A comparative study of experimental and theoretical refractive index of binary liquid mixtures using mathematical methods

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A comparative study of experimental and theoretical refractive index of binary liquid mixtures using mathematical methods

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Abstract. A comparative study of refractive index of binary liquid mixtures such as Cyclohexane+O-xylene, PEG200+Water, PPG400+toluene having industrial applications are analysed at temperature 303K for different concentrations [0 to 1%]. In the present study experimental values are taken from literature and there values are compared with theoretical values obtained by various mathematical equations such as Lorentz – Lorenz relation, Gladstone-Dale equation, Weiner’s relation, Heller’s (H) equation, Arago-Biot equation. Thus the present study reveals the nature of interaction between component molecules in the mixtures and enables us to identify a suitable mathematical model for predicting the refractive index of various binary liquid mixtures.

1. Introduction
The general applicability of refractive index in chemical analysis and industry are revealed in literature survey. Many researchers have been studied the theoretical refractive index measurements by the refractive index mixing rules [1-4]. The generally used theoretical rules are Arago-biot, GladstoneDale, Lorentz-Lorentz, Weiner, Heller, Newton and Eyring-John. The validity of the mixing rules has been tested by several researchers and pointed out the importance of mixing rules [1-5]. In the present study, we report the experimental and theoretical refractive index of binary mixtures such as Cyclohexane+O-xylene, PEG200+Water, PPG400+toluene and from these the validity of the mixing rules have been analyzed.

2. Methods and Materials
The binary mixtures are prepared by dissolving Cyclohexane+O-xylene, PEG200+water, PPG400+toluene to get desired concentrations. Magnetic stirrer [REMI make] was used for this purpose at a rate of 1000 rpm. Refractive index values are measured using thermostatically controlled Abbe Refractometer having accuracy less than 0.0001 units. Density values are measured using specific gravity method. The mass of the liquid is measured using a K-ROY make electronic balance, with an accuracy of ±0.001gm.

3. Results and Discussions
In the present study, refractive index is determined for aqueous mixtures of Cyclohexane+O-xylene, PEG200+water, PPG400+toluene for different concentrations (0 to 1%) at a temperature 303K. The
experimental refractive index values of these mixtures are compared with theoretical refractive indices by mathematical models like Lorentz-Lorenz equation, Gladstone-Dale equation, Newton’s equation, Arago-Biot (AB) equation, Heller equation and Weiner equation which are listed below.

**Lorentz-Lorenz (L-L)**

Lorentz-Lorenz (L-L) relation for refractive index is based on the change in the molecular interaction with volume fraction:
\[
\frac{(n_m^2 - 1)/(n_m^2 + 2)}{(n_1^2 - 1)/(n_1^2 + 2) + \phi_2 (n_2^2 - 1)/(n_2^2 + 2)}
\]

where, \(\phi_1 = w_1/\rho_1\) and \(\phi_2 = w_2/\rho_2\), \(w_1\) and \(w_2\) are the weight fractions of the pure components 1 and 2 respectively, and, \(\rho_m\), \(\rho_1\) and \(\rho_2\) are the density of the mixture, and densities of the pure components 1 and 2 respectively and \(n_m\), \(n_1\) and \(n_2\) are the refractive index of the mixture, refractive indices of the pure components 1 and 2 respectively.

**Gladstone-Dale relation (G-D)**

The Gladstone-Dale relation is used for optical analysis (the determination of composition from optical measurements), or to calculate the density of a liquid for use in fluid dynamics. The relation has also been used to calculate refractive index. Gladstone-Dale (G-D) equation for predicting the refractive index of a binary liquid mixture is as follows
\[
(n_m - 1) = \phi_1(n_1 - 1) + \phi_2(n_2 - 1)
\]

Where, \(n_m\), \(n_1\) and \(n_2\) are the refractive index of the mixture, refractive indices of the pure components 1 and 2 respectively.

**Weiner’s relation (W)**

Weiner’s (W) relation may be represented as
\[
\frac{(n_m^2 - n_1^2)/(n_m^2 + 2n_1^2)}{(n_2^2 - n_1^2)/(n_2^2 + 2n_1^2)\phi_2}
\]

where, \(\phi_2 = w_2/\rho_2\) and, \(w_2\) is the weight fraction of the pure component and \(\rho_2\) is the density of the pure component 2 and \(n_m\), \(n_1\) and \(n_2\) are the refractive index of the mixture, refractive indices of the pure components 1 and 2 respectively.

**Heller’s equation (H)**

Heller’s (H) equation is given by
\[
\frac{(n_m - n_1)}{n_1} = \frac{3}{2}[\frac{(n_2^2 - n_1^2)/(n_2^2 + 2n_1^2)}{\phi_2}
\]

where, \(m = n_2/n_1\), \(\phi_1 = w_1/\rho_1\), \(w_2\) is the weight fraction of the pure component 2 and \(\rho_2\) is the density of the pure component 2 and \(n_m\), \(n_1\) and \(n_2\) are the refractive index of the mixture, refractive indices of the pure components 1 and 2 respectively.

**Arago-Biot (A-B)**

Arago-Biot (A-B), assuming volume additively, proposed the following relation for refractive index of binary liquid mixtures
\[
n_m = \phi_1 n_1 + \phi_2 n_2
\]

where, \(\phi_1 = w_1/\rho_1\) and \(\phi_2 = w_2/\rho_2\), \(w_1\) and \(w_2\) are the weight fractions of the pure components 1 and 2 respectively, and, \(\rho_m\), \(\rho_1\) and \(\rho_2\) are the density of the mixture, and densities of the pure components 1 and 2 respectively and \(n_m\), \(n_1\) and \(n_2\) are the refractive index of the mixture, refractive indices of the pure components 1 and 2 respectively.

**Newton (N)**

Newton (N) gave the following equation
\[
(n_m^2 - 1) = \phi_1(n_1^2 - 1) + \phi_2(n_2^2 - 1)
\]

where, \(\phi_1 = w_1/\rho_1\) and \(\phi_2 = w_2/\rho_2\), \(w_1\) and \(w_2\) are the weight fractions of the pure components 1 and 2 respectively, and, \(\rho_m\), \(\rho_1\) and \(\rho_2\) are the density of the mixture, and densities of the pure components 1 and 2 respectively.
and 2 respectively and \( n_m \), \( n_1 \) and \( n_2 \) are the refractive index of the mixture, refractive indices of the pure components 1 and 2 respectively.

**Average percentage error**

The percentage of deviation is calculated by the following equation

\[
APE = \frac{1}{n} \sum \left( \frac{R.I._{\text{exp}} - R.I._{\text{cal}}}{R.I._{\text{exp}}} \right) \times 100
\]

Where \( n \) is the number of data used, \( R.I._{\text{exp}} \) is the experimental refractive index and \( R.I._{\text{cal}} \) is the theoretical refractive index. The experimentally measured refractive index and the estimated refractive index from various mathematical models for the binary liquid mixture Cyclohexane+O-Xylene at different concentrations at 303K are presented in the Table 1.

**Table 1.** Experimental and mathematical values of Refractive index Cyclohexane + O-Xylene

| Conc(%) | EXP | A-B | G-D | L-L | W | H |
|---------|-----|-----|-----|-----|---|---|
| 0.0000  | 1.4200 | 1.4200 | 1.4200 | 1.4200 | 1.4200 | 1.4200 |
| 0.0908  | 1.4333 | 1.4423 | 1.4409 | 1.4265 | 1.4287 | 1.4284 |
| 0.1835  | 1.4422 | 1.4604 | 1.4606 | 1.4335 | 1.4373 | 1.4368 |
| 0.2781  | 1.4495 | 1.4851 | 1.4793 | 1.4413 | 1.4458 | 1.4452 |
| 0.3747  | 1.4556 | 1.4976 | 1.4968 | 1.4499 | 1.4544 | 1.4536 |
| 0.4734  | 1.4606 | 1.5232 | 1.5127 | 1.4589 | 1.4631 | 1.4622 |
| 0.5742  | 1.4654 | 1.5345 | 1.5261 | 1.4651 | 1.4715 | 1.4705 |
| 0.6772  | 1.4702 | 1.5487 | 1.5387 | 1.4733 | 1.4799 | 1.4790 |
| 0.7824  | 1.4792 | 1.5509 | 1.5496 | 1.4787 | 1.4880 | 1.4872 |
| 0.8900  | 1.4919 | 1.5673 | 1.5598 | 1.4880 | 1.4966 | 1.4959 |
| 1.0000  | 1.4950 | 1.5780 | 1.5685 | 1.4950 | 1.5048 | 1.5043 |

**Table 2.** Average percentage values of Cyclohexane + O-Xylene

| Conc(%) | EXP | %A-B | %G-D | %L-L | %W | %H |
|---------|-----|------|------|------|----|----|
| 0.0908  | 1.4333 | -0.6279 | -0.5302 | 0.4744 | 0.32093 | 0.3418 |
| 0.1835  | 1.4422 | -1.2619 | -1.2758 | 0.60324 | 0.33975 | 0.3744 |
| 0.2781  | 1.4495 | -2.4560 | -2.0558 | 0.56571 | 0.2552 | 0.2966 |
| 0.3747  | 1.4556 | -2.8854 | -2.8304 | 0.39159 | 0.0824 | 0.1374 |
| 0.4734  | 1.4606 | -4.2859 | -3.5670 | 0.11639 | -0.1711 | -0.1095 |
| 0.5742  | 1.4654 | -4.7154 | -4.1422 | 0.02047 | -0.4162 | -0.3480 |
| 0.6772  | 1.4702 | -5.3394 | -4.6592 | -0.2108 | -0.6597 | -0.5985 |
| 0.7824  | 1.4792 | -4.8472 | -4.7593 | 0.03380 | -0.5949 | -0.5408 |
| 0.89    | 1.4919 | -5.0539 | -4.5512 | 0.26141 | -0.3150 | -0.2681 |
| 1.0000  | 1.495  | -5.5518 | -4.9163 | 0.0000 | -0.6555 | -0.6220 |
| AVG     | 3.3659 | -3.0261 | 0.20510 | -0.1649 | -0.1215 |
From Table 1, it is observed that the experimental values of refractive index increases with increase in concentration. Arago-Biot relation, Weiner relations, Gladstone relations shows good agreement with theoretical values of binary liquid mixture Cyclohexane + O-Xylene. The limitations and approximations incorporated in these theories are responsible for the deviations of theoretical values from experimental values.

For the binary liquid mixture Cyclohexane+O-Xylene at 303K the average percentage values are given in Table 2 Further from the table 2 the deviations are more in Lorentz-Lorenz relation. At all concentrations the values obtained from Glad-Stone relations and Arago-Biot relations are found to be nearer. Exactly Lorentz-Lorenz relations performs the best of all methods.

The experimentally measured refractive index and the estimated refractive index from various mathematical models for the binary liquid mixture PEG200+Water at different concentrations at 303K are presented in the Table 3.

**Table 3.** Experimental and mathematical values of Refractive index PEG 200 + Water

| Conc(%) | EXP  | A-B   | G-D   | L-L   | W    | H     |
|--------|------|-------|-------|-------|------|-------|
| 2      | 1.341| 1.3458| 1.3416| 1.3418| 1.3397| 1.3383|
| 4      | 1.343| 1.3454| 1.3418| 1.3419| 1.3399| 1.3385|
| 6      | 1.346| 1.3457| 1.3419| 1.342 | 1.3401| 1.3387|
| 8      | 1.348| 1.3456| 1.342 | 1.3421| 1.3403| 1.3389|
| 10     | 1.350| 1.3455| 1.3422| 1.3422| 1.3405| 1.3391|

**Table 4.** Average percentage values of PEG 200 + Water

| Conc(%) | %EXP  | %A-B  | %G-D  | %L-L  | %W   | %H   |
|--------|-------|-------|-------|-------|------|------|
| 2      | 1.341 | -0.3579| -0.0444| -0.0597| 0.0969| 0.2013|
| 4      | 1.343 | -0.1787| 0.0894 | 0.0819 | 0.2308| 0.3350|
| 6      | 1.346 | 0.0223 | 0.3046 | 0.2972 | 0.4383| 0.5423|
| 8      | 1.348 | 0.1780 | 0.4451 | 0.4377 | 0.5712| 0.6751|
| 10     | 1.350 | 0.3333 | 0.5778 | 0.5778 | 0.7037| 0.8074|
| AVG    | -0.006| 0.2744 | 0.2670 | 0.4082 | 0.5122|

From Table 3, it is observed that the experimental values of refractive index vary with increase in concentration. In Gladstone values the refractive indices first decreases and suddenly increases and further decreases with increase in concentration. It shows that Arago-Biot relation, L-L relations, Gladstone relations shows good agreement with theoretical values.

Average percentage values for binary liquid mixture PEG 200 + Water is given in Table 4 Further in the Table 4 the deviations are more in Heller’s relation. At all concentrations the values obtained from L-L reaitions and Arago-Biot relations are found to be nearer. Particularly Arago-Biot relations perform the best of all methods.

The experimentally measured refractive index and the estimated refractive index from the various mathematical models like Arago-Biot, Gladstone-Dale, Lorentz-lorencz, Weiner equation, Heller
equation for the binary liquid mixture of PPG 400 + toluene at five different concentrations at 303K are summarized in the Table 5.

**Table 5. Experimental and mathematical values of Refractive index PPG 400 + toluene**

| Conc(%) | EXP  | A-B   | G-D   | L-L   | W    | H    |
|---------|------|-------|-------|-------|------|------|
| 2       | 1.494| 1.4935| 1.4939| 1.4942| 1.4947| 1.4944|
| 4       | 1.493| 1.4945| 1.4937| 1.4945| 1.4944| 1.4942|
| 6       | 1.492| 1.4955| 1.4935| 1.4947| 1.4942| 1.494 |
| 8       | 1.49 | 1.4965| 1.4933| 1.4949| 1.494  | 1.4938 |
| 10      | 1.489| 1.4975| 1.4932| 1.4951| 1.4938 | 1.4935 |

From Table 5 it is observed that the experimental values of refractive index decreases with increase in concentration. Whereas the Arago-Biot relation increases with increase in concentration. This table reveals that Arago-Biot relation, L-L relations, Gladstone relations shows good agreement with theoretical values. The limitations and approximations incorporated in these theories are responsible for the deviations of theoretical values from experimental values.

For the binary liquid mixture PPG 400 + Toluene at 303K the average percentage values are given in Table 6. Also from the Table 6 the deviations are more in Glad-Stone relation. At all concentrations the values obtained from L-L realtions and Arago-Biot relations are found to be nearer. Altogether Arago-Biot relations perform the best of all methods.

**Table 6. Average percentage values of PPG 400 + toluene at 303K**

| Conc(%) | %EXP | %A-B | %G-D | %L-L | %W | %H |
|---------|------|------|------|------|----|----|
| 2       | 1.494| 0.0335| 0.0067| -0.0134| -0.0469| -0.0268|
| 4       | 1.493| -0.1005| -0.0469| -0.1005| -0.0938| -0.0804|
| 6       | 1.492| -0.2346| -0.1005| -0.1810| -0.1475| -0.1341|
| 8       | 1.49 | -0.4362| -0.2215| -0.3289| -0.2685| -0.2550|
| 10      | 1.489| -0.5709| -0.2821| -0.4097| -0.3224| -0.3022|
| AVG     | 1.489| -0.2617| -0.1289| -0.2067| -0.1758| -0.1597|

**4. Conclusion**

In this present study the experimental refractive index of binary liquid mixtures such as Cyclohexane + O-xylene, PEG200 + water, PPG400 + toluene are compared with their theoretical refractive index for different concentrations at a temperature 303K. From these it may be concluded that the binary mixtures PEG200 + water, PPG400 + toluene showed Arago-Biot relation as the best suitable method for calculating the refractive index in the liquid systems.

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