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Estimation of the refractive indices of some binary mixtures

Isehunwa S. O.*, Olanisebe E. B., Ajiboye O. O. and Akintola S. A.

Department of Petroleum Engineering, University of Ibadan, Nigeria.

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Refractive index is a useful fluid characterization parameter with widespread industrial applications. The values for many pure liquids are known or readily available in literature. However, when experimental data are not available, the refractive indices of binary and multi-component liquids are often estimated from the pure components using mixing rules which are sometimes not accurate. This study was designed to measure the refractive indices and evaluate the accuracy of some commonly used mixing rules when applied to benzene-toluene, heptane-hexane, hexane-acetone, heptane-acetic acid and acetic acid-acetone binary mixtures at varying volume fractions and temperatures between 20 and 60°C. A simpler relation based on modified Kay or Arago-Biot mixing rule was demonstrated to have wider range of applicability because of the explicit temperature-dependence term.

Key words: Refractive index, mixing rule, binary mixtures, excess volume, refractometer.

INTRODUCTION

Refractive index is a fundamental physical property which measures the speed of light in a material and characterizes its optical properties (Singh, 2002). It has been used for many years for accurate identification and characterization of pure fluids and mixtures (Ebatco, 2013). Sharma et al. (2007) and Vural et al. (2011) noted that refractive index, density and viscosity are essential for the characterisation and understanding of the thermodynamic properties of fluids. The molecular interaction in a fluid mixture can also be assessed from the refractive index and density of its pure components (Leron et al., 2012; Rilo et al., 2012).

Refractive index is useful in the indirect measurement of density and salinity and in the detection of structural properties of liquid-liquid mixtures. Its application has also led to the development of alternatives in fuel substitutes, additives, and treatment of oils with chemicals (Rushton, 1955). Wankhede (2011) used mixing rule to determine the composition of an unknown mixture and the presence of molecular interactions in binary mixtures. Several researchers have noted that deviation between theoretical and experimental values of the refractive indices of mixtures can be reduced by considering the concept of excess volume (Mehra, 2003; Ali and Tariq 2006, Sharma et al., 2007; Meenachi and Krishnamurthi, 2013).

The refractive indices of pure, binary and multi-component fluids can readily be measured directly using refractometers. However, there are times when the experimental values are not available and it is desirable to estimate the refractive index of binary or multi-component liquids from the pure components by using

*Corresponding author. E-mail: Sunday.isehunwa@gmail.com

mixing rules. The most commonly used mixing rules are the Lorentz-Lorenz equation, Weiner relation, Heller's and Gladstone-Dale equations. These mixing rules apply the concept of excess molar properties, a measure of thermodynamic interaction changes with physical forces in polar molecules (Vural et al., 2011). They therefore require rigorous procedures.

The aim of this study was to develop an accurate mixing rule that is simpler to apply than the commonly used relations. The refractive indices of pure components and mixtures were measured at different temperatures and volume fractions and the results were used to develop a simple equation based on the modification of the Kay or Arago-Biot mixing rule. The resultant temperature-dependent relation proved accurate and easy to use.

Theoretical basis

In the process of mixing two or more components effects such as the structural re-orientation occurs due to the differences in shape and size of component molecules and the interaction between molecules (Ali et al., 2008). If we assume that volumes of the pure components can be added when analyzing fluid mixtures (Andrew et al., 1986) and using the mean polarizability which approximates the average possible orientations of a molecule, the Lorentz-Lorenz (1979) relation can be obtained which for a binary mixture is expressed as:

$$\frac{n_m^2 - 1}{n_m^2 + 2} = y_1 \frac{n_1^2 - 1}{n_1^2 + 2} + y_2 \frac{n_2^2 - 1}{n_2^2 + 2} \quad (1)$$

The Weiner relation is given as:

$$\frac{n_m^2 - n_1^2}{n_m^2 + 2n_1^2} = y_2 \frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2} \quad (2)$$

While Heller relation is:

$$\frac{n_m - n_1}{n_1} = \frac{3}{2} y_2 \frac{m^2 - 1}{m^2 + 2} \quad (3)$$

Where, $m = n_2/n_1$

And, the Gladstone-Dale equation can be expressed as:

$$\frac{n_m - 1}{\rho_m} = \left(\frac{n_1 - 1}{\rho_1}\right) w_1 + \left(\frac{n_2 - 1}{\rho_2}\right) w_2 \quad (4)$$

Where: $n_m = refractive\ index\ of\ mixture$,
$n_1, n_2 = Refractive\ index\ of\ pure\ components$,
$y_1\ and\ y_2 = volume\ fractions$,
$w_1\ and\ w_2 = weight\ fractions$,
$\rho_m = density\ of\ mixture$,

If we assume that there is volume additivity during mixing, we can use the simple Arago-Biot relation:

$$n_m = n_1 y_1 + n_2 y_2 \quad (5)$$

However, for most fluid mixtures, $\sum_i y_i \neq 1$ since there is volume change during mixing (Brocos et al, 2003). Therefore, adapting the method of Leron et al (2012), we propose a modified Arago-Biot equation as:

$$n_m = (y_1 n_1 + m_{d1}) + (y_2 n_2 + m_{d2}) \quad (6)$$

Where,

$$m_{di} = \frac{y_i (\sqrt{n_m})}{1000} \quad (7)$$

i= 1, 2

$$and\ m_{di}\ and\ m_{dj} = 0\ \ for\ pure\ components$$

MATERIALS AND METHODS

Samples of pure benzene, toluene, heptane, hexane, acetone and acetic acid manufactured by Messer Griesheim were obtained and their purity ascertained at 99.9% using standard procedures. Different binary mixtures were prepared from the pure components by mixing at varying volumes of 1 to 0 ml, 7.5 to 2.5 ml, 5 to 5 ml, 2.5 to 7.5 ml and 0 to 1 ml. The Abbe refractometer double prism system (Model 300778) with monochromatic light source of 589 nm for illumination and with accuracy of 0.0001 was used in measuring the refractive indices. The refractometer was calibrated at 20°C using distilled water as well as samples of the five pure fluids used. Using a heating water bath connected to the refractometer, the refractive indices of the pure components and binary mixtures were measured at 20, 40 and 60°C using procedures similar to Bhatia et al. (2002). Results were replicated to ensure consistency. Deviations of the measured and estimated results were determined using the following equations:

$$D = cal_i - exp_i \quad (8)$$

$$AAD = ABS\left\{\frac{1}{N} \sum_{I=1}^{N} calc_i - exp_i\right\} \quad (9)$$

Where "exp_i" is the experimental value, "$calc_i$" is the calculated value for point *i* and *N* is the number of points.

RESULTS AND DISCUSSION

The temperature-dependent modified Arago-Biot mixing rule, Equation (6), accounts for the non-ideal molecular interactions which occurs during mixing. This should represent an improvement over Gladstone-Dale, Arago-Biot and other similar relations. Table 1 gives some of the physical properties of the pure components used for the

Table 1. Physical properties of selected pure compounds.

Compounds	Purity (%)*	Boiling point, (°C)	Refractive index at (20°C)
benzene	99.90	80.1	1.5000
toluene	99.90	110.6	1.4900
heptane	99.50	98.0	1.3800
hexane	99.50	69.0	1.3700
acetic acid	99.90	118.0	1.3700
acetone	99.95	56.0	1.3600

*Supplied by Messer Griesheim.

Table 2. Refractive Index of benzene + toluene at 20°C.

y_i	Experimental (This work)	Lorentz-Lorenz	Weiner	Heller relation	Gladstone-Dale	Arago-Biot (Calculated)	Modified Arago-Biot
0.00	1.4900	1.4900	1.4900	1.4900	1.4900	1.4900	1.4900
0.25	1.4937	1.4909	1.4909	1.4909	1.4921	1.4925	1.4937
0.50	1.4962	1.4949	1.4949	1.4949	1.4945	1.4950	1.4962
0.75	1.4988	1.4989	1.4989	1.4989	1.4972	1.4975	1.4987
1.00	1.5000	1.5000	1.5000	1.5000	1.5000	1.5000	1.5000

Table 3. Refractive Index of Heptane + Hexane mixture at 40°C.

y_i	Experimental (This work)	Lorentz-Lorenz	Weiner	Heller relation	Gladstone-Dale	Arago-Biot (Calculated)	Modified Arago-Biot
0.00	1.3599	1.3600	1.3600	1.3599	1.3600	1.3600	1.3612
0.25	1.3637	1.3609	1.3609	1.3609	1.3625	1.3625	1.3637
0.50	1.3662	1.3649	1.3649	1.3649	1.3650	1.3650	1.3662
0.75	1.3688	1.3689	1.3689	1.3689	1.3675	1.3675	1.3687
1.00	1.3698	1.3700	1.3700	1.3700	1.3700	1.3700	1.3712

Table 4. Refractive Index of Heptane + Acetic Acid at 20°C.

y_i	Experimental (This work)	Lorentz-Lorenz	Weiner	Heller relation	Gladstone-Dale	Arago-Biot (Calculated)	Modified Arago-Biot
0.00	1.3700	1.3700	1.3700	1.3700	1.3700	1.3700	1.3700
0.25	1.3737	1.3709	1.3709	1.3709	1.3746	1.3725	1.3736
0.50	1.3763	1.3749	1.3749	1.3749	1.3772	1.3750	1.3762
0.75	1.3787	1.3789	1.3789	1.3789	1.3788	1.3775	1.3787
1.00	1.3800	1.3800	1.3800	1.3800	1.3800	1.3800	1.3800

experiments as obtained in literature and confirmed during calibration.

Tables 2 to 6 and Figures 1 to 6 shows the results obtained from the experiments. A close observation of these results shows that refractive indices of the pure liquids and mixtures decreased as temperature increased. This agrees with results of previous researchers such as Bhatia et al. (2002), Mehra (2003) and Navendra et al (2011) and can be attributed to the changes in fluid density with temperature. At higher temperatures, liquid dense decreases, causing light to travel faster in the medium resulting in lower refractive index. The variation of refractive indices with temperature can also be attributed to the structural changes which occur during

Table 5. Predictive Refractive Index correlation at varying mole fractions.

$y_i + y_j$	a	b	c
B + T	-0.0056	0.0156	1.4800
Hep + Hx	-0.0054	0.0154	1.3600
Hx + Ac	-0.0053	0.0153	1.3500
Hep + Ac	-0.0054	0.0154	1.3600
AcA + Ac	-0.0053	0.0153	1.3500

$B = benzene, T = toluene, Hp = heptane, Hx = hexane, Ac = acetone, AcA = acetic\ Acid$

Table 6. Predictive Refractive index correlation at varying temperatures (°C).

$y_i + y_j$	K	$x_1 = 0$	$x_1 = 0.25$	$x_1 = 0.5$	$x_1 = 0.75$	$x_1 = 1.0$
		d				
Be + To	-0.0005	1.5000	1.5037	1.5062	1.5087	1.5100
Hep + Hx	-0.0005	1.3800	1.3837	1.3862	1.3887	1.3900
Hx + Ac	-0.0005	1.3700	1.3737	1.3762	1.3787	1.3800
Hep + Ac	-0.0005	1.3800	1.3837	1.3862	1.3887	1.3900
AcA + Ac	-0.0005	1.3700	1.3737	1.3762	1.3787	1.3800

$Be = Benzene, To = Toluene, Hp = heptane, Hx = Hexane, Ac = Acetone, AcA = Acetic\ Acid$

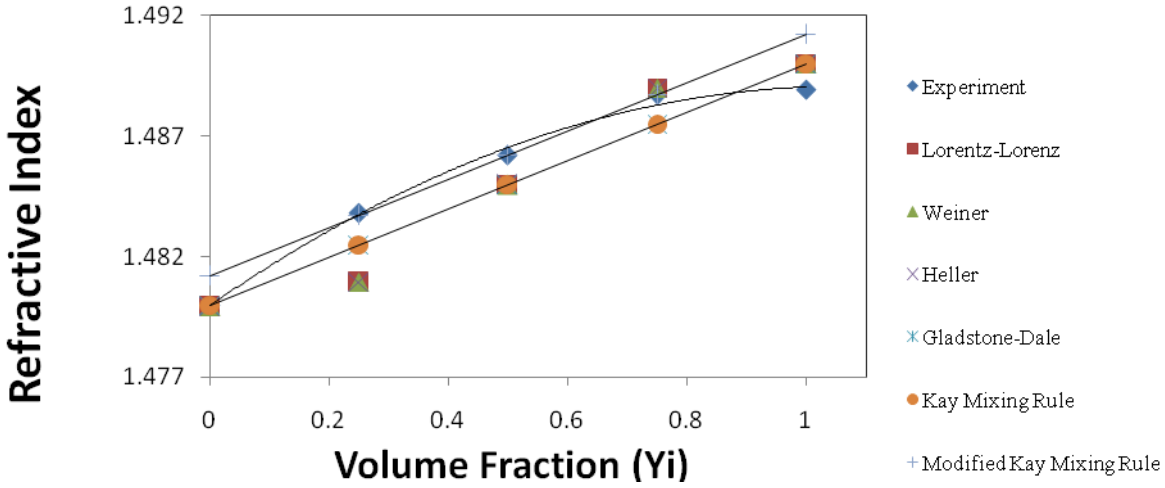

Figure 1. Refractive index versus volume fraction of benzene-toluene at 40°C.

mixing. The experimental results were also used to validate the commonly used mixing rules and the modified Arago-Biot equation. The results show that all estimated refractive indices using the mixing rules were reasonably close to measured values for the binary mixtures.

Furthermore, all the mixing rules considered showed remarkable changes in refractive indices of the mixtures with increasing temperature between 20 and 40°C except the Hexane-Acetone and Heptane-Acetic Acid mixture which were almost constant. This could be as a result of vaporization of acetone and hexane at temperatures close to 56 and 69°C, their boiling points respectively. However, mixtures which contain alkanes were not expected to exhibit structural changes at elevated temperatures between 40 and 60°C, in line with the observation by Mehra (2003) that no effect of increase in chain length was observed in alkanes and alkanols.

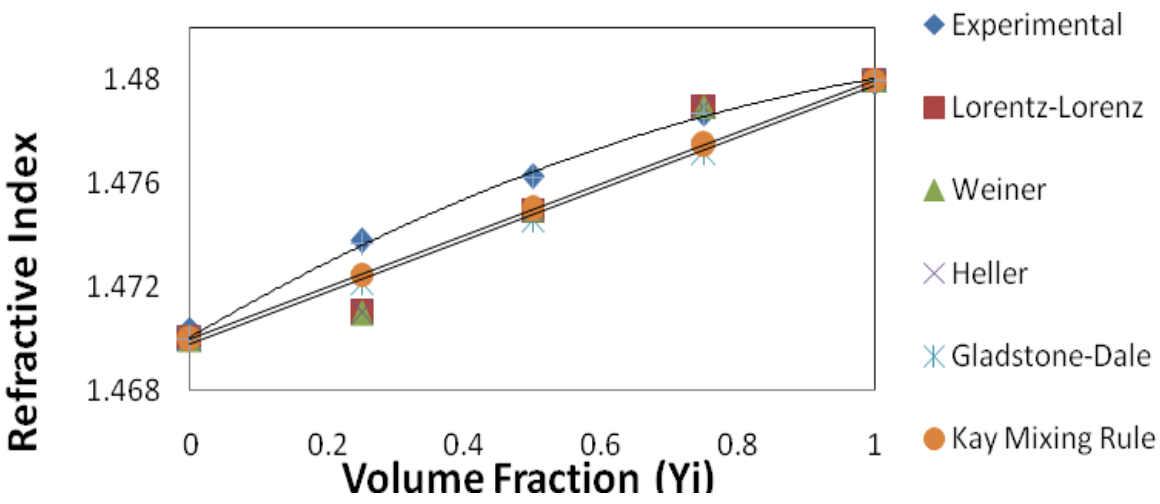

Figure 2. Refractive index versus volume fraction of benzene-toluene at 60°C.

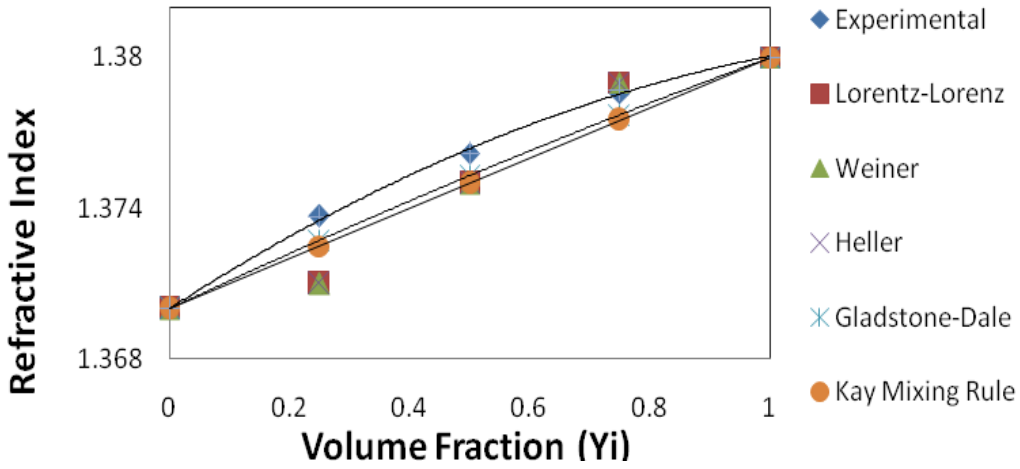

Figure 3: Refractive index versus volume fraction of heptane-hexane at 20°C.

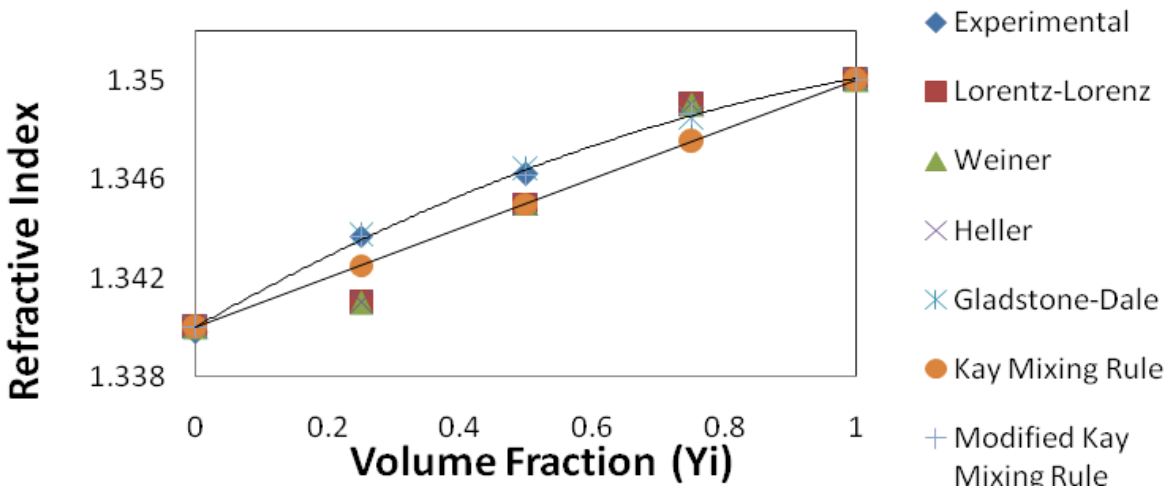

Figure 4. Refractive index versus volume fraction of hexane-acetone at 60°C.

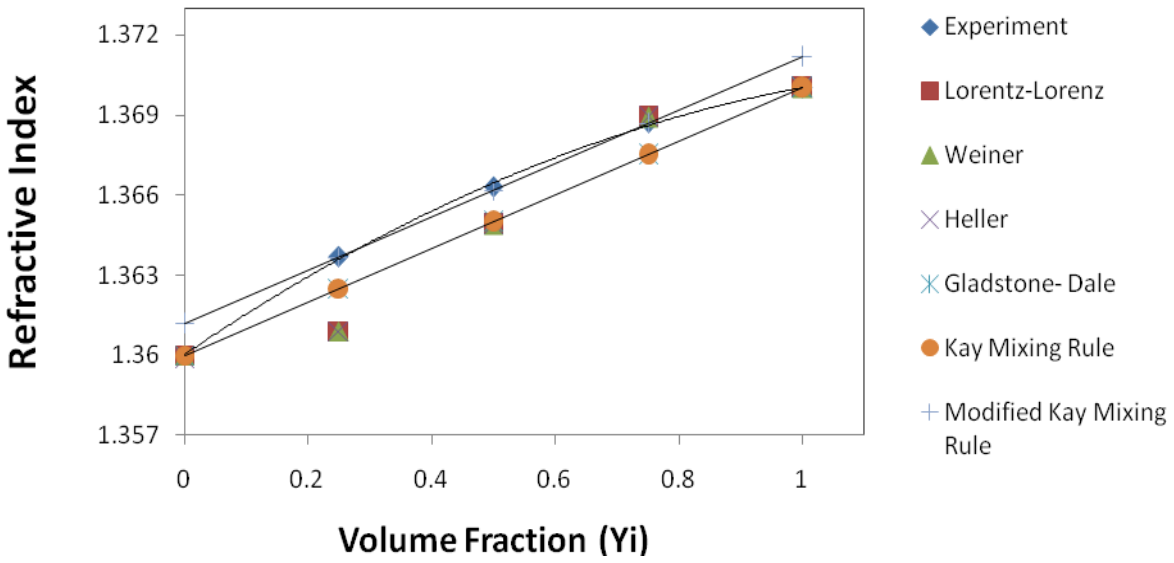

Figure 5. Refractive index against volume fraction of heptane-acetone at 40°C.

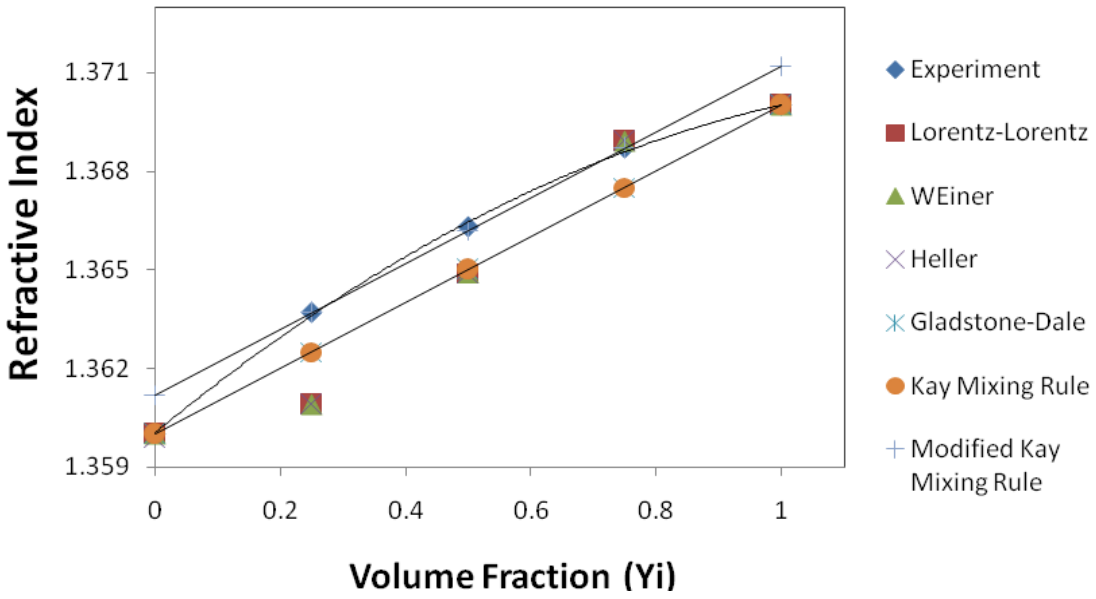

Figure 6. Refractive index versus volume fraction of acetic acid-acetone at 20°C.

Using the experimental data, the refractive indices of the selected binary mixtures at 20°C were related to volume fraction by equation (10):

$$n = ay_i^2 + by_i + c \quad (10)$$

Where, y_i is volume fraction of component 'i', while a, b and c are empirical constants as defined in Table 4.

Furthermore, the variation of refractive index with temperature was clearly established in this study in agreement with previous researchers (Bhatia et al., 2002). Therefore, we propose the estimation of the refractive indices of the mixtures at elevated temperatures using Equation (11):

$$n_t = d + KT \quad (11)$$

Where, K = Temperature correction factor = 0.0005/°C, d = Constant as given in Table 5, n_t = Refractive index at any temperature T °C other than base temperature.

Conclusion

Based on this work, the following conclusion can be made:

(1) The refractive indices of selected binary mixtures have been determined and presented.
(2) Refractive indices of the pure components and binary mixtures investigated in this study decrease with increasing temperature. Similar trends are expected in other similar compounds.
(3) The modified Arago-Biot mixing rule which includes temperature effects is simple to use and has wider range of application than some of the existing relations in literature. Therefore, an accurate mixing rule should not only be volume fraction-dependent, but explicit in temperature.

Conflict of Interest

The authors have not declared any conflict of interest.

ACKNOWLEDGEMENT

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NOMENCLATURE:

$n_m = refractive\ index\ of\ mixture$,
$n_1, n_2 = Refractive\ index\ of\ pure\ components$,
$\emptyset_1\ and\ \emptyset_2 = volume\ fractions$,
$w_1\ and\ w_2 = weight\ fractions$,
$\rho_m = density\ of\ mixture$,
$\rho_1, \rho_2 = density\ of\ pure\ components$,
K= $Temperature\ correction\ factor$,
$n = Refractive\ index$,
$n_D = Refractive\ index\ of\ mixture$,
$\rho = Density\ of\ the\ mixture$,
$\rho_i = Density\ of\ component\ 'i'$,
$M_i = Sum\ of\ components\ mass$,
$V = Total\ volume\ occupied\ by\ fluid\ mixture$,
$y_i = mole\ fraction\ of\ component\ 'i'$,
$m_{dn} = Mixing\ deviation\ for\ pure\ components$
$n = Refractive\ index\ of\ mixture$,
$n_t = Refractive\ Index\ of\ component\ mixture\ at\ a\ specific\ temperature$,
$n_{t_i}' = Temperature\ dependent\ Refractive\ index\ of\ component\ 'i'$,
$T = Temperature, oC$.

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