Research Paper

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Comparison of Various Mixing Rules for Refractive Index and Data Analysis for Some Liquid Mixtures

Physics

KEYWORDS : Refractive index, Lorentz–Lorentz relation; Heller relation; Weiner

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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 realtion (N) with following organic binary liquid mixtures of Cyclohexylmethane (CH) + 1,2Dimethylbenzene(2D), + 1,3Dimethylbenzene(3D),+1,4-Dimethylbenzene(4D), 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.

Cyclohexylmethane(CH) + 1,2-Dimethylbenzene(2D)

Cyclohexylmethane(CH) + 1,3-Dimethylbenzene(3D)

Cyclohexylmethane(CH) + 1,4-Dimethylbenzene(4D)

2. THEORY

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

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

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

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

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

Weiner relation (W) is given by

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

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

Heller (H) equation is given by –

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

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

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

In above equations n_m, n_1, n_2 respectively represents the refractive index of mixture, solvent and solute respectively φ_1 and φ_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 (CH+D) it is observed that Lorentz - Lorentz (L-L) and Heller's relations gives positive values of APD over all three temperature while other relation give negative values of APD for all three temperature values. Similar results are observed by system (CH+3D) also. All the theoretical relation exhibits well agreement with experiment values of refractive index. Minimum value of APD for (CH+2D) and (CH+3D) system are due to Newton (N) relation against all the three values of temperature. For system (CH+4D), APD values exhibits both positive and negative trends and minimum value of APD is due to N, G-D and A-B for temperature 293K, 298K and 303K respectively. It is also observed that at temperature 298K, all APD values corresponded to theoretical relations are positive while for 293K and 303K they have both positive and negative values.

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.

Table-1.Values of APD for various mixtures

Mixture	T (K)	GD	AB	LL	W	H	N
CH+2D	293	-0.0163	-0.0166	0.0074	-0.0074	0.0113	-0.0393
	298	-0.0161	-0.0165	0.0085	-0.0068	0.0114	-0.0376
	303	-0.0062	-0.0062	0.0176	0.0028	0.0216	-0.0290
CH+3D	293	-0.0125	-0.0125	0.0068	-0.0062	0.0102	-0.0297
	298	-0.0051	-0.0051	0.0120	0.0022	0.0154	-0.0228
	303	-0.0120	-0.0122	0.0062	-0.0057	0.0097	-0.0291
CH+4D	293	-0.0120	-0.0120	0.0062	-0.0062	0.0102	-0.0291
	298	.03324	.03441	0.3752	0.1623	0.4222	0.7437
	303	-0.2342	-0.2364	0.1122	-0.1324	0.1665	-0.5287

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.

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