Analytical study for mixing rules for refractive index and data analysis for some binary liquid mixtures

Sheeraz Akbar

Assistant professor, Department of Physics, Vssd College,Kanpur,U.P.India

ABSTRACT

In this paper we have made an Analytical study to discuss about relative validity and importance of various mixing rules viz. Arago-Biot (A-B), Gladstone–Dale (G–D, Lorentz–Lorentz (L–L), Weiner (W), Heller (H), and Newton's realtion (N) with following binary liquid mixtures of Ethyl Ethanoate (E) + Benzene (BN)+ Toluene (T),+ Xylene (X), at (293,298,303) K over the entire mole fraction range. Comparison of various mixing rules has been expressed in terms of (APD) average percentage deviation.

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

---

1. INTRODUCTION

For a mixture of liquids of different refractive indices, refractive index gives very useful information about the proportion in which they are mixed. It is well known that for transparent materials, Refractive index is an important characteristic constant. By determining this characteristic we can find the changes in amplitudes of reflected and transmit light beams. Using these measurements we can also determine the purity of liquid samples. It is now well established that the measurement of refractive index is used as an important tool of investigation in the field of Analytical Chemistry. When we make a liquid mixture of different organic liquids then molecules of liquid mixtures rearrange themselves and the study of refractive index can predict this molecular rearrangement due to mixing of organic liquids. Inside a matter there exists small atomic oscillators and since refractive index is very strongly related with the orientations of these oscillators this is the reason that why it is said that variation of refractive index of liquid mixtures with temperature and composition can give very useful information about molecular rearrangement arises due to mixing of different organic liquids. There are many workers who have examined the mixing rules of refractive index for pure liquids and also for binary liquid mixtures [3-8]. There exist the definite expansion and/or contraction of liquid when the mixing takes place and also densities become changed and due to this density change, we observe considerable variation in refractive index. This was firstly examined by Laplace and later by Gladstone-Dale who gave a formula for the determination of refractive index of a liquid mixture by using the properties of their pure components [9, 11]. We have many numbers of theoretical mixing rules and it is find out that rules due to Lorentz-Lorentz and Weiner are extensively used [10,12].Various empirical and semi-empirical relations have been formulated in this connection and also relative merits of these mixing rules have been discussed by various workers[15,16,17,19]. It is important to mention here that there exists drawback of these mixing rules in their inability to account for changes in volume and refractivity during mixing; this is because of volume additivity. In the light of above description, it is fully feasible to make discussion for these mixing rules for the mixtures taken in this study, given as follows. We have already report [13] the various properties such as refractive index, density, excess molar volumes, excess molar refraction etc. for the binary mixture under investigation.

Ethyl Ethanoate (E) + Benzene (BN)

Ethyl Ethanoate (E) + Toluene (T)

Ethyl Ethanoate (E) + Xylene (X)

2. THEORY

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

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

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

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

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

Weiner relation (W) is given by

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

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

Heller (H) equation is given by –

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

This relation is limiting case of Weiner’s relation.

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

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

Newton relation (N) is given by

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

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

Calculated Values of refractive index and average percentage deviation (APD) for system (E + BN), (E + T), and (E + X) at various temperatures for all the relations are listed in Table1 to table-4 respectively. By the close observation of table1 to table4 we can make discussion as follows. First of all its is very important to mention here that all the mixing relations for the prediction of refractive indices are in well agreement with the corresponding value of refractive index which are find out experimentally for all the systems under present study. For the binary liquid mixtures taken here i.e. (E+BN), (E+T) and (E+X) it is found that number of theoretical relations gives negative values for APD at all three temperatures. It is interesting to see that all relations give a systematic behavior with the variation of temperature. For (E+BN) system G-D, A-B, N and W gives the APD values in increasing order as temperature increase while L-L and H shows exactly opposite behavior as their APD values decreases with temperature increasing. Minimum value of APD is due to Newton's (N) relation for (E+BN), for system (E+T) G-D, A-B, W and N gives negative values of APD while L-L and H give positive values, minimum value of APD for this system is due to G-D for all three temperature values. For system (E+X) similar trends are observed as found for (E+T) system with the change that now Newton (N) relation gives minimum APD values. There is no systematic variation for APD values, found with temperature variation for system (E+T) and (E+X). With the above analysis it is concluded that all the mixing rules relations give good results that are in well agreement. However in this study Gladstone-Dale relation gives minimum values of APD for most cases.

As we have difference between theoretical values and experimental values it is necessary to discuss about this. Although there are number of reasons for this difference but it is strongly due to mixture formation because when the mixture of liquid is formed then the physical properties of liquid mixture becomes change and they are significantly different from the properties of the original components[1,2]. As we know that very low compressibility and lack of shear rigidity are the two main properties of matter in liquid phase hence we can say that matter in liquid phase shows both type of nature as shows by solids and gases because the very low compressibility and lack of shear rigidity are the fundamental properties of solids and gases respectively. This is attributed to limitation to these mixing rules theories. It is assumed normally that all the molecules are perfectly spherical in shape but every time this is not true. In Nomoto theory [18] it is assumed that the volume does not change on mixing of liquid mixtures, hence there exist no interactions. In the similar manner the assumption for the formation of ideal mixing relation is that the ratio of specific heats of ideal mixtures is equal to the ratio of specific heats of the components and the volumes are also equal, this also indicates that no molecular interaction is taken in account [14]. When mixing of two liquids takes place, the presence of various types of forces such as dispersion forces, dipole-dipole, charge transfer, hydrogen bonding, and dipole-induced dipole interactions, are responsible for the interaction between molecules of liquids [17]. From whole above discussion it may be concluded that difference between theoretical values and experiment values of refractive index indicates that molecular interaction between the molecules in liquid mixture is present.

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. Here we have also discussed about the temperature dependence of these relations. From above, it is clear that various mixing rules considered here are interrelated. Size and nature of molecules are different, that is why particular relation gives good agreement in some systems but shows deviation in others, and as a result we find preferential use of one model over other model.

Table-1 Refractive index of (E+BN) mixture at various temperatures by different mixing rules.

X_1	n_m	G-D	A-B	L-L	W	H	N
293K							
0.0000	1.4991	1.4991	1.4991	1.4991	1.4991	1.4969	1.4991
0.0623	1.49	1.4904	1.4904	1.49	1.4902	1.4883	1.4907
0.1531	1.477	1.4778	1.4778	1.477	1.4775	1.476	1.4786
0.2478	1.4639	1.465	1.465	1.4639	1.4645	1.4634	1.4661
0.3468	1.4505	1.4519	1.4519	1.4505	1.4513	1.4505	1.4532
0.4456	1.4375	1.439	1.439	1.4375	1.4384	1.4378	1.4404
0.5573	1.4233	1.4247	1.4247	1.4233	1.4242	1.4238	1.4261
0.6499	1.4119	1.4131	1.4131	1.4119	1.4126	1.4124	1.4144
0.7609	1.3985	1.3995	1.3995	1.3985	1.3991	1.399	1.4005
0.8574	1.3872	1.3879	1.3879	1.3872	1.3876	1.3876	1.3886
0.9952	1.3716	1.3717	1.3717	1.3716	1.3716	1.3716	1.3717
1.0000	1.3711	1.3711	1.3711	1.3711	1.3711	1.3711	1.3711
298K							
0.0000	1.4978	1.4978	1.4978	1.4978	1.4978	1.4956	1.4978
0.0623	1.4891	1.4891	1.4891	1.4887	1.4889	1.487	1.4894
0.1531	1.4757	1.4765	1.4765	1.4757	1.4762	1.4747	1.4773
0.2478	1.4632	1.4637	1.4637	1.4625	1.4632	1.4621	1.4648
0.3468	1.4492	1.4505	1.4505	1.4492	1.45	1.4491	1.4519
0.4456	1.4377	1.4377	1.4377	1.4362	1.4371	1.4365	1.4391
0.5573	1.4220	1.4234	1.4234	1.422	1.4228	1.4225	1.4248
0.6499	1.4113	1.4118	1.4118	1.4106	1.4113	1.4111	1.4131
0.7609	1.3982	1.3982	1.3982	1.3972	1.3978	1.3977	1.3992
0.8574	1.3859	1.3866	1.3866	1.3859	1.3863	1.3863	1.3873
0.9952	1.3703	1.3704	1.3704	1.3703	1.3703	1.3703	1.3704
1.0000	1.3698	1.3698	1.3698	1.3698	1.3698	1.3698	1.3698
303K							
0.0000	1.4965	1.4965	1.4965	1.4965	1.4965	1.4943	1.4965
0.0623	1.4876	1.4878	1.4878	1.4874	1.4876	1.4857	1.4881
0.1531	1.4734	1.4752	1.4752	1.4744	1.4749	1.4734	1.476
0.2478	1.4635	1.4624	1.4624	1.4612	1.4619	1.4608	1.4635
0.3468	1.4478	1.4492	1.4492	1.4479	1.4487	1.4478	1.4506
0.4456	1.4358	1.4364	1.4364	1.4349	1.4358	1.4352	1.4378
0.5573	1.4212	1.4221	1.4221	1.4207	1.4215	1.4212	1.4235
0.6499	1.4118	1.4105	1.4105	1.4092	1.4100	1.4098	1.4118
0.7609	1.3965	1.3969	1.3969	1.3959	1.3965	1.3964	1.3979
0.8574	1.3850	1.3853	1.3853	1.3846	1.3850	1.3850	1.3860
0.9952	1.3691	1.3691	1.3691	1.3690	1.3690	1.3690	1.3691
1.0000	1.3685	1.3685	1.3685	1.3685	1.3685	1.3685	1.3685

Table-2 Refractive index of (E+T) mixture at various temperatures by different mixing rules**.**

X_1	n_m	G-D	A-B	L-L	W	H	N
293K							
0.0000	1.4945	1.4945	1.4945	1.4945	1.4945	1.4924	1.4945
0.0574	1.4877	1.4879	1.4879	1.4877	1.4878	1.486	1.4882
0.1478	1.4772	1.4775	1.4775	1.4768	1.4772	1.4757	1.4781
0.2643	1.4623	1.4638	1.4638	1.4628	1.4634	1.4623	1.4648
0.3556	1.4524	1.4529	1.4529	1.4517	1.4524	1.4515	1.4541
0.4311	1.4424	1.4438	1.4438	1.4424	1.4432	1.4426	1.445
0.5849	1.4243	1.4248	1.4248	1.4235	1.4243	1.4239	1.4261
0.6598	1.4146	1.4154	1.4154	1.4141	1.4149	1.4146	1.4166
0.7389	1.4042	1.4053	1.4053	1.4042	1.4049	1.4047	1.4064
0.8552	1.3900	1.3903	1.3903	1.3896	1.3900	1.3899	1.3910
0.9505	1.3776	1.3777	1.3777	1.3774	1.3776	1.3776	1.3780
1.0000	1.3711	1.3711	1.3711	1.3711	1.3711	1.3711	1.3711
298K							
0.000	1.4929	1.4929	1.4929	1.4929	1.4929	1.4909	1.4929
0.0574	1.4862	1.4864	1.4864	1.4861	1.4862	1.4844	1.4866
0.1478	1.4742	1.4759	1.4759	1.4753	1.4757	1.4742	1.4765
0.2643	1.4632	1.4623	1.4623	1.4612	1.4619	1.4607	1.4632
0.3556	1.4500	1.4514	1.4514	1.4502	1.4509	1.45	1.4526
0.4311	1.4417	1.4423	1.4423	1.4409	1.4417	1.4411	1.4435
0.5849	1.4225	1.4233	1.4233	1.422	1.4228	1.4225	1.4246
0.6598	1.4152	1.4139	1.4139	1.4127	1.4135	1.4132	1.4152
0.7389	1.4035	1.4039	1.4039	1.4028	1.4035	1.4033	1.405
0.8552	1.3886	1.3889	1.3889	1.3882	1.3886	1.3886	1.3896
0.9505	1.3767	1.3764	1.3764	1.3761	1.3763	1.3763	1.3767
1.0000	1.3698	1.3698	1.3698	1.3698	1.3698	1.3698	1.3698
303K							
0.0000	1.4918	1.4918	1.4918	1.4918	1.4918	1.4897	1.4918
0.0574	1.4850	1.4852	1.4852	1.485	1.4851	1.4833	1.4855
0.1478	1.4745	1.4748	1.4748	1.4741	1.4745	1.473	1.4754
0.2643	1.4596	1.4611	1.4611	1.4601	1.4607	1.4596	1.4621
0.3556	1.4497	1.4502	1.4502	1.449	1.4497	1.4488	1.4514
0.4311	1.4398	1.4411	1.4411	1.4398	1.4405	1.4399	1.4424
0.5849	1.4216	1.4221	1.4221	1.4208	1.4216	1.4212	1.4234
0.6598	1.4120	1.4127	1.4127	1.4115	1.4122	1.412	1.4139
0.7389	1.4016	1.4027	1.4027	1.4016	1.4022	1.4021	1.4037
0.8552	1.3873	1.3876	1.3876	1.3869	1.3873	1.3873	1.3883
0.9505	1.3750	1.3751	1.3751	1.3748	1.375	1.375	1.3754
1.0000	1.3685	1.3685	1.3685	1.3685	1.3685	1.3685	1.3685

Table-3 Refractive index of (E+X) mixture at various temperatures by different mixing rules.

X_1	n_m	G-D	A-B	L-L	W	H	N
293K							
0.0000	1.4947	1.4947	1.4947	1.4947	1.4947	1.4926	1.4947
0.0562	1.4889	1.4891	1.4891	1.4889	1.4890	1.4872	1.4893
0.1511	1.4791	1.4794	1.4794	1.4788	1.4791	1.4776	1.4800
0.2643	1.4657	1.4673	1.4673	1.4663	1.4669	1.4657	1.4682
0.3532	1.4568	1.4573	1.4573	1.4561	1.4568	1.4559	1.4584
0.4449	1.4453	1.4466	1.4466	1.4453	1.4461	1.4454	1.4479
0.5504	1.4332	1.4338	1.4338	1.4324	1.4332	1.4327	1.4351
0.6727	1.4173	1.4181	1.4181	1.4168	1.4175	1.4173	1.4193
0.7467	1.4070	1.4081	1.4081	1.4070	1.4076	1.4075	1.4092
0.8538	1.3927	1.393	1.3930	1.3922	1.3927	1.3927	1.3938
0.9614	1.3769	1.377	1.3770	1.3768	1.3770	1.3769	1.3773
1.0000	1.3711	1.3711	1.3711	1.3711	1.3711	1.3711	1.3711
298K							
0.0000	1.4931	1.4931	1.4931	1.4931	1.4931	1.491	1.4931
0.0562	1.4873	1.4875	1.4875	1.4873	1.4874	1.4856	1.4878
0.1511	1.4776	1.4778	1.4778	1.4772	1.4776	1.4760	1.4784
0.2643	1.4641	1.4657	1.4657	1.4648	1.4653	1.4641	1.4666
0.3532	1.4553	1.4558	1.4558	1.4546	1.4553	1.4544	1.4569
0.4449	1.4438	1.4451	1.4451	1.4438	1.4446	1.4439	1.4464
0.5504	1.4318	1.4323	1.4323	1.4309	1.4318	1.4313	1.4336
0.6727	1.4158	1.4166	1.4166	1.4154	1.4161	1.4158	1.4179
0.7467	1.4056	1.4067	1.4067	1.4056	1.4062	1.4061	1.4078
0.8538	1.3914	1.3917	1.3917	1.3909	1.3914	1.3913	1.3925
0.9614	1.3756	1.3757	1.3757	1.3755	1.3756	1.3756	1.3760
1.0000	1.3698	1.3698	1.3698	1.3698	1.3698	1.3698	1.3698
303K							
0.0000	1.4918	1.4918	1.4918	1.4918	1.4918	1.4897	1.4918
0.0562	1.4860	1.4862	1.4862	1.486	1.4861	1.4843	1.4865
0.1511	1.4763	1.4765	1.4765	1.4759	1.4763	1.4747	1.4771
0.2643	1.4628	1.4644	1.4644	1.4635	1.4640	1.4628	1.4653
0.3532	1.4540	1.4545	1.4545	1.4533	1.4540	1.4531	1.4556
0.4449	1.4425	1.4438	1.4438	1.4425	1.4433	1.4426	1.4451
0.5504	1.4305	1.4310	1.4310	1.4296	1.4305	1.4300	1.4323
0.6727	1.4145	1.4153	1.4153	1.4141	1.4148	1.4145	1.4166
0.7467	1.4043	1.4054	1.4054	1.4043	1.4049	1.4048	1.4065
0.8538	1.3901	1.3904	1.3904	1.3896	1.3901	1.3900	1.3912
0.9614	1.3743	1.3744	1.3744	1.3742	1.3743	1.3743	1.3747
1.0000	1.3685	1.3685	1.3685	1.3685	1.3685	1.3685	1.3685

Table-4 Values of APD for various mixtures

Mixture	T (K)	GD	AB	LL	W	H	N
E+BN	293	-0.0558	-0.0550	-0.0145	-0.0325	0.0186	-0.1100
	298	-0.0308	-0.0300	0.0258	-0.0077	0.0436	-0.0850
	303	-0.0186	-0.0180	0.0378	0.0046	0.0559	-0.0730
E+T	293	-0.0389	-0.0389	0.0145	-0.0174	0.0348	-0.0907
	298	-0.0180	-0.0160	0.036	0.0040	0.0552	-0.0680
	303	-0.0370	-0.0370	0.0145	-0.0150	0.0340	-0.0897
E+X	293	-0.0390	-0.0390	0.0133	-0.0174	0.0354	-0.0905
	298	-0.0383	-0.0380	0.0130	-0.0170	0.0366	-0.0900
	303	-0.0380	-0.0383	0.0133	-0.0174	0.0366	-0.0907

5. REFERENCES

[1] T.M. Aminabhavi, K. Banerjee and R.H. Balundgi, Ind. J. Chem. 38A (1999) 768
[2] Pal and R.K. Bharadwaj, Ind. J. Chem. 41(A) (2002) 706.
[3] A.P. Mishra and S.K. Gautam, Ind. J. Chem. 41(A)(2002) 845
[4] T.M. Aminabhavi and K. Banerjee, J. Chem. Engg. Data 43 (1998) 509.
[5] A Krishnaiah, K N Surendranath and D S Vishwanath *J. chem.. Eng.* Data 39, (1994) 756
[6] Isht Vibhu *PhD Thesis* (Lucknow University, India) (2003)
[7] J G Nath and J. D Pandey *J. Chem. Eng. Data* 41, (1996) 844
[8] J N Nayak, M I Aralaguppi, B V K Naidu and T. M Aminabhavi *J. Chem. Eng. Data* 49, (2003) 468
[9] W.J. Heller, J. Phys. Chem. 69 (1965) 1123.
[10] Lorentz H A 1906 Theory of electrons (Leipzig).
[11] J.H. Gladstone and T.P. Dale, Phil. Trans. 153 (1863) 317.
[12] O. Wiener, Leipzig Ber. 62 (1910) 256.
[13] Akbar S and kumar M, *Indian j of applied research* 1,5 (2012) 197
[14] P.S. Kalsi, Spectroscopy of Organic Compound, New Age International (P) Ltd., Publishers, New Delhi (2002).
[15] Mehra R, *proc Ind Acad Sci*, 115 (2003) 147
[16] J N Nayak, M I Aralaguppi and T M Aminabhavi *J chem Eng Data* 48 (2003) 1489
[17] J.N. Nayak, M. I. Aralguppi and T.M. Aminabhavi, J. Chem. Eng. Data, 47 (2002) 964.
[18] O. Nomoto, J. Phys. Soc. Japan 11 (1956) 1146.
[19] J.D. Pandey, Y. Akhtar and A.K. Sharma, Ind. J. chem. 37A (1998) 1095.