RESEARCH ARTICLE

APPLICATION OF REFRACTIVE INDEX MIXING PRINCIPLES IN BINARY SYSTEMS AT T=298.15, 308.15 AND 318.15K

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Manuscript Info	*Abstract*
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Binary liquid mixes of 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol with hexadecane and heptadecane have had their densities and refractive indices experimentally determined at 298.15, 308.15, and 318.15 K. To determine whether the Lorentz-Lorenz (L-L), Weiner-Heller (W-H), and Gladstone-Dale (G-D) relations for predicting the refractive index of a liquid are valid for the eight binaries over the entire mole fraction range of hexadecane and heptadecane at the three temperatures, a comparative study of these relationships has been conducted. The average percentage deviation has been used to compare different mixing rules. Comparatively speaking, the Weiner and Gladstone-Dale relations perform better than the Lorentz-Lorenz and Heller relations.

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Introduction:-

Prediction of refractive indices of binary liquid mixtures is essential for the determination of composition of binary liquid mixtures. Refractive index measurements in combination with density, boiling point, melting point and other analytical data are very useful industrially also for common substances which include oils, waxes, sugar syrups etc. An exhaustive literature survey reveals that there is no such data on these systems, the components of which have wide applicability in chemical analyses and industry. The most widely used theoretical rules for predicting refractivity of binary liquid mixtures are due to Lorentz–Lorenz(1980,1909) and Weiner(1910).Various empirical and semi-empirical relations have been formulated earlier and tested by Heller3 and Gladstone–Dale(1858). Recently, researchers Faiza, Ouaaret.al.,(2020);Fisnik,Aliaj.et.al.(2020);Moodley,Kuveneshan.(2020);and Azarang, Nasim.et.al.(2020)have examined the applicability of these mixing rules in several binary systems. By Pandey et al.(1992), the relative advantages of these mixing rules have been explored. Since these mixing rules are only based on volume additivity, they cannot take into consideration changes in volume and refractivity that occur during mixing. Aminabhaviet.al. (1984) made a point about how mixing rules can be used to calculate binary refractive indices and density information.The complete composition range of hexadecane and heptadecane at 298.15, 308.15, and 318.15 K has been studied in the current paper using four refractive index mixing rules for eight binary liquid mixtures. These rules have not before been studied in the literature. The relative reliability of each of these rules has been assessed by comparing with experimental data.

Experimental

The compounds, which were of Anal R grade purity greater than 99%, were bought from Merck. The credibility of the current results is established by the close agreement between experimental values and those described in the literature. To avoid evaporation losses, the mixtures were made by mixing calibrated amounts of the components in

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hermetically stoppered bottles. Denver Instruments' electronic balance, with a readability of 0.0001 gramme, was used for the weighing. Using a bilimbedPyknometer with an 18 ml bulb, density measurements were taken. With a measurement uncertainty of 0.024%, the experimentally estimated densities using this method corresponded well with literature values. Using Abbe's refractometer, which has the fewest moving components and hence the lowest likelihood of error owing to strain, the refractive indices of the liquids and the mixtures were calculated. To verify the veracity of the findings, the refractive indices of pure liquids including benzene, cyclohexane, and n-hexane were tested. The values measured and those from the literature showed good agreement. Refractive index readings were found to be 0.006% uncertain.

Resultsanddiscussion:-

These mixing principles for refractive index are based on the electromagnetic theory of light, which treats molecules as dipoles or collections of dipoles in the presence of an external field. In the current study, an effort has been made to examine the viability of four mixing rules for predicting the refractivity of eight binary mixtures that contain hexadecane or hepta-decane as the first component and 1-butanol, 1-pentanol, 1-hexanol, or 1-heptanol as the second component, over the full mole fraction range of hexadecane and heptadecane in their respective systems. Below are a number of equations for calculating refractive index.

The mixing rule known as Lorentz-Lorenz is the one that is most usually applied when analyzing data on refractive indices.

$$\frac{n_{12}^2 - 1}{n_{12}^2 - 2} = \emptyset_1 \frac{n_{12}^2 - 1}{n_{12}^2 - 2} + \emptyset_2 \frac{n_{12}^2 - 1}{n_{12}^2 - 2}$$

Here, n1 and n_2 are the corresponding refractive indices of the pure components; 1 and 2 are volume fractions. n_{12} is the refractive index of the mixture of x_1 (n-alkane) and x_2 (1-alkanol). The volume fraction can be calculated using the formula $1 = x_1 v_1 / x_1 v_1$, where x is the mole fraction and v is the component i's molar volume.

Weiner connection It proposes volume additivity, is applicable to isotropic bodies with spherically symmetrical shapes, and is given by

$$\frac{n_{12}^2 - n_1^2}{n_{12}^2 - 2n_1^2} = \emptyset_2 \frac{n_{12}^2 - n_1^2}{n_{12}^2 - 2n_1^2}$$

Heller relation: Heller (1945) assumed equivalence of light-scattering equations of Debye and Rayleigh and derived the following equation:

$$\frac{n_{12}^2 - n_1}{n_1} = \frac{3}{2} \emptyset_2 \frac{m^2 - 1}{m^2 + 2}$$

where m = n_2/n. The Heller relation is based on the approximation:

$$\frac{m^2 - 1}{m^2 + 2} = \left(\frac{2}{3} m\right) m - 1$$

i.e. $n_2 = n_1$.

Gladstone–Dale equation: This can be referred to as specific refraction and can be formulated as;

$$\frac{n_{12}^2 - n_1}{\rho_{12}} = \left(\frac{n_1 - 1}{\rho_1}\right) w_1 + \left(\frac{n_2 - 1}{\rho_2}\right) w_2$$

where w_1 and w_2 are the weight fractions of pure components.

Utilising refractive index mixing principles such Lorentz-Lorenz, Heller, Weiner, and Gladstone-Dale relations, the refractive indices for the systems chosen for inquiry were calculated at 298.15, 308.15, and 318.15 K. Tables 1-4 show the experimental results on the density and refractive indices of the eight binaries at 298.15 K. Hexadecane plus one butanol's refractive index information for the three temperatures under consideration is shown in Table 2.

Other systems have seen a similar fluctuation. The experimentally determined binary mixture indices were compared to the anticipated outcomes of the mixing principles put forward by Lorentz-Lorenz, Weiner, Heller, and Gladstone-Dale. Table 3 displays the average percentage deviations found to evaluate their validity. Utilising refractive index mixing principles such Lorentz-Lorenz, Heller, Weiner, and Gladstone-Dale relations, the refractive indices for the systems chosen for inquiry were calculated at 298.15, 308.15, and 318.15 K. Table 1 shows the experimental results on the density and refractive indices of the eight binaries at 298.15 K. Hexadecane plus one butanol's refractive index information for the three temperatures under consideration is shown in Table 2. Other systems have seen a similar fluctuation. The experimentally determined binary mixture indices were compared to the anticipated outcomes of the mixing principles put forward by Lorentz-Lorenz, Weiner, Heller, and Gladstone-Dale. Table 3 displays the average percentage deviations found to evaluate their validity. In systems including alcohol, hydrogen bonding contributes to lowering experimental refractive index values, which also produces negative deviation values.

While the Heller relation yields generally good results, variations are more noticeable in the systems where refractive index values predicted from the Lorentz-Lorenz relation show great agreement with the experimental values.

Table1:- Refractiveindicesofbinarysystemsofhexadecanewith1-butanoland 1-pentanol at298.15.

x	ρ/gcm^{-3}	n	x	ρ/gcm^{-3}	n
Hexadecane +1-butanol			Hexadecane + 1-pentanol		
0.000	0.8078	1.3985	0.000	0.8110	1.4095
0.0903	0.7997	1.3988	0. 0831	0.8072	1.4101
0.1969	0.7971	1.4009	0.1842	0.8029	1.4124
0.2528	0.7952	1.4032	0.2892	0.7988	1.4173
0.3988	0.7911	1.4112	0.3684	0.7956	1.4108
0.4806	0.7893	1.4170	0.4612	0.7919	1.4259
0.5726	0.7861	1.4210	0.5614	0.7880	1.4298
0.6757	0.7853	1.4277	0.6462	0.7851	1.4325
0.7925	0.7824	1.4216	0.7584	0.7811	1.4339
0.9259	0.7776	1.4338	0.8492	0.7778	1.4345
0.9628	0.7755	1.4347	0.9314	0.7746	1.4341
1.000	0.7732	1.4348	1.000	0.7733	1.4348

Table2:- Refractiveindicesofbinarysystemsofhexadecanewith1-hexanol and 1-heptanolat298.15.

x	ρ/gcm^{-3}	n	x	ρ/gcm^{-3}	n
Hexadecane +1-hexanol			Hexadecane +1-heptanol		
0.0000	0.8152	1.4103	0.0000	0.8205	1.4120
0.0791	0.8112	1.4105	0.0893	0.8157	1.4123
0.1751	0.8067	1.4130	0.1944	0.8101	1.4148
0.2940	0.8015	1.4180	0.3041	0.8048	1.4189
0.3647	0.7985	1.4217	0.3743	0.8014	1.4228
0.4451	0.7949	1.4258	0.4543	0.7974	1.4266
0.5371	0.7909	1.4263	0.5512	0.7927	1.4300
0.6435	0.7868	1.4299	0.6531	0.7883	1.4328
0.7679	0.7817	1.4338	0.7703	0.7828	1.4340
0.8384	0.7788	1.4342	0.8301	0.7800	1.4344
0.9184	0.7755	1.4347	0.9242	0.7756	1.4346
1.0000	0.7733	1.4348	1.000	0.7733	1.4348

Table3:- Refractiveindicesofbinarysystemsofheptadecanewith1-butanol and 1-pentanolat298.15.

x	ρ/gcm^{-3}	n	x	ρ/gcm^{-3}	n
Heptadecane +1-butanol			Heptadecane +1-pentanol		
0.000	0.8078	1.3985	0.000	0.8110	1.4095

0.0867	0.8045	1.3996	0.1400	0.8094	1.4103
0.1704	0.8026	1.4027	0.1472	0.8063	1.4117
0.2817	0.7996	1.4106	0.2530	0.8034	1.4160
0.3539	0.7973	1.4163	0.3550	0.7997	1.4216
0.4421	0.7951	1.4226	0.4855	0.7952	1.4286
0.5521	0.7927	1.4285	0.5948	0.7946	1.4323
0.6932	0.7896	1.4246	0.6583	0.7902	1.4338
0.7799	0.7881	1. 4348	0.7291	0.7813	1. 4349
0.8810	0.7860	1.4356	0.8084	0.7864	1.4356
0.9379	0.7853	1.4357	0.8980	0.7853	1.4357
1.000	0.7846	1.4358	1.000	0.7846	1.4358

Table4:- Refractiveindicesofbinarysystemsofandheptadecanewith1-hexanol and 1-heptanolat298.15.

x	ρ/gcm^{-3}	n	x	ρ/gcm^{-3}	n
Heptadecane +1-hexanol			Heptadecane +1-heptanol		
0.0000	0.8152	1.4173	0.000	0.8205	1.4231
0.0961	0.8136	1.4189	0.1062	0.8183	1.4236
0.1667	0.8103	1.4198	0.1828	0.8154	1.4245
0.2819	0.8063	1.4212	0.3050	0.8121	1.4268
0.3895	0.8033	1.4243	0.4162	0.8093	1.4298
0.4747	0.8004	1.4279	0.5025	0.8062	1.4314
0.5739	0.7963	1.4299	0.6008	0.8031	1.4335
0.6907	0.7932	1.4313	0.7139	0.8004	1.4348
0.7575	0.7907	1. 4348	0.7771	0.7964	1. 4353
0.8302	0.7894	1.4352	0.8453	0.7921	1.4356
0.9107	0.7864	1.4356	0.9194	0.7874	1.4357
1.0000	0.7846	1.4358	1.000	0.7846	1.4358

Table5:- Refractive indices and densities of hexadecane (x_1) + 1-butanol (x_2) at 298.15, 308.15 and 318.15 K.

	298.15		308.15		318.15	
x	ρ/gcm^{-3}	n	ρ/gcm^{-3}	n	ρ/gcm^{-3}	n
0.0000	0.8078	1.3985	0.8009	1.3970	0.7848	1.3956
0.0903	0.7997	1.3988	0.7958	1.3974	0.7787	1.3960
0.1969	0.7971	1.4009	0.7899	1.3995	0.7725	1.3981
0.2528	0.7952	1.4032	0.7865	1. 4017	0.7696	1.4003
0.3988	0.7911	1.4112	0.7765	1.4096	0.7629	1.4082
0.4809	0.7893	1.4170	0.7739	1.4151	0.7601	1.4136
0.5726	0.7861	1.4210	0.7705	1.4201	0.7567	1.4189
0.6757	0.7853	1.4277	0.7673	1.4257	0.7530	1.4242
0.7925	0.7824	1.4216	0.7643	1.4294	0.7498	1.4279
0. 9259	0. 7776	1.4338	0. 7611	1.4317	0. 7468	1.4302
0.9628	0.7755	1.4347	0.7603	1.4325	0.7441	1.4310
1.000	0.7733	1.4348	0.7597	1.4327	0.7429	1.4312

Weiner and Gladstone-Dale relations have been used to produce theoretical results. The performance of the Lorentz-Lorenz equation is the best of all because the deviation with concentration varies monotonically without reaching a maximum or changing its sign. Without assuming a change in molecular polarizabilities on component mixing, the volume dilation explains the minor negative deviations. Therefore, the systems can be viewed as being almost perfect for testing various different mixing rules. The observed variations are predicted and can be attributed to the volume additive mixing process, since liquid mixes' surplus volume, which serves as a gauge of molecular interactions, would completely disappear otherwise. For the systems under investigation, the extra molar volumes have already been published by many workers Arago, D.F.J.(1860);Tasic, A. Z.et.al.(1992);Pandey, J.D.et.al.(1992); Mehra, R., and Israni. R.(2000); and Oster, G.(1980).Aminabhavi has also suggested that by accounting for the

surplus volume in the various mixing procedures, the difference between theoretical values and experimental ones can be minimized(1979).These projected refractive index values of multi-component systems are necessary for physicochemical calculations involving multiple phase systems. Refractive indices using molar refraction can be used to integrate the structure of liquids and liquid mixtures. For both symmetric and asymmetric molecules, molar refraction rises with molecular weight. Refractive index and density are influenced by molecular weight and the type of substituents.

Weiner and Gladstone-Dale relations for all eight binary mixtures showed negative departures at all temperatures that were likewise larger in size than the deviations found for the Lorentz and Heller equations. Weiner's relation shows a larger negative divergence. It only applies to isotropic substances with spherically symmetrical shapes, and it suggests volume additivity as the cause of the Weiner relation's deviations. Additionally, when the temperature rises and the length of the alkane and alkanol chains increases, the negative deviations shortenNath,J.et.al.(a1980;b1980);Aminabhavi T. M.(1994);and Riggio, R., Ubeda, Ramos, M. H.(1980) Compared to the Lorentz-Lorenz and Weiner relations, the Gladstone-Dale (GD) connection has a narrower range of applications. If the solutions are very diluted and the solvent and solute's refractive indices are both very similar, the G-D relation yields findings that are equal to those from the Weiner relation.

However, at lower alkanol concentrations, regardless of all other variables like volume additivity, volume expansion, volume reduction, refractivity, and temperature, all four mixing rules may be successfully employed. For all the systems under consideration, Weiner's relation and the Gladstone Dale equation do not produce satisfactory results at larger concentrations of alkanols; as a result, they cannot be used to liquids of diverse types, especially those with notable differences in molecular size. Alkanol and alkane chain length increases and temperature increases have little impact on the observed variances.

Table 6:- Average percentage deviations in Lorentz –Lorenz (L –L), Heller (H), Weiner (W) and G ladstone–Dale (G–D) relations in binary mixtures of hexadecane and heptadecane with 1 -butanol, 1 -pentanol, 1 -hexanol and 1 - heptanol at different temperatures.

Compone nt	T=298.15K				T=308.15K				T=318.15K			
	L-L Relat ion	Helle r	Wei ner	Glads tone- Dale	L-L Rel atio n	Helle r	Wein er	Glads tone- Dale	L-L Relat ion	Helle r	Wein er	Glad stone -Dale
Hexadecane+ 1-butanol	0.010	0.005	-0.660	-0.841	0.010	0.005	-0.63	-0.981	0.010	0.005	-0.600	-0.800
Hexadecane+ 1-butanol	0.016	0.007	-0.350	-0.380	0.010	0.002	-0.32	-0.362	0.014	0.002	-0.193	-0.186
Hexadecane+ 1-butanol	0.014	0.005	-0.208	-0.210	0.014	0.005	-0.231	-0.243	0.016	0.004	-0.220	-0.248
Hexadecane+ 1-butanol	0.019	0.002	-0.187	-0.197	0.010	0.011	-0.142	-0.186	0.012	0.016	-0.133	-0.149
Heptadecane +1-butanol	0.010	0.015	-0.403	-0.183	0.012	0014.	-0.358	-0.034	0.012	0.008	-0.308	-0.316
Heptadecane +1-pentanol	0.013	0.017	-0.275	-0.286	0.015	0.015	-0.142	-0.168	0.015	0.015	-0.058	-0.161
Heptadecane +1-hexanol	0.013	0.015	-0.040	-0.050	0.012	0.015	-0.071	-0.084	0.009	0.012	-0.103	-0.109
Heptadecane +1-heptanol	0.013	0.016	-0.012	-0.080	0.015	0.020	-0.026	-0.034	0.015	0.014	-0.020	-0.060

Conclusion:-
The four theoretical mixing rules given are related in a straightforward quantitative way from the aforementioned investigation, and they function well within the bounds of experimental error. If the idea of excess volume (V^E), which is an indirect measure of interaction, is taken into account in various mixing procedures, the difference between the theoretical and observed values of refractive index for all the systems chosen for inquiry may be decreased.

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