes	25–35	[50, 51]
Cyclohexanone-alkanes	25–35	[52]
Dioxane-alkanes	25–35	[53-55]
Ethanol-alkanes	15–45	[56-61]

4. RESULTS AND DISCUSSION

4.1. Single compounds

The measured refractive index (n) values of the pure n -alkanes considered are reported in the Supplementary Material and plotted in Figure 1. For any fixed temperature, the refractive index increases with alkane chain length. The temperature dependence was perfectly linear over the full measurement range, i.e., it could be represented by

$$n(T) = n^{\circ} + m(T - T^{\circ}) \quad (23)$$

where n° is the refractive index of the compound at the reference temperature T° and m is the slope of the refractive index line when plotted against temperature.

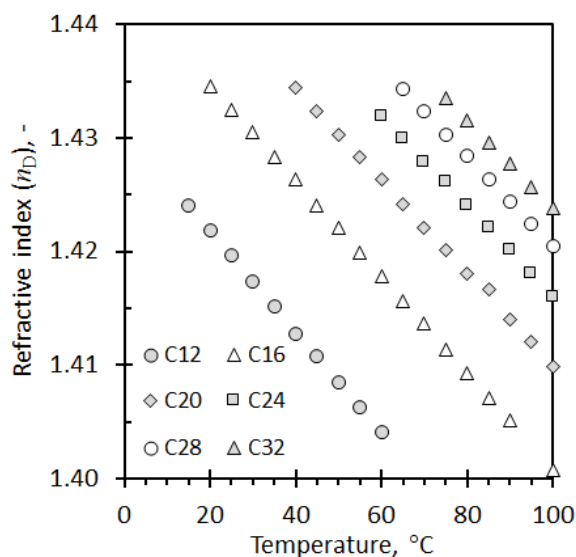


Figure 1. Measured refractive index values for measured for selected linear n -alkanes: C12 Dodecane; C16 Hexadecane; C20 Eicosane; C24 Tetracosane; C28 Octacosane; C32 Dotriacontane.

Figure 2(a) shows data plots of the molar refraction, R , calculated from equation (4) with refractive index and density data extracted from the sources listed in Table 4. The scaled molar refraction R/M data are reported in Figure 2(b). The results corroborate the assertions related to the virtual temperature independence of the molar refraction, defined by equation (4), and, for the n -alkanes, the molar mass scaled version as expressed by equation (5). The R/M values observed in Figure 2(b) are very close to one third. Nevertheless, the data trends suggest a very weak linear temperature dependence. In the temperature range displayed, the R/M values, as well as the temperature slope, decrease with alkane chain length. The slope is positive for dodecane, hexadecane and eicosane but negative for the longer alkane members. However, the variation with temperature, in the range considered, is negligible as it amounts to

less than $\pm 0.2\%$. For all practical purposes, the molar refraction values, R , may therefore be assumed to be constants.

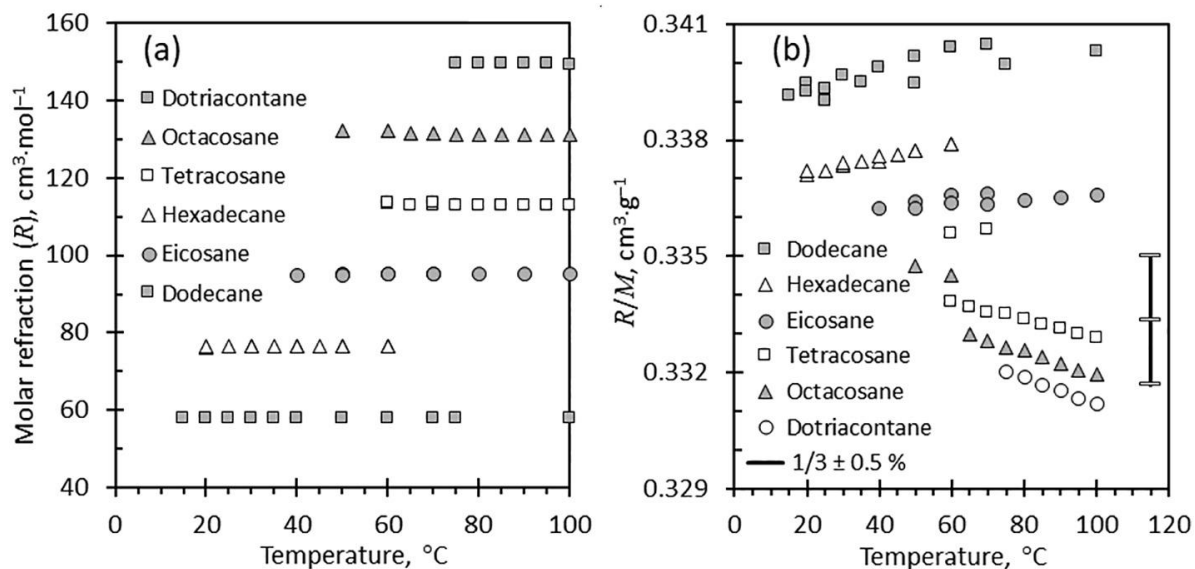


Figure 2. Data for (a) the molar refraction R , and (b) the molar-mass scaled form R/M for selected alkanes in the liquid state. The scale bar in (b) shows a $\pm 0.5\%$ deviation from one third.

If this is the case, the Lorentz–Lorenz relationship of equation (5) allows the calculation of the liquid density from refractive index measurements.

$$\rho = \frac{M}{R} \left(\frac{n^2 + 2}{n^2 - 1} \right) = \frac{M}{R} N \quad (24)$$

The applicability of this approach was tested on the n -alkanes together with data for some additional compounds. The results are summarised in Table 5. Experimental values for the densities and refractive indices over certain temperature ranges were obtained from the literature as per Table 4. These values were used to calculate the molar volume and molar refraction at each data point. The calculated values obtained were averaged over the whole temperature range. Subsequently the mean value for R obtained for each component was used to calculate its density over the temperature range considered with equation (24). Table 5 lists the R values and the mean and maximum absolute average deviations (AAD) for the density prediction errors obtained by applying equation (24). Table 5 indicates that the molar refraction is less affected by the system temperature than the molar volume. The standard deviation (s), expressed as a relative percentage, averaged 0.14% for R and 1.14% for the molar volume over the temperature ranges considered. The variation in R is therefore almost order of magnitude smaller in value compared to V .

The utility of applying the Looyenga and modified Eickman proposals using this approach was also investigated. This was done by replacing the expression for N , i.e., $(n^2-1)/(n^2+2)$, in the Lorentz-Lorenz expression with either n^p-1 or with $(n^2-1)/(n^2+d)$, respectively. Setting $p = 2/3$ or $d = 0.4$ resulted in slightly larger standard deviations in the R values compared to the Lorentz-Lorenz approach. Only minor improvements were observed when allowing these adjustable parameters to vary. At best, the performance was the same as for the Lorentz-Lorenz equation. Surprisingly, the results were rather insensitive to the actual values assigned to the parameters d and p . Density predictions covered a wide range of values and agreed, on average, within 0.2 %, with a maximum deviation of less than 1 %. Subsequently, equation (24) proves to be applicable for calculating pure component temperature-dependent density values in the absence of experimental data or correlations, provided that at least a single density point at a reference temperature is available to allow for the calculation of R . This is useful in correlations where pure component density data are required to predict the mixture composition and only refractive index measurements are available.

Table 5. Pure components: Average values of the molar volumes and molar refractions with the density predicted from the latter

Compound	T-range, °C	Molar volume, cm ³ ·mol ⁻¹			Lorentz-Lorenz molar refraction, cm ³ ·mol ⁻¹			Density errors	
		$V \pm s$	$s, \%$		$R \pm s$	$s, \%$		Max %	AAD %
Benzene	8–50	89.9 ± 1.28	1.43		26.22 ± 0.04	0.16		0.28	0.15
Acetone	20–45	74.3 ± 1.20	1.61		16.16 ± 0.04	0.23		0.43	0.15
DMA	25–45	94.0 ± 0.94	1.00		24.34 ± 0.02	0.09		0.09	0.06
Anisole	20–30	109.3 ± 0.52	0.47		32.93 ± 0.07	0.22		0.24	0.16
Cyclohexanone	25–35	104.7 ± 0.51	0.49		27.93 ± 0.01	0.05		0.05	0.03
Dioxane	25–35	86.2 ± 0.48	0.56		21.69 ± 0.01	0.06		0.07	0.04
Ethanol	15–45	59.1 ± 0.71	1.19		12.91 ± 0.01	0.05		0.08	0.04
Dodecane	20–100	232.7 ± 5.88	2.53		57.86 ± 0.08	0.14		0.23	0.12
Hexadecane	20–60	297.9 ± 3.73	1.25		76.43 ± 0.06	0.08		0.12	0.07
Eicosane	40–100	373.1 ± 6.09	1.63		95.06 ± 0.04	0.04		0.06	0.03
Tetracosane	60–100	442.1 ± 4.26	0.96		113.0 ± 0.33	0.29		0.58	0.21
Octacosane	50–100	509.3 ± 5.21	1.02		131.4 ± 0.39	0.29		0.56	0.22
Dotriacontane	75–100	580.4 ± 3.76	0.65		149.5 ± 0.14	0.09		0.12	0.07
Average (max)			1.14			0.14		(0.58)	0.10

4.2. Binary mixtures containing an *n*-alkane

Figure 3 shows that all the binary mixtures of acetone with alkanes appear to behave like ideal mixtures with respect to both the molar refraction and the molar volume. This also holds for other compounds in mixtures with *n*-alkanes as demonstrated by the data in the Supplementary Material.

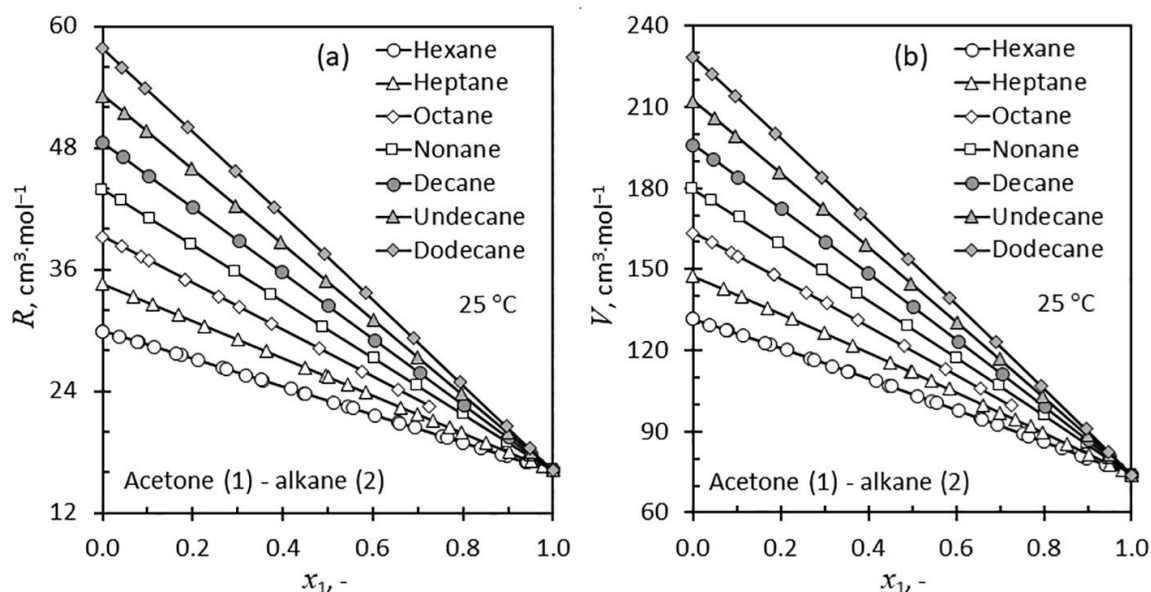


Figure 3. The Lorentz-Lorenz molar refraction R and molar volume at 25 °C for binary mixtures of acetone with selected alkanes calculated using the data sources listed in Table 4.

Figure 4 shows the temperature dependence of the molar refraction and the molar volume for mixtures of 1,4-dioxane with *n*-hexane. The R data for measurements conducted at temperatures of 25 °C, 30 °C and 35 °C, all lie on the same straight line. However, the corresponding molar volume data values lie on three separate parallel lines. Similar observations hold for the other binary systems listed in Table 4. The Supplementary Material includes a plot that confirms this for benzene mixtures with alkanes. This confirms the notion that the molar refraction can be interpreted as a temperature-invariant scaled molar volume. The results presented above appear to be generally valid for alkanes in binary combinations with aromatic and/or polar compounds such as benzene, chlorobenzene, ethanol, anisole, cyclohexanone, and 1,4-dioxane. The key realisation from these results is that the molar refraction R varies linearly with composition expressed in terms of mole fractions and that it is, for practical purposes, temperature invariant.

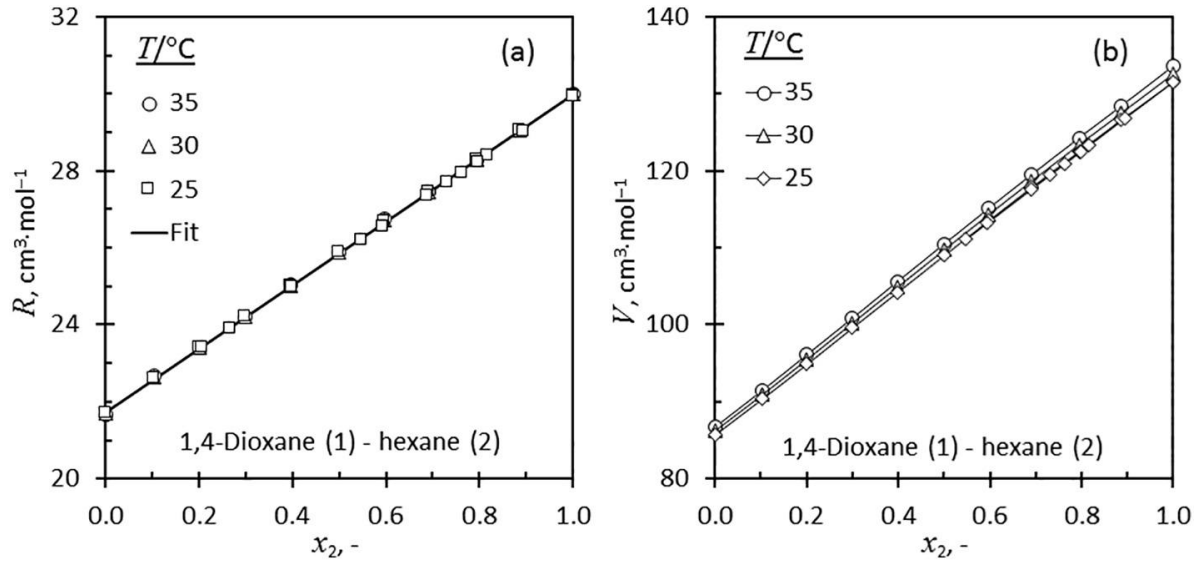


Figure 4. The temperature dependence of the Lorentz-Lorenz molar refraction R and molar volume for binary mixtures of 1,4-dioxane with n -hexane

For the discussion to follow, it is advantageous to have a look at a few specific examples of the variation of the actual refractive index with mixture composition. First a “brute force” test of the mixing rules presented in Table 2 was done. The models with a linear composition dependence fall in two groups corresponding to whether the mole fractions or the volume fractions are used as the composition descriptors:

$$g(n) = g(n_1)x_1 + g(n_2)x_2 \quad (25a)$$

and

$$f(n) = f(n_1)\varphi_1 + f(n_2)\varphi_2 \quad (25b)$$

Where $g(n_i)$ and $f(n_i)$ represent the functional dependence of the parameter N on refractive index suggested by the different investigators as listed in Table 2. These equations can be rearranged in a format that facilitates plotting all data from all systems on a single graph. This method also allows the performance of the Heller and Wiener mixture laws to be compared:

$$X \equiv \frac{g(n) - g(n_1)}{g(n_2) - g(n_1)} = x_2 \quad (26a)$$

and

$$\Phi \equiv \frac{f(n) - f(n_1)}{f(n_2) - f(n_1)} = \varphi_2 \quad (26b)$$

It should be noted that a volume fraction is an ill-defined concept because only nominal values based on the pure component properties are used. The true volume of the mixture differs slightly from the molar volume calculated using the linear mixing rule. Mole fractions are therefore preferred. If the model is able to represent the experimental data, the plots of Φ vs. φ_2 or of X vs. x_2 should yield a straight line with slope of unity that passes through the origin. Figure 5(a) shows that this is indeed the case for equation (6) and equation (9a) on plots vs. the mole fraction. This means that the molar volume and the Lorentz-Lorenz molar refraction measured, for all the systems considered presently, do follow the linear mixing rule with mole fraction as the composition descriptor.

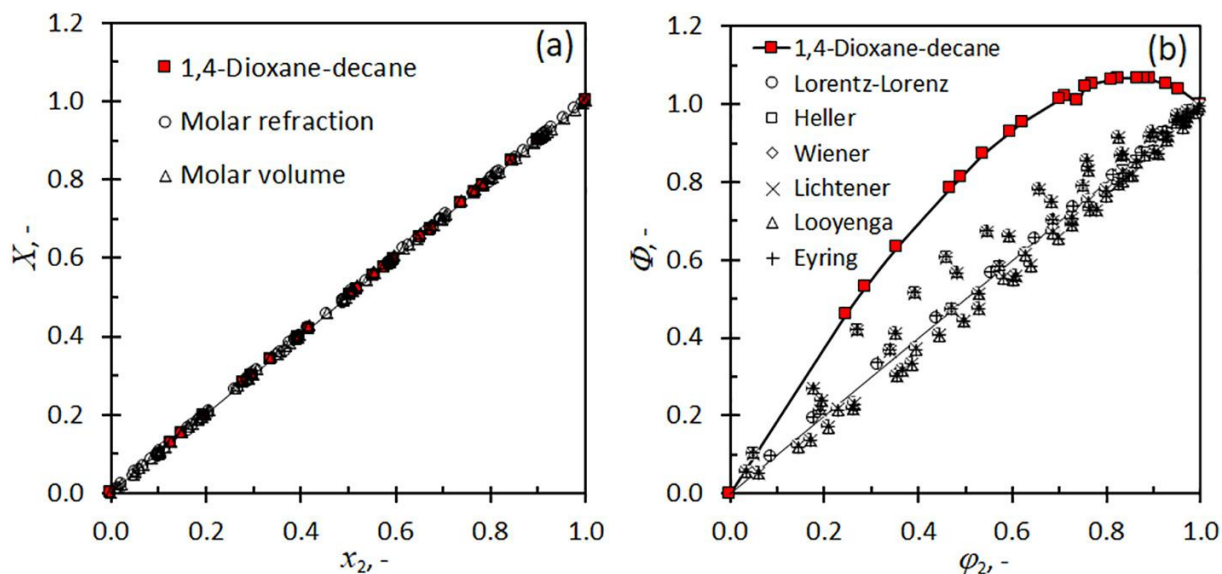


Figure 5. Testing the applicability of the linear mixture models using the binary data of all systems. (a) Equation (26a) applied to the molar volume (equation (6)) and the Lorentz-Lorenz molar refraction (equation (9a)). (b) Equation (26b) applied to the mixing rules that assume linear variation with volume fraction.

Figure 5(b) shows the plots of the models that are based on linear expressions in the volume fractions. Interestingly, all of the mixture models return data pairs that are very close to each other. The differences were smaller than the size of the symbols used to denote them and lie on top of each other in the graph. Unfortunately, none of them are able to correlate the data from all systems. This is indicated by the considerable scatter of the data points at distances quite far away from the diagonal line. The plot of the data from the 1,4-dioxane-decane binary appears to represent the greatest deviations. These data points were calculated using the Eyring equation and they are highlighted by the red squares that are connected with a solid line. It is clear that this data set cannot be represented by any of the models tested in Figure 5(b). The calculations even yield Φ values that exceed unity. This is in stark contrast with the results shown in Figure 5(a) where the 1,4-dioxane-decane data fall precisely on the required straight line

when the models based on mole fraction are used. Interestingly, it did not matter whether the Lorentz-Lorenz or Looyenga expression for N was used. The results were identical.

In order to better understand the reasons for this failure, it is useful to consider actual plots of the refractive index vs. volume fraction. Figure 6 shows representative plots that reveal some of the data trends that were found in the systems studied. In this figure, the data are plotted and shown together with the predictions of the two Lorentz-Lorenz equations. The predictions of the $L-L-R$ -mixing rules are indicated by the solid lines. It is clear that they represent the data trends quite well. However, the $L-L-N$ mixture model predictions, represented by dashed lines, fail to adequately describe all three systems considered. While the refractive index data for the chlorobenzene-decane system varies almost linearly with the mole fraction, both the ethanol-octane and the 1,4 dioxane-decane system data deviates from linear behaviour. The $L-L-N$ mixture model adequately corrects for the small deviations from linear behaviour for the chlorobenzene-decane system, but it underpredicts the refractive index values of the ethanol-octane system and overpredicts the values for the 1,4 dioxane-decane system.

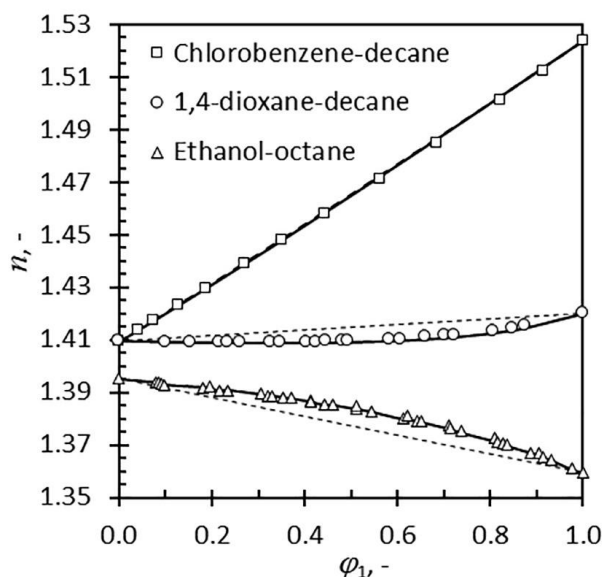


Figure 6. Refractive index data obtained at 25 °C. The solid lines and dashed lines are predictions obtained by applying equation (9) (the $L-L-R$ -mixing rule) and equation (13) (the $L-L-N$ -mixing rule), respectively. The two lines for the chlorobenzene-decane system virtually coincide.

Examination of all the different proposals for defining revised expressions for the N variable show that they all are strictly increasing functions of the refractive index n . In addition, they all assume a linear variation of N with composition expressed in volume fractions. This means that none of these models can represent a minimum in a refractive index vs. composition plot—as is in fact observed in the data of the

1,4 dioxane-decane system. This also explains the values of Φ that exceed unity in Figure 5. They arise from refractive index values in mixtures that are lower than those of both pure compounds.

However, the $L-L-R$ model represents even the data for the dioxane-decane system quite well. Recall that both the molar refraction and the molar volume follow the linear mixing rule in mole fractions. Therefore, equation (9) can be rearranged as follows:

$$N = (R_1x_1 + R_2x_2)/V \quad (27)$$

Note that for the mixture the left-hand side is fully determined by the measured refractive index values. Similarly, the right-hand side is fully determined by the density measurements that yield the molar volume of the mixture V . Figure 7 shows plots of these two quantities for binary mixtures of 1,4-dioxane with selected alkanes. The values coincide for all the systems. This implies that variations in the mixture density are accounted for by concomitant changes in the refractive index in such a way that molar refraction volume retains a linear composition dependence in the mole fractions. This then also suggests that it is possible to obtain estimates for the excess molar volume on the basis of equation (27):

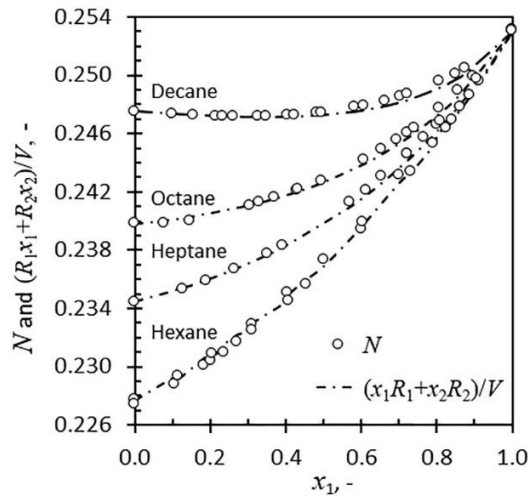


Figure 7. Plots illustrating the link between the Lorentz-Lorenz expression $N = (n^2-1)/(n^2+2)$ and the molar volume of binary mixtures of 1,4-dioxane with some alkanes.

$$V^E = V - V_1x_1 - V_2x_2 = (R_1/N - M_1/\rho_1)x_1 + (R_2/N - M_2/\rho_2)x_2 \quad (28)$$

The right-hand side is fully defined by the refractive indices of the mixture and the pure components, as well as the densities of the latter.

It can therefore be regarded as a predictive relationship for the excess molar volume of the system. Figure 8 shows such predictions for binary mixtures containing 1,4-dioxane. The predictions in Figure 8(a) follow the trends observed for the excess molar volume. However, they overestimate it for the mixture with decane and underestimate it for heptane.

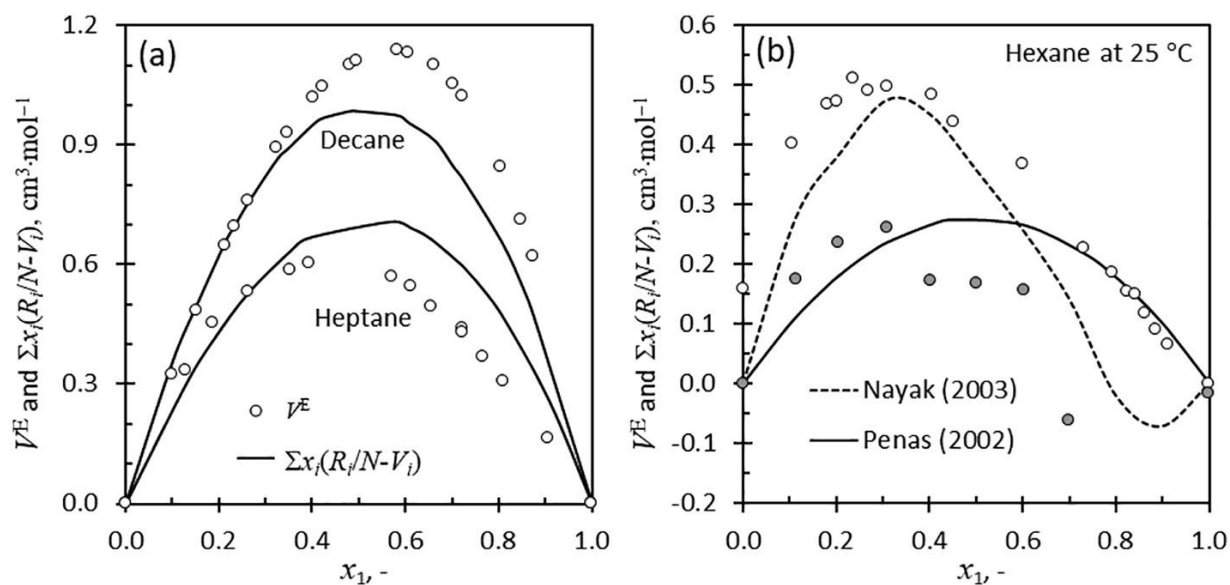


Figure 8. Comparison of the excess molar volume at 25 °C of 1,4-dioxane mixtures with alkanes with the predictions obtained from refractive index measurements. (a) Heptane and decane measurements from Penas, Calvo, Pintos, Amigo and Bravo [53]; (b) Hexane system: Solid line predictions and open markers, for excess molar volume, are based on data reported by Penas, Calvo, Pintos, Amigo and Bravo [53] while dashed line and filled markers (V^E) are based on data published by Nayak, Aralaguppi and Aminabhavi [55].

The results in Figure 8(b)—for mixtures with *n*-hexane—are rather curious. The V^E data from Penas, Calvo, Pintos, Amigo and Bravo [53] show good agreement with the predictions at high concentrations of dioxane but better agreement with the results extracted from Nayak, Aralaguppi and Aminabhavi [55] at low concentrations. The reverse is true for the plots derived from the Nayak, Aralaguppi and Aminabhavi [55] results. It should be considered that the excess molar volume is but a small fraction of the total molar volume, in the order of just 1 %. The striking differences between the two data sets reported for the dioxane-hexane system can have many different explanations. There might have been differences in the purity of the compounds, their moisture content and even the actual compositions of the mixtures. The accuracy of the temperature, density and refractive index measurements might have differed slightly. Therefore, very accurate measurements of high purity compounds in well-defined mixture ratios are required in order to generate meaningful results that will allow proper testing of the validity of equation (5). Previous investigators have explored the use of refractive index measurements for predicting the

excess volumes [13, 26]. They found a strong correlation between the density and refractive index of binary mixtures but used approaches that differed significantly from the method indicated by equation (27).

4.3. Mixture models requiring only refractive index information

The investigation done so far indicates that the $L-L-R$ mixture model provides exceptional predictive power. Unfortunately, this model additionally requires density data for the mixture. This is not always convenient to obtain. It is true that the $L-L-N$ mixture model works adequately for some binary systems, e.g., the chlorobenzene-decane system. It is then of interest to determine whether better performance can be achieved for other systems (that are not adequately described by this model) in order that the measurement of the refractive index of the mixture will suffice for composition determinations. In this regard, it is also conspicuous that the proposals for the power index p for the power mean-based mixture models, listed in Table 1, vary over such a considerable range, i.e., from zero to two. Such disparate values cannot simultaneously apply to all cases. However, these suggestions were previously supported by experimental results. This suggests that the nature of binary mixtures varies to such an extent that individual systems require unique power indices for proper data representation. Two approaches for adjustment of the mixture models were investigated. The power-mean mixture models were considered which treat the power index p as an adjustable constant. Also, the modified Eykman expression [17] which allows the parameter d to vary, was considered. Least squares regression was used to determine the best data fit for each possibility.

The outcome of this exercise is shown in Figure 9 as a Φ vs. φ_2 plot. The values of the adjustable parameters and the Φ - φ_2 correlation coefficients are listed in Table 6. It is clear that, except for the anisole-dodecane system, better performance is possible with these approaches than is possible with the $L-L-N$ mixture model.

Table 6. Φ - φ_2 correlation coefficients and values for the adjustable parameters for the modified Eyckman and volume fraction weighted power mean models

System	Lorentz-Lorenz-N	Power mean		Modified Eykman	
	r	p	r	d	r
Acetone-dodecane	0.99953	-4.174	0.99980	-0.682	0.99980
Anisole-dodecane	0.99924	-4.082	0.99891	-0.738	0.99874
Benzene-hexadecane	0.98809	-26.74	0.99921	-1.83	0.99919
Chlorobenzene-decane	0.99990	-0.790	0.99995	0.927	0.99995
Cyclohexanone-dodecane	0.99577	-34.09	0.99963	-1.82	0.99961
Ethanol-octane	0.99823	-16.82	0.99929	-1.50	0.99928

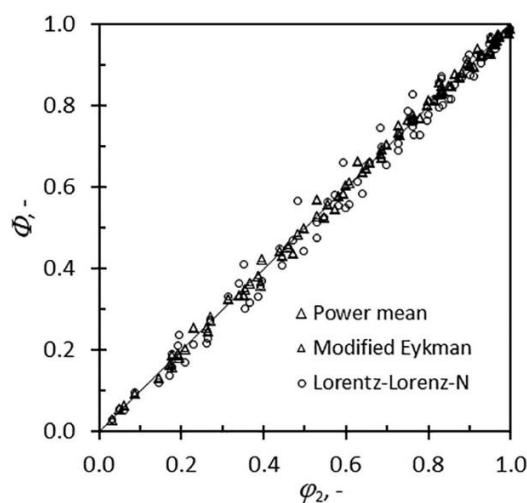


Figure 9. Performance of the Modified Eykman and volume fraction weighted power mean model for correlating the data for the binary systems listed in Table 6.

5. CONCLUSIONS

Experimental data of binary mixtures of *n*-alkanes with polar hydrocarbons were considered to evaluate the suitability of mixture models using refractive index and density measurements to predict mixture composition. For these systems both the mixture molar volume and molar refraction follow a linear mixing rule in mole fraction. While the linear trend in molar refraction is independent of temperature, a slight temperature dependence is observed when mixture molar volume is considered. Furthermore, pure component refractive index data of alkanes show that the Lorentz-Lorenz molar refraction may be assumed virtually independent of temperature. This can be leveraged to calculate pure component density data with an accuracy of within 0.2 % where temperature dependent measurement of this property is not available.

A review of published refractive index mixture models that cover the full composition range shows that, with the exception of the Wiener mixture rule, all suggest linear mixing in either mole fractions or volume fractions. The non-linear Wiener equation follows a Padè type mixing rule and the expression that proves this definition is explicitly presented. The advantage of mixture models that are linear in volume fraction is that a mixture density measurement is not required in order to allow prediction of the mixture composition. Unfortunately, comparison of predictive performance of both types of linear mixture models show that linear mixture models in volume fraction fail to represent the real data trends. Mixture refractive index data reveals that both positive and negative deviations from linear behaviour in this property with volume fraction can occur—which explains the inability of linear models in volume fraction to be generally applicable. However, it was shown that the performance of the Eykman and

power mean mixture models can be improved by allowing the adjustable constant in both to vary depending on the binary system evaluated.

The only model that is generally applicable to all the systems considered here, is the Lorentz-Lorenz molar refraction model that is linear in mole fraction. This can be explained by considering that the molar refraction is a physical quantity that combines refractive index and density in a single parameter. It is speculated that changes in density with temperature are compensated for by complementary changes in density. This explains the virtual temperature independence of pure component molar refraction as well as the observation that the real mixtures behave ideally when this property is considered. Subsequently, the Lorentz-Lorenz molar refraction linear mixing rule in mole fractions allows fully predictive composition estimates from combined density and refractive index measurements on mixtures. Based on this evidence a new method for calculating the excess mixture volume is suggested. However, more accurate refractive index measurements are needed to confirm its validity.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft (DFG) under Grant AN 212/22-1, is gratefully acknowledged.

REFERENCES

- [1] M. Martens, M.J. Hadrich, F. Nestler, M. Ouda, A. Schaadt, *Chemie Ingenieur Technik* 92 (2020) 1474 DOI: <https://doi.org/10.1002/cite.202000058>.
- [2] A. Shehadeh, A. Evangelou, D. Kechagia, P. Tataridis, A. Chatzilazarou, F. Shehadeh, *Food Chemistry* 329 (2020) DOI: 10.1016/j.foodchem.2020.127085.
- [3] A. Basgumus, F.E. Durak, A. Altuncu, G. Yilmaz, *IEEE Photonics Technology Letters* 28 (2016) 171 DOI: 10.1109/LPT.2015.2488040.
- [4] X.U. Zhang, D.J. Faber, A.L. Post, T.G. van Leeuwen, H.J.C.M. Sterenborg, *Journal of Biophotonics* 12 (2019) DOI: 10.1002/jbio.201900019.
- [5] A. Postnikov, *Measurement Science and Technology* 32 (2021) DOI: 10.1088/1361-6501/abb5da.
- [6] V. Krishna, C.H. Fan, J.P. Longtin, *Review of Scientific Instruments* 71 (2000) 3864 DOI: 10.1063/1.1288236.
- [7] J.M. Prausnitz, R.N. Lichtenthaler, E. Gómez de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*. Prentice-Hall, New Jersey, USA, 1999.
- [8] W. Heller, *The Journal of Physical Chemistry* 69 (1965) 1123 DOI: 10.1021/j100888a006.
- [9] F.M. Vargas, W.G. Chapman, *Fluid Phase Equilibria* 290 (2010) 103 DOI: <https://doi.org/10.1016/j.fluid.2009.12.004>.
- [10] P. Brocos, Á. Piñeiro, R. Bravo, A. Amigo, *Physical Chemistry Chemical Physics* 5 (2003) 550 DOI: 10.1039/b208765k.

- [11] A.Z. Tasic, B.D. Djordjevic, D.K. Grozdanic, N. Radojkovic, *Journal of Chemical & Engineering Data* 37 (1992) 310 DOI: 10.1021/je00007a009.
- [12] R.K. Krishnaswamy, J. Janzen, *Polymer Testing* 24 (2005) 762 DOI: <https://doi.org/10.1016/j.polymertesting.2005.03.010>.
- [13] M.A. Iglesias-Otero, J. Troncoso, E. Carballo, L. Romani, *The Journal of Chemical Thermodynamics* 40 (2008) 949 DOI: <https://doi.org/10.1016/j.jct.2008.01.023>.
- [14] H. Eyring, M.S. John, *Significant liquid structure*. Wiley Inter Science, New York, 1969.
- [15] W. Heller, *Physical Review* 68 (1945) 5 DOI: 10.1103/PhysRev.68.5.
- [16] J.F. Eykman, A.F. Holleman, *De Erven Loosjes*, (1919).
- [17] Á. Piñeiro, P. Brocos, A. Amigo, M. Pintos, R. Bravo, *The Journal of Chemical Thermodynamics* 31 (1999) 931 DOI: <https://doi.org/10.1006/jcht.1999.0517>.
- [18] G. Oster, *Chemical Reviews* 43 (1948) 319 DOI: 10.1021/cr60135a005.
- [19] H. Looyenga, *Molecular Physics* 9 (1965) 501 DOI: 10.1080/00268976500100671.
- [20] D.F.J. Arago, J.B. Biot, *Mem. Acad. Fr., 1806, , Mémoires de l'Académie (royale) des sciences de l'Institut (imperial) de France* (1806) 7.
- [21] T.P. Dale, J.H. Gladstone, *Philosophical Transactions of the Royal Society of London* 148 (1858) 887 DOI: doi:10.1098/rstl.1858.0036.
- [22] S.S. Kurtz, A.L. Ward, *Journal of the Franklin Institute* 222 (1936) 563 DOI: [https://doi.org/10.1016/S0016-0032\(36\)90986-9](https://doi.org/10.1016/S0016-0032(36)90986-9).
- [23] O. Wiener, *Berichte über die Verhandlungen der Königlich-Sächsischen Gesellschaft der Wissenschaften zu Leipzig, Mathematisch-Physische Klasse* 62 (1910) 256.
- [24] A.Ž. Tasić, B.D. Djordjević, D.K. Grozdanlić, M. Radojkovič, *Journal of Chemical and Engineering Data* 37 (1992) 310 DOI: 10.1021/je00007a009.
- [25] J.D. Pandey, A.K. Shukla, N.K. Soni, K.K. Tiwari, N. Pandey, *Journal of the Indian Chemical Society* 84 (2007) 674.
- [26] J.M. Vuksanović, D.M. Bajić, G.R. Ivaniš, E.M. Živković, I.R. Radović, S.P. Šerbanović, M.L. Kijevčanin, *Journal of the Serbian Chemical Society* 79 (2014) 707.
- [27] F. Sirbu, D. Dragoescu, A. Shchamialiou, T. Khasanshin, *The Journal of Chemical Thermodynamics* 128 (2019) 383 DOI: <https://doi.org/10.1016/j.jct.2018.08.036>.
- [28] I.R. Radović, M.L. Kijevčanin, M.Z. Gabrijel, S.P. Šerbanović, B.D. Djordjević, *Chemical Papers* 62 (2008) 302 DOI: 10.2478/s11696-008-0027-x.
- [29] R. Mehra, *Journal of Chemical Sciences* 115 (2003) 147 DOI: 10.1007/BF02716982.
- [30] C.L. Yaws, R.W. Pike, in: C.L. Yaws (Ed.) *Thermophysical Properties of Chemicals and Hydrocarbons*, William Andrew Publishing, Norwich, NY, 2009.
- [31] M.L.L. Paredes, R.A. Reis, A.A. Silva, R.N.G. Santos, M.H.A. Ribeiro, P.F. Ayres, *The Journal of Chemical Thermodynamics* 54 (2012) 377 DOI: <https://doi.org/10.1016/j.jct.2012.05.023>.
- [32] D.R. Caudwell, J.P.M. Trusler, V. Vesovic, W.A. Wakeham, *International Journal of Thermophysics* 25 (2004) 1339 DOI: 10.1007/s10765-004-5742-0.
- [33] L.M. Casás, A. Touriño, B. Orge, G. Marino, M. Iglesias, J. Tojo, *Journal of Chemical & Engineering Data* 47 (2002) 887 DOI: 10.1021/je0103059.
- [34] J.M. Pardo, C.A. Tovar, D. González, E. Carballo, L. Romani, *Journal of Chemical & Engineering Data* 46 (2001) 212 DOI: 10.1021/je000197a.
- [35] A.J. Queimada, I.M. Marrucho, J.A.P. Coutinho, E.H. Stenby, *International Journal of Thermophysics* 26 (2005) 47 DOI: 10.1007/s10765-005-2352-4.
- [36] S. Dutour, J.-L. Jean-Luc Daridon, B. Lagourette, *High Temperatures High Pressures* 33 (2001) 371 DOI: DOI:10.1068/htjr007.
- [37] G. Marino, M.M. Piñeiro, M. Iglesias, B. Orge, J. Tojo, *Journal of Chemical & Engineering Data* 46 (2001) 728 DOI: 10.1021/je000200q.

- [38] J. Acosta, A. Arce, E. Rodil, A. Soto, *Journal of Chemical & Engineering Data* 46 (2001) 1176 DOI: 10.1021/je0100490.
- [39] G. Marino, M. Iglesias, B. Orge, J. Tojo, M.M. Piñeiro, *Journal of Chemical Thermodynamics* 32 (2000) 483.
- [40] N. Calvar, E. Gómez, B. González, Á. Domínguez, *The Journal of Chemical Thermodynamics* 41 (2009) 939 DOI: <https://doi.org/10.1016/j.jct.2009.03.009>.
- [41] A.S. Al-Jimaz, J.A. Al-Kandary, A.-H.M. Abdul-latif, A.M. Al-Zanki, *The Journal of Chemical Thermodynamics* 37 (2005) 631 DOI: <https://doi.org/10.1016/j.jct.2004.09.021>.
- [42] B. Orge, G. Marino, M. Iglesias, J. Tojo, M.M. Piñeiro, *Journal of Chemical Thermodynamics* 32 (2000) 617 DOI: doi:10.1006/jcht.1999.0625.
- [43] J.H. Dymond, K.J. Young, *International Journal of Thermophysics* 2 (1981) 237 DOI: 10.1007/BF00504187.
- [44] A.S. Teja, P. Rice, *Journal of Chemical & Engineering Data* 21 (1976) 173 DOI: 10.1021/je60069a010.
- [45] K. Ridgway, P.A. Butler, *Journal of Chemical & Engineering Data* 12 (1967) 509 DOI: 10.1021/je60035a012.
- [46] M. Díaz Peña, J. Nuñez Delgado, *The Journal of Chemical Thermodynamics* 7 (1975) 201 DOI: [https://doi.org/10.1016/0021-9614\(75\)90269-4](https://doi.org/10.1016/0021-9614(75)90269-4).
- [47] T.M. Letcher, *The Journal of Chemical Thermodynamics* 16 (1984) 805 DOI: [https://doi.org/10.1016/0021-9614\(84\)90027-2](https://doi.org/10.1016/0021-9614(84)90027-2).
- [48] K. Lal, N. Tripathi, G.P. Dubey, *Journal of Chemical & Engineering Data* 45 (2000) 961 DOI: 10.1021/je000103x.
- [49] B. González, E.J. González, I. Domínguez, A. Domínguez, *Physics and Chemistry of Liquids* 48 (2010) 514 DOI: 10.1080/00319100903161499.
- [50] A. Tourino, A. Gayol, M. Hervello, V. Moreno, M. Iglesias, *Physics and Chemistry of Liquids* 42 (2004) 63 DOI: 10.1080/00319100310001604858.
- [51] A. Gayol, A. Touriño, M. Iglesias, *Physics and Chemistry of Liquids* 48 (2010) 661 DOI: 10.1080/00319104.2010.481764.
- [52] M.I. Aralaguppi, C.V. Jadar, T.M. Aminabhavi, *Journal of Chemical & Engineering Data* 44 (1999) 435 DOI: 10.1021/je9802266.
- [53] A. Penas, E. Calvo, M. Pintos, A. Amigo, R. Bravo, *Journal of Chemical & Engineering Data* 45 (2000) 682 DOI: 10.1021/je000038r.
- [54] E. Calvo, P. Brocos, R. Bravo, M. Pintos, A. Amigo, A.H. Roux, G. Roux-Desgranges, *Journal of Chemical & Engineering Data* 43 (1998) 105 DOI: 10.1021/je9701691.
- [55] J.N. Nayak, M.I. Aralaguppi, T.M. Aminabhavi, *Journal of Chemical & Engineering Data* 48 (2003) 1152 DOI: 10.1021/je030107c.
- [56] A. Gayol, M. Iglesias, J.M. Goenaga, R.G. Concha, J.M. Resa, *Journal of Molecular Liquids* 135 (2007) 105 DOI: <https://doi.org/10.1016/j.molliq.2006.11.012>.
- [57] A. Blanco, A. Gayol, D. Gómez, J.M. Navaza, *Physics and Chemistry of Liquids* 51 (2013) 233 DOI: 10.1080/00319104.2012.737792.
- [58] L. Segade, J. Jiménez de Llano, M. Domínguez-Pérez, Ó. Cabeza, M. Cabanas, E. Jiménez, *Journal of Chemical & Engineering Data* 48 (2003) 1251 DOI: 10.1021/je034053i.
- [59] B. Orge, A. Rodríguez, J.M. Canosa, G. Marino, M. Iglesias, J. Tojo, *Journal of Chemical & Engineering Data* 44 (1999) 1041 DOI: 10.1021/je9900676.
- [60] B. Orge, M. Iglesias, A. Rodríguez, J.M. Canosa, J. Tojo, *Fluid Phase Equilibria* 133 (1997) 213 DOI: [https://doi.org/10.1016/S0378-3812\(97\)00031-9](https://doi.org/10.1016/S0378-3812(97)00031-9).
- [61] E. Jiménez, H. Casas, L. Segade, C. Franjo, *Journal of Chemical & Engineering Data* 45 (2000) 862 DOI: 10.1021/je000060k.

Graphical abstract

Looyenga refractive index mixing rule:

$$NV = N_1V_1x_1 + N_2V_2x_2 \quad \text{with } N_i = n_i^{2/3} - 1$$

where n_i , V_i and x_i are the refractive index, molar volume and mole fraction of component i respectively.

Provides near perfect fit of binary data for mixtures of alkanes in combination with polar or aromatic compounds

