Research Paper

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# Application of Various Mixing Rules for Refractive Index and Data Analysis of Some Binary Mixtures

Physics

**KEYWORDS :** Refractive index, Lorentz–Lorentz relation; Heller relation; Weiner relation; Gladstone–Dale relation, Arago-Biot, Newton's relation.

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## ABSTRACT

*In this paper we have made an attempt to discuss about relative validity of various mixing rules viz. Lorentz–Lorentz (L–L), Weiner (W), Heller (H), Gladstone–Dale (G–D, Arago-Biot (A-B) and Newton's relation (N) with following organic binary liquid mixtures of 1,4Dioxane (D)+Ethyl Ethanoate (EE), + Ethanoic Acid (EA),+ Butanol (B), at (293,298,303) K over the entire mole fraction range. Comparison of various mixing rules has been expressed in terms of average percentage deviation.*

## 1. INTRODUCTION

Various properties of the organic liquid and liquid mixtures are studied with the help of refractive index. It measures, in quantitative manner, the behavior of the medium to the electromagnetic radiations. It depends on the temperature, pressure and nature of liquid for a given wavelength. It also finds applications over many physico-chemical multiphase systems. Measurement of refractive index of a mixture of liquids of different refractive indices gives information about the proportion in which they are mixed. Prediction of refractive indices of binary liquid mixtures is essential for the determination of composition of binary liquid mixtures. As far as the physical property of medium is concerned we can divide them into two broad categories; macroscopic and microscopic. Under the macroscopic scale the internal structure of matter is immaterial as in it matter possesses a continuum with certain properties defined by well set up measuring operations. On the other hand, under the microscopic point of view, we study the composition of matter in deep . In this work the investigation of variation of these macroscopic physical properties of liquid mixtures have been carried out. These measurements can be used to determine the purity of liquid sample. In fact the measurement of refractive index is used as an important tool of investigation in the field of Analytical Chemistry.

There are many numbers of theoretical mixing rules which can predict the refractive index. The validity of these mixing rules has been tested by various workers and they also study the relative merits of these mixing rules. In this paper, as a continuation of our research work, we have made an attempt to discuss about relative validity and importance of various mixing rule with following organic binary liquid mixtures, for which we have already report[5-8] the various properties such as refractive index, density, excess molar volumes etc.

1,4-Dioxane (D) + Ethyl Ethanoate (EE)

1,4-Dioxane (D) + Ethanoic acid (EA)

1,4-Dioxane (D) + Butanol(B)

## 2. THEORY

Lorentz-Lorentz relation (L-L) is given by

$$\frac{(n_m^2-1)}{(n_m^2-2)}=\phi_1\frac{(n_1^2-1)}{(n_1^2+2)}+\phi_2\frac{(n_2^2-1)}{(n_2^2+2)} \quad \text{........................ (1)}$$

This is most frequently used mixing rule in analysis of refractive index.

Gladstone-Dale relation (G-D) is given as

$$(n_m-1)=\phi_1(n_1-1)+\phi_2(n_2-1) \quad \text{......... (2)}$$

Weiner relation (W) is given by

$$\frac{(n_m^2-n_1^2)}{(n_m^2-2n_1^2)}=\phi_2\frac{(n_2^2-n_1^2)}{(n_2^2+2n_1^2)} \quad \text{.................... (3)}$$

It applies to isotropic bodies of spherically symmetrical shape and proposes volume additivity.

Heller (H) equation is given by –

$$\frac{n_m-n_1}{n_1}=\frac{3}{2}\phi_2\frac{(n_2^2-n_1^2)}{(n_2^2+2n_1^2)} \quad \text{.................... (4)}$$

This relation is limiting case of Weiner's relation.

Arago - Biot relation (A-B) is given by

$$n_m=\phi_1 n_1+\phi_2 n_2 \quad \text{.................... (5)}$$

Newton relation (N) is given by

$$(n_m^2-1)=(n_1^2-1)\phi_1+(n_2^2-1)\phi_2 \quad \text{.................... (6)}$$

In above equations $n_m$, $n_1$, $n_2$ respectively represents the refractive index of mixture, solvent and solute respectively $\varphi_1$ and $\varphi_2$ are the volume fractions of solvent and solute respectively.

## 3. Results and Discussion

Values of APD at various temperatures for all the relations are listed in Table1. By the close observation of table1 we can make discussion as follows. First of all its is to be pointed that all the theoretical relations for the prediction of refractive indices are in well agreement with the corresponding value of refractive index, find out experimentally for all the systems under consideration in this work. For system (D+EE) at temperature 293K APD values have both negative and positive values. For (G-D), A-B and N, APD values are negative while for other it is positive. Minimum value of APD is due to Newton's (N) relation while maximum value of APD is due to Heller (H) Hence it is concluded that Newton's relation shows best agreement among all the theoretical relations for (D+EE) mixture at temperature 293K. At temp 298K for (D+EE) system G-D, A-B, L-L, W and H relation are in excellent agreement to each other. It is also equally important to state here that Newton (N) relation gives the minimum APD values for (D+EE) combination for all three temperatures. For (D+EE) system, again, the minimum value of APD is due to Newton relation (N) for all three temperature like as for system (D+EE), this system also have positive and negative values of APD. Over all values of APD for system (D+EA) due to G-D, A-B, L-L, W and H it are very close to each other. Similar trend is followed by (D+B) system for which weiner and Heller's relation are very prominent as they have lowest value at 298K.

At last we concluded that all the relations give good results that are in well agreement. However in this study Newton's relation gives minimum values of APD for most cases.

The deviations of theoretical values from experimental one are due to number of reasons. When the mixture of an organic liquid is formed then the various physical properties change and they are quite different from the properties of the original components. As, qualitatively, in liquid phase of matter there is lack of shear rigidity and exist very low compressibility, we can say that liquid phase of the matter exhibits both type of nature as exhibited by gases and solids because the lack of shear rigidity and very low compressibility are the properties of gases and solids respectively. The limitation to these theories is responsible for it. It is assumed that all the molecules are spherical in shape which is not true every time. In Nomoto theory it is supposed that the volume does not change on mixing. Therefore no interaction takes place. Similarly the assumption for the formation of ideal mixing relation is that the ratio of specific heats of the components is equal to the ratio of specific heats of ideal mixtures and the volumes are also equal, again no molecular interaction is taken in account. But on mixing of two liquids the interaction between molecules of liquids takes place because of the presence of various types of forces such as dispersion forces, change transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole interactions. Thus the observed deviation of theoretical values of refractive index from experiment values shows that the molecular interaction is taking place between the molecules in liquid mixture.

## 4. CONCLUSION

In this paper, it is attempted to study the relative validity and importance of six mixing rules for the prediction of refractive index of binary liquid mixture. Temperature dependence of these relations has also been discussed. From above, it is concluded that these rules are interrelated. The different size and nature of molecules has been taken consideration hence particular relation gives very good agreement in some systems but deviates in others. This can provide the preferential use of one model over other.

**Table-1:Values of APD for various mixtures**

| Mixture | T (K) | GD | AB | LL | W | H | N |
|---|---|---|---|---|---|---|---|
| D+EE | 293 | -0.0520 | -0.0650 | 0.1380 | 0.0265 | 0.1530 | -0.1960 |
| | 298 | -0.0810 | -0.0850 | 0.0530 | -0.0540 | 0.0940 | -0.2670 |
| | 303 | -0.6250 | -0.6203 | -0.5150 | -0.6670 | -0.4820 | -0.7805 |
| D+EA | 293 | -0.1130 | -0.1154 | 0.0463 | -0.0630 | 0.0440 | -0.2780 |
| | 298 | -0.0230 | -0.0290 | 0.0940 | 0.0130 | 0.0870 | -0.1650 |
| | 303 | -0.0650 | -0.0637 | -0.0250 | -0.0580 | -0.0170 | -0.0840 |
| D+B | 293 | 0.1028 | 0.1034 | 0.1042 | 0.1032 | 0.1023 | 0.1027 |
| | 298 | 0.0052 | 0.0014 | 0.0236 | 0.0054 | 0.0037 | 0.0329 |
| | 303 | -0.0630 | -0.0660 | 0.0760 | -0.0470 | 0.0780 | -0.2640 |

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