Application of Refractive Index Mixing Rules to Binary System

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ABSTRACT
Refractive index, \( n \), and density, \( \rho \), data of diethyl carbonate + aniline binary mixture have been measured as a function of composition at temperatures 293.15 K, 303.15 K and 313.15 K. A comparative study of Arago-Biot (A-B), Eykman (E), Eyring and John (E-J), Gladstone-Dale (G-D), Heller (H), Lorentz-Lorentz (L-L), Newton (N), Oster (Os) and Weiner (W) relations for predicting the refractive index of a liquid has been carried out to test the validity for the binary mixtures over the entire composition range of aniline at three temperatures. Comparision of various mixing rules has been expressed in terms of average percentage deviation.

Keywords: diethyl carbonate, refractive index, aniline, refractive index mixing rules.

INTRODUCTION
In combination with density and other analytical data refractive index measurements are very useful in industry and also for common substances like oils, waxes, syrup etc. The prediction of refractive index is essential for the determination of composition of binary liquid mixtures [1,2]. No such data on these mixtures is available in literature. Here we report the experimental values of density and refractive index for the binary mixture diethyl carbonate + aniline at temperatures 293.15 K, 303.15 K and 313.15 K over the entire composition range. The deviation in molar refraction have been calculated from the experimental data and fitted with Redlich-Kister polynomial equation. The experimental values of refractive indices are compared with the values of refractive indices calculated from various theoretical relations. The most widely used theoretical rules for predicting the refractivity of binary liquid mixtures are Arago-Biot [3], Eykman [4], Eyring and John [5], Gladstone-Dale [6], Heller [7], Lorentz-Lorentz [8], Newton [9], Oster [10] and Weiner [11]. The relative applicability of these mixing rules has been tested by many researchers [12-16]. The major drawback of these mixing rules is their inability to account for change in volume and refractivity during mixing as they are based only on volume additivity [17].

MATERIALS AND METHODS
Anton Paar DSA 5000 density and sound analyser provided with two Pt 100 platinum thermometer is used for measuring the densities of pure liquids and mixtures. The density is extremely sensitive to temperature,
so the apparatus was controlled to ±0.001 K by a built in solid state thermostat. To avoid evaporation, the mixtures prepared by mass were kept in special airtight stoppered glass bottles. The weighings were done with an electronic balance with a precision of ±0.01mg. 

Refractive indices of the mixtures at the sodium D-line were determined with an Abbe refractometer equipped with a circulating water bath permitting to maintain the sample at constant temperature to within ±0.1K. The instrument is calibrated by measuring the refractive index of deionised water. The sample support was rinsed with acetone and dried with a paper towel.

**THEORY:** Mixing rules for refractive index of liquid mixtures are listed below—Arago-Biot (A-B), assuming volume additivity, proposed the following relation for refractive index of binary mixtures

\[ n_m = \phi_1 n_1 + \phi_2 n_2 \]  

(Eykman’s (E) relation is represented as

\[ \left( \frac{n^2_m - 1}{n^2_m + 2} \right) \phi = \left( \frac{n^2_m - 1}{n^2_m + 2} \right) \frac{m}{\rho_m} \left( \frac{n^2_1 - 1}{n^2_1 + 2} \right) \frac{M_1 x_1}{\rho_1} + \left( \frac{n^2_2 - 1}{n^2_2 + 2} \right) \frac{M_2 x_2}{\rho_2} \]  

where, symbols have their usual meaning.

Eyring and John (E-J) relation

\[ n = n_1 \phi_1^2 + 2(n_1 n_2)^{1/2} \phi_1 \phi_2 + n_2 \phi_2^2 \]  

Gladstone-dale (G-D) equation for predicting the refractive index of a binary mixture is as follows

\[ (n_m - 1) = \phi_1 (n_1 - 1) + \phi_2 (n_2 - 1) \]  

Heller’s (H) relation is given by

\[ \left( \frac{n_m - n_1}{n_1} \right) = \frac{3}{2} \left( \frac{m^2 - 1}{m^2 + 2} \right) \phi_2 \]  

Where \( m = \frac{n_2}{n_1} \)

The Lorentz-Lorentz (L-L) relation for refractive index is based on the change in the molecular polarizability with volume fraction

\[ \left( \frac{n^2_m - 1}{n^2_m + 2} \right) \frac{1}{\rho_m} = \left( \frac{n^2_1 - 1}{n^2_1 + 2} \right) \frac{w_1}{\rho_1} + \left( \frac{n^2_2 - 1}{n^2_2 + 2} \right) \frac{w_2}{\rho_2} \]  

Newton (N) gave the following equation

\[ (n_m^2 - 1) = \phi_1 (n_1^2 - 1) + \phi_2 (n_2^2 - 1) \]  

Oster (Os) relation

\[ \frac{(n^2 - 1)(2n^2 + 1)}{n^2} = \frac{(n^2 - 1)(2n^2 + 1)}{n^2} \phi_1 + \frac{(n^2 - 1)(2n^2 + 1)}{n^2} \phi_2 \]  

Weiner’s (W) relation is represented as

\[ \left( \frac{n^2_m - n^2_1}{n^2_m + 2n^2_1} \right) = \left( \frac{n^2_2 - n^2_1}{n^2_2 + 2n^2_1} \right) \phi_2 \]  

In the above equations, \( n_m \) is the refractive index of the mixture; \( n_1 \) and \( n_2 \) are the refractive indices of the pure components 1 and 2 respectively. \( \phi_i \) is volume fraction of component i, \( \phi_i = x_i V_i / \sum x_i V_i \), \( V_i \) is the molar volume of component i and \( x_i \) is the mole fraction of component i.

The \( n_m \) data of the mixtures have been used to calculate the excess refractive index using

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\[ n^E = n_m - (x_1n_1 + x_2n_2) \]  

(10)

The refractive index is related to molar refraction, \( R_m \), by

\[ R_m = \left( \frac{n^2_m - 1}{n^2_m + 2} \right) V_m \]

(11)

where, \( V_m = (x_1M_1 + x_2M_2)/\rho \) is the molar volume.

The deviations were further fitted to the Redlich-Kister polynomial equation [18]

\[ X^E = x_i(1-x_i) \sum_{i=1}^{n} A_i (1-2x_i)^i \]

(12)

where \( X^E \) is the deviation in parameters and \( x_i \) is the mole fraction of diethyl carbonate. The values of Redlich-Kister polynomial coefficients, \( A_i \), were evaluated by the method of least squares and the standard deviation \( \sigma (X^E) \) was calculated as

\[ \sigma (X^E) = \left[ \frac{1}{m-n} \sum_{i=1}^{n} (X_{\text{expt}} - X_{\text{cal}})^2 \right]^{1/2} \]

(13)

Where \( m \) and \( n \) are the number of data points and parameters, respectively.

**RESULTS AND DISCUSSION**

The experimental data on density and refractive index of the binary system diethyl carbonate + aniline at 293.15, 303.15 and 313.15 K has been given in table 1. The adjustable parameters along with standard deviations are given in table 2. The average percentage deviations determined to assess their validity are shown in table 3. A close look of the table 1 reveals that the refractive index values of the pure components and mixtures decrease with rise in temperature.

**Table 1.** Experimental values of density, \( \rho \) and refractive index, \( n \) for binary mixtures at different temperatures.

<table>
<thead>
<tr>
<th>( x_1 )</th>
<th>( \rho ) (Kg m(^{-3}))</th>
<th>( n )</th>
<th>( \rho ) (Kg m(^{-3}))</th>
<th>( n )</th>
<th>( \rho ) (Kg m(^{-3}))</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T = 293.15 K</td>
<td></td>
<td>T = 303.15 K</td>
<td></td>
<td>T = 313.15 K</td>
<td></td>
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<tr>
<td>0.00000</td>
<td>1021.401</td>
<td>1.58530</td>
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<td>1.56738</td>
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<td>0.16517</td>
<td>1014.687</td>
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<td>1005.686</td>
<td>1.539855</td>
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<td>0.25373</td>
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<td>1.52532</td>
<td>1001.755</td>
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<td>0.33866</td>
<td>1007.334</td>
<td>1.50736</td>
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<td>1.501972</td>
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<td>0.44318</td>
<td>1002.841</td>
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<td>1.475802</td>
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<tr>
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<td>988.083</td>
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<tr>
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<td>982.646</td>
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<tr>
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<td>987.764</td>
<td>1.42735</td>
<td>977.289</td>
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<td>966.732</td>
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<td>981.296</td>
<td>1.40479</td>
<td>970.438</td>
<td>1.400012</td>
<td>959.494</td>
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<tr>
<td>1.00000</td>
<td>974.699</td>
<td>1.38470</td>
<td>963.468</td>
<td>1.380170</td>
<td>952.134</td>
<td>1.375586</td>
</tr>
</tbody>
</table>

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Table 2. Adjustable parameters $A_i$ with the standard deviations $\sigma$ for excess refractive index for binary mixtures at temperatures $T = (293.15, 303.15$ and $313.15) \text{ K}$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$A_4$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>-0.04044</td>
<td>-0.01463</td>
<td>-0.00098</td>
<td>0.00419</td>
<td>0.0001149</td>
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<tr>
<td>303.15</td>
<td>-0.04124</td>
<td>-0.01547</td>
<td>-0.00009</td>
<td>0.00530</td>
<td>0.0001102</td>
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<tr>
<td>313.15</td>
<td>-0.03790</td>
<td>-0.01595</td>
<td>0.00463</td>
<td>0.01180</td>
<td>0.0002575</td>
</tr>
</tbody>
</table>

Table 3. Average percentage deviation values of various empirical/semi-empirical relations of refractive index of binary liquid mixtures at varying temperatures.

<table>
<thead>
<tr>
<th>Relation</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293.15</td>
</tr>
<tr>
<td>Arago-Biot</td>
<td>0.162362</td>
</tr>
<tr>
<td>Eykmann</td>
<td>0.484646</td>
</tr>
<tr>
<td>Eyring-John</td>
<td>0.230205</td>
</tr>
<tr>
<td>Gladstone-Dale</td>
<td>0.162362</td>
</tr>
<tr>
<td>Heller</td>
<td>0.312750</td>
</tr>
<tr>
<td>Lorentz-Lorentz</td>
<td>0.310482</td>
</tr>
<tr>
<td>Newton</td>
<td>0.026606</td>
</tr>
<tr>
<td>Oster</td>
<td>0.567769</td>
</tr>
<tr>
<td>Weiner</td>
<td>0.224339</td>
</tr>
</tbody>
</table>

The basis of these mixing rules of refractive index is Electromagnetic theory of light, which treats the molecules as dipoles or assemblies of dipoles by an external field. Refractive index dependent on the nature of liquid, pressure and temperature and is directly related to a number of physical parameters of the liquid such as dielectric constant, density, molar refractivity etc. Here an attempt has been made to study the validity of nine mixing rules for predicting the refractivity of binary liquid system, over the entire mole fraction range.

The deviations of theoretical values from experimental ones are temperature-independent. This may be attributed to the fact that variation in refractive index with temperature is compensated by the change in density of the liquid mixture. However, in cases where the variation is significant with change in temperature, it can be used for interpreting the structure and interactions in the liquid by computing other dielectric, optical and acoustical properties using experimental data. If the concept of excess volume (which is an indirect measure of interaction) is taken into consideration in various mixing rules, the deviation between the observed and theoretical values of refractive index may be reduced [19].

**APPLICATIONS**

Density and refractive index values are measured experimentally and various mixing rules of refractive index were useful to test their validity for binary mixtures.

**CONCLUSIONS**

It may be concluded that all the mixing rules discussed are interrelated in a simple quantitative manner and perform well within the limits of experimental error. Negative and positive deviations are observed between experimental and theoretical values calculated by using various theories/models.

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REFERENCES