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Study of Mixing Rules for Refractive Index for Organic Liquid Mixtures under Different Temperature Range

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Abstract

Various mixing rules viz. Arago-Biot (A-B), Lorentz–Lorentz (L–L), Weiner (W), Heller (H), Gladstone–Dale (G–D), and Newton’s relation (N) are studied for following organic binary liquid mixtures of Hexahydrotoluene (H) + o-Xylene(O), + m-Xylene(M),+ p-Xylene (P), at different temperatures (295,300,305) K over the entire mole fraction range. Comparison of various mixing rules has been expressed in terms of average percentage deviation.

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

Introduction

Refractive index gives very useful information about the various properties of the organic liquid and liquid mixtures. It gives the behavior of the medium to the electromagnetic radiations and depends on the temperature, pressure and nature of liquid for a given wavelength. Refractive index also finds applications over many multiphase systems. Refractive index of an organic liquid mixture of liquids of different refractive indices gives useful information about the proportion in which they are mixed. Prediction of refractive indices of binary organic liquid mixtures is very useful for the determination of composition of binary liquid mixtures. For the study of physical property of medium we can divide them into two broad categories; macroscopic and microscopic. Macroscopic scale gives information about the external structure of matter. On the other hand, under the microscopic study, we deal with the composition of matter. In this work the study of variation of macroscopic physical properties of liquid mixtures have been performed. The main use of this study is that with the help of this study we can analyze the purity of liquid sample. It is important to mention here that in the field of Analytical Chemistry, it is used as very important tool of investigation. 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. Hexahydrotoluene (H) + o-Xylene (O) Hexahydrotoluene (H) + m-Xylene (M) Hexahydrotoluene (H) + p-Xylene (P)

Theory

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

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

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

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

$$(n_m - 1) = \phi_1 (n_1 - 1) + \phi_2 (n_2 - 1) \dots\dots\dots (2)$$

Weiner relation (W) is given by

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

It applies to isotropic bodies of spherically symmetrical shape and proposes volume additivity. Heller (H) equation is given by –

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

This relation is limiting case of Weiner’s relation.

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

$$n_m = \phi_1 n_1 + \phi_2 n_2 \dots\dots\dots (5)$$

Newton relation (N) is given by

$$(n_m^2 - 1) = (n_1^2 - 1)\phi_1 + (n_2^2 - 1)\phi_2 \dots\dots\dots (6)$$

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.

Results and Discussion

Average percentage deviation (APD) at various temperatures for all the mixing rules are listed in Table1. With the help of table1 we can make discussion as follows it is clear that all the theoretical relations for the prediction of refractive indices are in good agreement with the corresponding value of refractive index which are find out experimentally for all the binary mixtures under consideration. For system (H+O) it is found that L-L and Heller’s relations gives positive values of APD for all three temperatures on the other hand other relations give negative values of APD over all the three temperature. Similar results are observed by system (H+M) also. It is observed that all the mixing rules shows well agreement with experiment values of refractive index. Minimum value of APD for (H+O) and (H+M) system are due to Newton (N) relation over all the values of temperature. For system (H+P), APD values shows both positive and negative trends, here we have minimum value of APD for Newton, Gladstone–Dale and Arago-Biot for all temperatures respectively. It is also observed that at temperature 300K, all APD values corresponded to theoretical relations are positive while for 295K and 305K they have both positive and negative values. It is found here that all the relations give good results and are in well agreement. However in

present study Newton’s relation gives minimum values of APD under most cases. The deviations of theoretical values from experimental values are due to many reasons as discussed here. When the mixture is formed, the various physical properties of an organic liquid become changed and they are quite different from the properties of the original ones. In liquid phase of matter there is lack of shear rigidity and exist very low compressibility, due to which liquid phase of the matter shows both type of nature as exhibited by gases and solids. The reason behind this is that the lack of shear rigidity and very low compressibility are the properties of gases and solids respectively. Here it is assumed that all the molecules of liquid and liquid mixture are perfectly spherical in shape but this is not true many times. Nomoto theory suggests that the volume does not change on mixing of organic liquids hence no interaction takes place. Similarly when mixture of organic liquid is formed, specific heats of the components is equal to the ratio of specific heats of ideal mixtures and the volumes are also equal, this again implies that no molecular interaction is taken in account. But actually interaction between molecules of liquids takes place because of the presence of various types of forces such as dispersion forces, charge transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole interactions. Hence it is concluded that the observed deviation of theoretical values from experiment values confirms that the molecular interaction is taking place between the molecules in binary organic liquid mixture.

Table-1. Values of APD for various mixtures

Mixture	T (K)	GD	AB	LL	W	H	N
H+O	295	-0.0153	-0.0162	0.0067	-0.0068	0.0114	-0.0387

	300	-0.0158	-0.0164	0.0083	-0.0064	0.0116	-0.0378
	305	-0.0061	-0.0057	0.0187	0.0029	0.0223	-0.0285
H+M	295	-0.0119	-0.0117	0.0070	-0.0059	0.0101	-0.0282
	300	-0.0047	-0.0046	0.0117	0.0024	0.0146	-0.0219
H+P	305	-0.0130	-0.0120	0.0065	-0.0059	0.0082	-0.0295
	295	-0.0126	-0.0118	0.0054	-0.0065	0.0105	-0.0297
	300	-0.0327	-0.0338	0.3759	0.1618	0.4234	0.7443
	305	-0.2341	-0.2359	0.1127	-0.1321	0.1654	-0.5282

Conclusion

It is attempted to study the relative validity and importance of various mixing rules for the prediction of refractive index of binary organic liquid mixture. Observed Temperature dependence also discussed. it is concluded that these rules are interrelated. Due to the different size and nature of molecules particular relation gives good agreement in some systems but deviates in others. In this way we find the preferential use of one rule over other.

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