

## Refractive Index of Multicomponent Systems Containing n-alkanes

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**Abstract.** Refractive indices and densities of three ternary toluene + n- heptane + n-hexane (I), Cyclohexane + n-heptane + n-hexane (II) and n-hexane + n-heptane + n-decane (III) systems have been measured experimentally. Relative merits and interrelations of various important mixing rules have been discussed. Fairly good agreement between theoretical and experimental values has been found.

### 1. Introduction

In the year 1965, Heller<sup>1</sup> for the first time, examined and tested the relative merits and interrelations of important mixing rules for refractive index of binary liquid mixtures. He, himself, proposed a new mixing rule while performing the test of various mixing rules for binary liquid mixtures. The most widely used relations for predicting the refractive indices of binary liquid mixtures are due to Lorentz-Lorenz (L-L)<sup>2</sup>, Gladstone - Dale (G-D)<sup>3</sup>, Wiener (W)<sup>4</sup>, Heller (H)<sup>1</sup>, Arago- Biot (A-B)<sup>5</sup>. Binary mixture data of density and refractive index were also analysed by Aminabhavi et al<sup>3-4</sup> to test their validity. They have also pointed out various drawback of the mixing rules. Refractive index of multicomponent systems have been estimated by Bertrand and Acree<sup>5</sup> and by Pandey et al<sup>6</sup> using data of their binary combination.

In the present paper we report the results of experimental measurements of refractive index and density of three ternary systems, namely toluene + n-heptane + n-hexane, cyclohexane + n-heptane + n-hexane and n-heptane + n-hexane + n-decane. The validity of various mixing rules have been tested for these multicomponent systems using experimental values of density and refractive index of pure components.

### 2. Experimental

All the liquids were of (AR)BDH grade. They were purified according to procedures available in the literature. All measurements were carried out in a thermostatically controlled water bath. The bath temperature was set and maintained with the use of Beckmann thermometer calibrated against platinum resistance thermometer. The precision in the temperature was not allowed to exceed  $\pm 0.01^\circ\text{C}$  during the measurements. The refractive indices of pure components and various liquid mixtures were measured using an Abbe refractometer. The temperature was kept constant by maintaining a constant flow of water from the thermostat through the outer jacket of the cell. Measured refractive indices are accurate to  $\pm 0.0002$  units. Densities were measured at  $(298.15 \pm 0.1) \text{ K}$  in a calibrated modified bicapillary pycnometer with an accuracy of  $\pm 0.3 \text{ kg m}^{-3}$  (approximately  $\pm 0.05$  per cent). The other details of the experimental methods are discussed elsewhere<sup>7</sup>. The experimental values of density and refractive index of pure liquids, toluene, cyclohexane, n-hexane, n-heptane and n-decane and their literature values<sup>8</sup> are presented in table-1.

### 3. Theoretical

All the theoretical mixing rules tested earlier<sup>2-8</sup> for predicting the refractive indices of binary liquid mixtures have been extended for multicomponent liquid system<sup>8-10</sup> after slight mathematical adjustments. Most of the mixing rules are fundamentally based on the electromagnetic theory of light with the restriction that molecules may be considered as dipoles or assemblies of dipole induced by an external field. We have considered the following mixing rules<sup>8-10</sup> for the present analysis.

$$(1) \quad \left( \frac{n_m^2 - 1}{n_m^2 + 2} \right) V_m = \sum \frac{n_i^2 - 1}{n_i^2 + 2} V_i \phi_i \quad (\text{Lorentz-Lorenz})$$

The above relation is valid for strict additivity. Changes of volume in mixing and refractivity are not considered. Here  $n_m$  and  $n_i$  are respectively the refractive indices of mixture and  $i^{\text{th}}$  component,  $V_m$  and  $V_i$  are the respective molar volumes. To account for the size differences between two mixing species the following relation is used

$$(1a) \quad \left( \frac{n_m^2 - 1}{n_m^2 + 2} \right) = \sum \frac{n_i^2 - 1}{n_i^2 + 2} \phi_i$$

where  $\phi_i = V_i / \sum X_i V_i$  is the volume fraction of  $i^{\text{th}}$  component in the mixture, and  $X_i$  the mole fraction. The Gladstone-Dale relation may similarly be expressed as:

$$(2) \quad \left[ \frac{n_m - 1}{n_m} \right] = \sum \frac{n_i^2 - 1}{n_i} W_i \quad (\text{Gladstone-Dale})$$

where  $W_i$  is the weight fraction of  $i^{\text{th}}$  component in the mixture.

$$(3) \quad \left[ \frac{n_m^2 - n_1^2}{n_m^2 + 2n_1^2} \right] = \sum_{i=1}^n \phi_i \frac{n_i^2 - n_1^2}{n_i^2 + 2n_1^2} \quad (\text{Wiener})$$

both L-L and  $W_n$  relations give identical results if the mixing process is accompanied by neither contraction nor expansion (i.e. ideal). Heller's relation (H) is written as:

$$(4) \quad \left[ \frac{n_m - n_1}{n_1} \right] = \frac{3}{2} \sum_{i=1}^n \phi_i \frac{n_i^2 - 1}{n_i^2 + 2} \quad (\text{Heller})$$

where  $m_i = \frac{n_i}{n_1}$ . The refractive index of the mixture is given by:

$$(5) \quad n_m = \sum \phi_i n_i \quad (\text{Arago-Biot})$$

In the case of volume additivity, most widely used G-D relation is found to be identical with A-B relation and assumes the limiting form of the Heller's (H) relation.

The theoretically predicted results were examined in the light of mean percentage deviations and standard percentage errors. The two parameters mean percentage deviation  $\sigma$  and standard percentage error  $\delta$  were calculated using the following equations:

$$(6) \quad \sigma = \frac{1}{N} \sum_{i=1}^N [(Z_{i\text{expt}} - Z_{i\text{calc}})/Z_{i\text{expt}}] \times 100$$

$$(7) \quad \delta = \left\{ \frac{1}{N} \sum_{i=1}^N [(Z_{i\text{expt}} - Z_{i\text{calc}}) \times 100 / Z_{i\text{expt}}]^2 \right\}^{1/2}$$

where  $Z$  is any measured and theoretically computed thermodynamic property and  $N$  is the total number of sets.

#### 4. Results and Discussion

From the experimental density and refractive index data we have computed refractive index of three ternary systems mentioned earlier using various theoretical mixing rules<sup>1-2</sup> and compared with the experimental values of refractive indices of mixture. The theoretical values of refractive indices ( $n_m$ ) obtained from various rules are compared with the experimentally determined values by calculating  $\sigma$  and  $\delta$  from equation (6) and (7). The results of comparison are recorded in Table-2, which are discussed under the following paragraphs:

**Toluene + n-heptane + n-hexane :** A close perusal of Table 2 shows that all the theoretical mixing rules provide excellent agreement with experimental values. In this system Wiener's and Heller's relation give best results with minimum standard errors of 0.25% and 0.33% respectively. These relations are followed by Gladstone-Dale (G-D), Lorentz-Lorenz (L-L) and Arago-Biot (A-B) relations. Arago-Biot's relation shows maximum deviation, which may be due to the involvement of simple volume additivity. In all these relations, the existence of excess volume is not considered, which is a measure of interactions in the liquid system.

Table 1. Parameters of the pure components at 298.15K

Component	Density / kg m <sup>-3</sup>		Refractive index	
	Expt. Value	Lit. Value	Expt. Value	Lit. Value
Toluene	862.6	862.5	1.4968	1.4961
Cyclohexane	773.6	779.8	1.4264	1.4266
n-hexane	654.8	655.0	1.3720	1.3723
n-heptane	679.0	679.5	1.3850	1.3852
n-decane	726.0	726.3	1.4092	1.4097

Table 2. Mean percentage deviation and standard percentage error of various mixing rules for ternary liquid systems.

	Systems	%Δ	G-D	L-L	W <sub>n</sub>	H	A-B
1.	Toluene + n-heptane + n-hexane	(σ)	3.37	3.73	-0.23	-0.31	10.61
		(δ)	3.38	3.74	0.25	0.33	10.62
2.	Cyclohexane + n-heptane + n-hexane	(σ)	-0.45	-0.39	-0.95	0.88	0.85
		(δ)	0.46	0.42	0.98	0.91	0.86
3.	n-Hexane + n-heptane + n-decane	(σ)	0.78	0.04	0.02	0.03	0.04
		(δ)	0.82	0.07	0.12	0.09	0.07

σ = Mean percentage deviation, δ = Standard percentage error.

**Cyclohexane + n-heptane + n-hexane** : In this system a close look at table 2 shows that L-L relation provides very good agreement with minimum standard error of 0.42% when the volume additivity is not considered during mixing. The small negative deviations are accounted due to the volume dilution without assuming a change in molecular polarizability on mixing of the components. This relation is followed by Gladstone-Dale, Arago-Biot, Heller and Wiener ( $W_n$ ) relations. Wiener's relation has been found to exhibit maximum deviation of -0.95 per cent.

**n-hexane + n-heptane + n-decane** : A close observation of table-2 shows that in this system all the five mixing rules give excellent performance. Lorentz-Lorenz (L-L) and Arago-Biot (A-B) relations shows minimum deviations of 0.07 per cent, which is followed by Heller (H), Gladstone-Dale (G-D) and Wiener ( $W_n$ ) relations. All the three components of this system belong to the same series and possess similar nature, only slightly different in their properties.

To conclude, it can be stated that all the five mixing rules are interrelated in simple quantitative manner and show excellent performance only at lower concentrations. Deviation can be minimized to some extent by considering the change of volume,  $V^E$ , of the liquid with refractivity during mixing because excess volume is well recognized as a thermodynamic property predicting the different types of interactions in multicomponent systems.

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