Application of refractive index mixing rules in binary systems of hexadecane and heptadecane with *n*-alkanols at different temperatures

RITA MEHRA

Department of Pure and Applied Chemistry, Maharshi Dayanand Saraswati University, Ajmer 305 009, India
e-mail: mehra_rita@rediffmail.com

Abstract. Density and refractive index have been experimentally determined for binary liquid mixtures of hexadecane and heptadecane with 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol at 298·15, 308·15 and 318·15 K. A comparative study of Lorentz–Lorenz (L–L), Weiner (W) and Heller (H), and Gladstone–Dale (G–D) relations for predicting the refractive index of a liquid has been carried out to test their validity for the eight binaries over the entire mole fraction range of hexadecane and heptadecane at the three temperatures. Comparison of various mixing rules has been expressed in terms of average percentage deviation. The performance of the Lorentz–Lorenz and Heller relations is relatively better than that of the Weiner and Gladstone–Dale relations.

Keywords. Hexadecane; heptadecane; refractive index; Lorentz–Lorenz relation; Heller relation; Weiner relation; Gladstone–Dale relation.

1. 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[1] and Weiner.[2] Various empirical and semi-empirical relations have been formulated earlier and tested by Heller[3] and Gladstone–Dale.[4] The validity of these mixing rules has been tested by researchers[5–9] for some binary systems. Relative merits of these mixing rules have been discussed by Pandey *et al*[10]. The major drawback of these mixing rules is their inability to account for changes in volume and refractivity during mixing as they are based only on volume additivity. Aminabhavi[11] pointed out the usefulness of mixing rules in determining binary refractive indices and density data.

   In the present paper, an attempt has been made to study four refractive index mixing rules for eight binary liquid mixtures covering the entire composition range of hexadecane and heptadecane at 298·15, 308·15 and 318·15 K, which are not available in

literature. The relative reliability of each of these rules has been assessed by comparing with experimental data.

2. Experimental

The chemicals were purchased from Merck and were of Analar grade of purity greater than 99%. The close agreement of experimental values with those reported in literature ascertain the reliability of the present results. The mixtures were prepared by mixing measured volumes of the components in airtight stoppered bottles to minimise evaporation losses. The weighing was done on an electronic balance (Denver Instruments) with a readability of 0·0001 gm. Density measurements were made using a bilimbed pyknometer, the bulb volume of which was 18 ml. The experimentally determined values of densities by this method agreed well with literature values, the uncertainty in measurements being 0·024%.

The refractive indices of the liquids and of the mixtures were determined using Abbe's refractometer which has the least number of moving parts; thus the chances of error arising due to strain are also minimal. Refractive indices of pure liquids such as benzene, cyclohexane and *n*-hexane were measured to ascertain the accuracy of the results. Good agreement was found between measured and literature values. Uncertainty in refractive index measurements was found to be 0·006%.

3. Results and discussion

Electromagnetic theory of light is the basis of these mixing rules of refractive index which treats the moleules as dipoles or assemblies of dipoles by an external field. In the present work, an attempt has been made to study the validity of four mixing rules for predicting the refractivity of eight binary mixtures comprising hexadecane or heptadecane as the first component and 1-butanol, 1-pentanol, 1-hexanol or 1-heptanol as the second component, over the entire mole fraction range of hexadecane and heptadecane in their respective systems. Various equations for determining refractive index are given below.

Lorentz–Lorenz: This is the most frequently used mixing rule in the analysis of refractive index data:

$$\frac{n_{12}^2-1}{n_{12}^2+2} = f_1 \frac{n_1^2-1}{n_1^2+2} + f_2 \frac{n_2^2-1}{n_2^2+2}.$$

Here, n_{12} is the refractive index of the mixture of x_1 (*n*-alkane) and x_2 (1-alkanol), n_1 and n_2 are the refractive indices of the pure components respectively, f_1 and f_2 are volume fractions. The volume fraction f may be obtained from $f_1 = x_1 v_1 / \sum x_1 v_1$, where x is the mole fraction and v is the molar volume of component i.

Weiner relation: It applies to isotropic bodies of spherically symmetrical shape and proposes volume additivity and is given by

$$\frac{n_{12}^2 - n_1^2}{n_{12}^2 + 2n_1^2} = f_2 \frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}.$$

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

$$\frac{n_{12} - n_1}{n_1} = \frac{3}{2} f_2 \frac{m^2 - 1}{m^2 + 2},$$

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

$$\frac{m^2 - 1}{m^2 + 2} \cong \left(\frac{2}{3}m\right)m - 1, \text{ i.e. } n_2 = n_1.$$

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

$$\frac{n_{12} - 1}{r_{12}} = \left(\frac{n_1 - 1}{r_1}\right)w_1 + \left(\frac{n_2 - 1}{r_2}\right)w_2,$$

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

The refractive index for the systems taken for investigation has been evaluated at 298·15, 308·15 and 318·15 K using refractive index mixing rules such as Lorentz–Lorenz, Heller, Weiner and Gladstone–Dale relations. The experimental data on refractive index and density of the eight binaries at 298·15 K has been given in table 1. Table 2 records the refractive index data of hexadecane + 1 butanol at the three temperatures studied. Similar variation has been observed for other systems. The experimental indices obtained for the binary mixture were compared with the predicted results for the mixing rules proposed by Lorentz–Lorenz, Weiner, Heller and Gladstone–Dale. The average percentage deviations determined to assess their validity are shown in table 3.

A close look of the tables reveals that the refractive indices of the pure components and mixtures decrease with rise in temperature. However, the deviations of theoretical values from experimental ones are temperature-independent except for the Weiner relation in the systems selected for investigation. This may be attributed to the fact that variation in refractive index with temperature is compensated for by the change in density of the liquid mixture. However, in cases where the variation is significant with change in temperature, it can be used for interpreting the structure and interactions in the liquid by computing other dielectric, optical and acoustic properties using the experimental data. No effect of increase in chain length of alkanols and alkanes on refractive index was observed. Hydrogen bonds play a role in reducing the experimental values of refractive index in alcohol-containing systems, which also results in negative values of deviations.

In all the systems, refractive index values predicted from Lorentz–Lorenz relation shows excellent agreement with the experimental values followed by the Heller relation, which gives fairly good results, whereas deviations are more pronounced in the

Table 1. Refractive indices of binary systems of hexadecane and heptadecane with 1-alkanols at 298·15 K.

x_1	n_{exp}	r (kg m^{-3})	x_1	n_{exp}	r (kg m^{-3})
Hexadecane + 1-butanol			*Hexadecane + 1-pentanol*		
0·0000	1·3985	807·8	0·0000	1·4095	811·0
0·0903	1·3988	799·7	0·0831	1·4101	807·2
0·1969	1·4009	797·1	0·1842	1·4124	802·9
0·2528	1·4032	795·2	0·2892	1·4173	798·8
0·3988	1·4112	791·1	0·3684	1·4108	795·6
0·4809	1·4170	789·3	0·4612	1·4259	791·9
0·5726	1·4210	786·1	0·5614	1·4298	788·0
0·6757	1·4277	785·3	0·6462	1·4325	785·1
0·7925	1·4216	782·4	0·7584	1·4339	781·1
0·9259	1·4338	777·6	0·8492	1·4345	777·8
0·9628	1·4347	775·5	0·9314	1·4341	774·6
1·0000	1·4348	773·3	1·0000	1·4348	773·3
Hexadecane + 1-hexanol			*Hexadecane + 1-heptanol*		
0·0000	1·4103	815·2	0·0000	1·4120	820·5
0·0791	1·4105	811·2	0·0893	1·4123	815·7
0·1751	1·4130	806·7	0·1944	1·4148	810·1
0·2940	1·4180	801·5	0·3041	1·4189	804·8
0·3647	1·4217	798·5	0·3743	1·4228	801·4
0·4451	1·4258	794·9	0·4543	1·4266	797·4
0·5371	1·4263	790·9	0·5512	1·4300	792·7
0·6435	1·4299	786·8	0·6531	1·4328	788·3
0·7679	1·4338	781·7	0·7703	1·4340	782·8
0·8384	1·4342	778·8	0·8301	1·4344	780·0
0·9184	1·4347	775·5	0·9242	1·4346	775·6
1·0000	1·4348	773·3	1·0000	1·4348	773·3
Heptadecane + 1-butanol			*Heptadecane + 1-pentanol*		
0·0000	1·3985	807·8	0·0000	1·4095	811·0
0·0867	1·3996	804·5	0·1400	1·4103	809·4
1·1704	1·4027	802·6	0·1472	1·4117	806·3
0·2817	1·4106	799·6	0·2530	1·4160	803·4
0·3539	1·4163	797·3	0·3550	1·4216	799·7
0·4421	1·4226	795·1	0·4855	1·4286	795·2
0·5521	1·4285	792·7	0·5948	1·4323	794·6
0·6932	1·4246	789·6	0·6583	1·4338	790·2
0·7799	1·4348	788·1	0·7291	1·4349	781·3
0·8810	1·4356	786·0	0·8084	1·4356	786·4
0·9379	1·4357	785·3	0·8980	1·4357	785·3
1·0000	1·4358	784·6	1·0000	1·4358	784·6
Heptadecane + 1-hexanol			*Heptadecane + 1-heptanol*		
0·0000	1·4173	815·2	0·0000	1·4231	820·5
0·0961	1·4189	813·6	0·1062	1·4236	818·3
0·1667	1·4198	810·3	0·1828	1·4245	815·4

Table 1. *(Contd...)*

x_1	n_{exp}	r (kg m^{-3})	x_1	n_{exp}	r (kg m^{-3})
0·2819	1·4212	806·3	0·3050	1·4268	812·1
0·3895	1·4243	803·3	0·4162	1·4298	809·3
0·4747	1·4279	800·4	0·5025	1·4314	806·2
0·5739	1·4299	796·3	0·6008	1·4335	803·1
0·6907	1·4313	793·2	0·7139	1·4348	800·4
0·7575	1·4348	790·7	0·7771	1·4353	796·4
0·8302	1·4352	789·4	0·8453	1·4356	792·1
0·9107	1·4356	786·4	0·9194	1·4357	787·4
1·0000	1·4358	784·6	1·0000	1·4358	784·6

Table 2. Refractive indices and densities of hexadecane (x_1) + 1-butanol (x_2) at 298·15, 308·15 and 318·15 K.

	Temperature (K)					
	298·15		308·15		318.15	
x_1	n_{exp}	r (kg m^{-3})	n_{exp}	r (kg m^{-3})	n_{exp}	r (kg m^{-3})
0·0000	1·3985	807·8	1·3970	800·9	1·3956	784·8
0·0903	1·3988	799·7	1·3974	795·8	1·3960	778·7
0·1969	1·4009	797·1	1·3995	789·9	1·3981	772·5
0·2528	1·4032	795·2	1·4017	786·5	1·4003	769·6
0·3988	1·4112	791·1	1·4096	776·5	1·4082	762·9
0·4809	1·4170	789·3	1·4151	773·9	1·4136	760·1
0·5726	1·4210	786·1	1·4201	770·5	1·4189	756·7
0·6757	1·4277	785·3	1·4257	767·3	1·4242	753·0
0·7925	1·4216	782·4	1·4294	764·3	1·4279	749·8
0·9259	1·4338	777·6	1·4317	761·1	1·4302	746·8
0·9628	1·4347	775·5	1·4325	760·3	1·4310	744·1
1·0000	1·4348	773·3	1·4327	759·7	1·4312	742·9

theoretical results obtained from the Weiner and the Gladstone–Dale relations. The Lorentz–Lorenz equation performs best of all, since the variation of the deviation with concentration is monotonic without a maximum or a change of sign. The small negative deviations are accounted for by the volume dilation without assuming a change in molecular polarizabilities on mixing of the components. The systems may therefore be considered as nearly ideal ones for the test of various other mixing rules. The observed deviations are expected and can be ascribed to the volume additivity during mixing without which the excess volume that is a measure of molecular interactions in liquid mixtures will completely vanish. The excess molar volumes for the systems under investigation have already been reported by us.[12–16] Aminabhavi has also suggested that the deviation of theoretical values from experimental ones can be reduced if the excess volume is taken into consideration in the various mixing rules.[17] Physico-chemical calculations involving multiple phase systems require these predicted refractive index values of multi-component systems. The structure of liquid and liquid mixtures can be integrated through refractive indices employing molar refraction. Molar refraction

Table 3. Average percentage deviations in Lorentz–Lorenz (L–L), Heller (H), Weiner (W) and Gladstone–Dale (G–D) relations in binary mixtures of hexadecane and heptadecane with 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol at different temperatures.

	$T = 298.15$ K				$T = 308.15$ K				$T = 318.15$ K			
	L–L	H	W	GD	L–L	H	W	GD	L–L	H	W	GD
cane + 1-butanol	0.010	0.005	−0.660	−0.841	0.010	0.005	−0.63	−0.981	0.01	0.005	−0.6	−0.800
-pentanol	0.016	0.007	−0.350	−0.380	0.010	0.002	−0.32	−0.362	0.014	0.002	−0.193	−0.186
-hexanol	0.014	0.005	−0.208	−0.210	0.014	0.005	−0.221	−0.243	0.016	0.004	−0.22	−0.248
-heptanol	0.019	0.002	−0.187	−0.197	0.010	0.011	−0.142	−0.186	0.012	0.016	−0.133	−0.149
-butanol	0.010	0.015	−0.403	−0.183	0.012	0.014	−0.358	−0.034	0.012	0.008	−0.308	−0.316
-pentanol	0.013	0.017	−0.275	−0.286	0.015	0.015	−0.142	−0.168	0.015	0.015	−0.058	−0.061
-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
-heptanol	0.013	0.016	−0.012	−0.080	0.015	0.020	−0.026	−0.034	0.015	0.014	−0.02	−0.060

increases with molecular weight for symmetric and asymmetric molecules. Density and refractive index are dependent on molecular weight and nature of substituents.

For all the eight binary mixtures, Weiner and Gladstone–Dale relations at all temperatures exhibited negative deviations which were also higher in magnitude than the deviations obtained for the Lorentz and Heller relations. Weiner relation exhibits negative deviation of higher magnitude. It strictly applies to isotropic bodies of spherically symmetrical shape and it proposes volume additivity which is the reason for the deviations obtained in case of the Weiner relation. Also, the negative deviations decrease with rise in temperature and increase in chain length of alkanes and alkanols.[18–21] The Gladstone–Dale (GD) relation is more limited in applicability then the Lorentz–Lorenz and Weiner relations. The G–D relation gives identical results with those obtained from the Weiner relation if, the solutions are very dilute and if, in addition, the refractive indices of solute and solvent are very similar.

However, all four mixing rules could be applied successfully at lower concentration of alkanols irrespective of all other factors such as volume additivity, volume expansion, volume reduction, refractivity and temperature. Weiner's relation and Gladstone Dale equation do not provide good results at higher concentrations of alkanols for all the systems under study and hence it cannot be satisfactorily applied for liquids of different nature particularly those that have significant difference in molecular size. The deviations observed are not affected by increase in the chain length of alkanol and alkanes or with rise of temperature.

4. Conclusion

From the above investigation it may be concluded that the four theoretical mixing rules discussed are interrelated in a simple quantitative manner and perform well within the limits of experimental error. The deviation between the theoretical and observed values of refractive index for all the systems taken for investigation may be reduced if the concept of excess volume (V^E), which is an indirect measure of interaction, is taken into consideration in various mixing rules.

References

1. Lorentz H A 1906 *Theory of electrons* (Leipzig)
2. Weiner O 1910 *Berichte* (*Leipzig*) **62** 256
3. Heller W 1945 *Phys. Rev.* **68** 5
4. Dale D and Gladstone F 1858 *Philos. Trans.* **148** 887
5. Saxena M C, Khare P and Shrivastav A 1995 *Oriental J. Chem.* **11** 286
6. Oswal S L and Palsanwala P P 1989 *Acoust. Lett.* **13** 66
7. Saxena M C 1998 *Indian J. Chem.* **10** 636
8. Tasic A Z, Djardjevic B D and Grozdonic D K 1992 *J. Chem. Eng. Data* **37** 310
9. Oster G 1948 *Chem. Rev.* **43** 319
10. Pandey J D, Rai R D, Shukla R K, Tiwari K P and Shukla R K 1992 *Indian J. Pure Appl. Phys.* **30** 94
11. Aminabhavi T M 1984 *J. Chem. Eng. Data* **29** 54
12. Mehra R and Israni R 2000 *Indian J. Pure Appl. Phys.* **38** 81
13. Mehra R and Israni R 2001 *J. Pure Appl. Ultrasonics* **23** 63
14. Mehra R and Israni R 1999 *Proc. of Int. Conf. and Exhibition on Ultrasonics* (*ICEU*) **1** 234
15. Mehra R and Israni R 2001 *J. Acoust. Soc. India* **29** 240
16. Mehra R and Israni R 2002 *Indian J. Chem. Technol.* **9** 341
17. Aminabhavi T M and Munk P 1979 *Macromolecules* **12** 1186

18. Nath J and Dubey S N 1980 *J. Phys. Chem.* **84** 2166
19. Kalyanasundaram S 1999 *Bull. Electrochem.* **15** 513
20. Aminabhavi T M, Phyde H T S, Khinnavar R S, Gopal Krishna B and Hansen K C 1994 *J. Chem. Eng. Data* **39** 251
21. Riggio R, Ubeda M H, Ramos J F and Martinez H E 1980 *J. Chem. Eng. Data* **25** 318