Asian Journal of Chemistry Vol. 4, No. 1 (1992), 120–127

Refractive Index of Ternary Liquid Mixtures of Toluene, Cyclohexane, Carbon Tetrachloride and Benzene at 298.15°K

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Refractive index values of two ternary liquid mixtures: toluene+cyclohexane+carbon tetrachloride(I) and toluene+cyclohexane+benzene(II) at 298.15°K have been measured experimentally. A comparative study to check the validity, merits and demerits of the five mixing rules *viz.*, Lorentz, Lorenz, Gladsone-Dale, Weiner, Heller and Arago-Biot relations have been made after analysing the experimental refractive indices data for these ternary liquid mixtures.

INTRODUCTION

A knowledge of refractive index of multicomponent system is often desirable in many applications of multiphase systems. Various theoretical mixing rules have been proposed for the estimation of the refractive index of binary liquid mixtures. The most widely used relations for the refractive index of binary liquid systems are Lorentz-Lorenz relations[1,2], Gladstone-Dales relation[3], Weiner's relation[4], Heller's relation[5] and Arago-Biot relation[6]. Recently several drawbacks of most of the mixing rules have been pointed out[7,8], and binary mixture data of density and refractive index were analysed to test their validity. Pandey *et al.*[8] have carried out this work recently concluding that (L–L), (G–D), (W), (H) and (A–B) relations performed well. Recently Bertrand *et al.*[9,10] have proposed an equation for the evaluation of physical properties of multicomponent systems from the knowledge of the properties of their binary combinations and applied for the estimation of refractive indices.

In the present paper an attempt has been made to extend the existing binary mixing rules for the refractive index of ternary liquid mixtures. The validity of these proposed relations have been tested using the only available density and refractive index data of ternary liquid mixtures.

EXPERIMENTAL

Toluene, cyclohexane, carbon tetrachloride and benzene were AR BDH (India) chemicals procured from Glaxo Laboratories (India) Ltd., Bombay, These chemicals were further purified by fractional distillation and drying before use. Pure component densities and refractive index were measured and compared with the literature[11] values to assure no significant effect due to impurities. Experimentally determined densities and refractive

index of these liquids were checked within allowed limits with the corresponding literature values Table 1. The distilled and deionized water having the electrical conductivity of 8.0×10^{-7} mho cm^{-1} was used as reference fluid to calibrate the pyknometer and Abbe's refractometer.

TABLE 1

PARAMETERS OF THE PURE COMPONENT LIQUIDS AT 298.15°K

Component liquid	Density (ρ) gm cc^{-1}	Refractive Index (n)
Toluene	.8625	1.4961
Cyclohexane	.7738	1.4266
Carbon tetrachloride	1.5143	1.4551
Benzene	0.8732	1.4980

The ternary liquid mixtures were prepared by weighing the respective components in a chemical balance with an accuracy of 0.0001 gm. The pyknometer was submerged in the thermostatic water bath. Refractive index was measured with the help of Abbe's refractometer. All measurements were carried out at 25°C. Densities were determined by pyknometer. Distilled conductivity grade water having the density values of 0.99707 was used for calibration. The capillary tube was thoroughly cleaned between mixtures and flushed several times with the new mixture before filling and knowing the component weight, we calculated the exact compositions.

Refractometer was connected with the water bath and has got the accuracy of ± 0.001. All the measurements were carried out in a water bath allowing sufficient time for attaining thermal equilibrium and minimizing evaporation. The temperature of water bath was set and monitored to 0.01°C with a Beckmann thermometer which had been standarized with a standard thermometer. The fluctuation in the bath temperature were always within the range of ± 0.01°C.

THEORETICAL

All the mixing rules tested earlier for predicting the refractive indices of binary liquid mixtures have been extended for ternary systems after slight mathematical adjustments. The most important mixing rules which are used here, can be formulated as:

Lorentz-Lorenz relation has widest applicability in predicting the refractive indices of mixtures from refractive index and density data of the pure components. The extension of (L–L) relation for ternary liquid

mixture with the knowledge of binary system requires an addition of the two terms, which accounts the change in polarizability $D=(n^2-1)/(n^2+2)$, with the volume fraction of all the components which can be written as:

$$\left[\frac{n_m^2-1}{n_m^2+2}\right]=\left[\frac{n_1^2-1}{n_1^2+2}\right]\phi_1+\left[\frac{n_2^2-1}{n_2^2+2}\right]\phi_2+\left[\frac{n_3^2-1}{n_3^2+2}\right]\phi_3 \quad (1)$$

where n_m, n_1, n_2 and n_3 are the refractive indices of mixture and pure components 1, 2 and 3 respectively.

Gladstone-Dale relation has wide applicability in predicting the refractive index of binary mixtures especially in the case of dilute solutions. Difference between the refractive index of pure components must be small for better performance of the relation. For the ternary liquid mixtures, this relation may be represented as

$$(n_m-1)=\phi_1(n_1-1)+\phi_2(n_2-1)+\phi_3(n_3-1)$$

The above relation may be expressed in the terms of specific refraction, *i.e.*

$$\left[\frac{n_m-1}{\rho_m}\right]=\left[\frac{n_1-1}{\rho_1}\right]W_1+\left[\frac{n_2-1}{\rho_2}\right]W_2+\left[\frac{n_3-1}{\rho_3}\right]W_3 \quad (2)$$

where ρ_m, ρ_1, ρ_2 and ρ_3 are the densities of mixture and pure components 1, 2 and 3 respectively.

Weiner's relation has been applied in the case of isotropic body of spherically symmetrical shape assuming volume additivity and can be expressed as

$$\left[\frac{n_m^2-n_1^2}{n_m^2+2n_1^2}\right]=\phi_2\left[\frac{n_2^2-n_1^2}{n_2^2+2n_1^2}\right]+\phi_3\left[\frac{n_3^2-n_1^2}{n_3^2+2n_1^2}\right] \quad (3)$$

Heller's relation is a simple limiting form of the Weiner's relation, which can be applied only in the case of dilute solutions. It can be obtained by assuming $n_m n_1$ and substituting in Weiner's relation for ternary system. Now it takes the following form:

$$\left[\frac{n_m-n_1}{n_1}\right]=\frac{3}{2}\left[\phi_2\left(\frac{m_1^2-1}{m_1^2+2}\right)+\phi_3\left(\frac{m_2^2-1}{m_2^2+2}\right)\right] \quad (4)$$

Arago-Biot relation for ternary liquid mixture can be obtained by adding the contribution of the third component in the binary equation. According to this relation, the refractive index of the mixture may be given as:

$$n_m=\phi_1 n_1+\phi_2 n_2+\phi_3 n_3 \quad (5)$$

RESULTS AND DISCUSSION

By using the refractive index and density of the pure components, the validity of the above discussed five theoretical mixing rules has been

tested. The present work has been carried out in two parts. Firstly, all the five relations proposed for the refractive index of binary liquid mixtures, were extended to ternary system. Secondly, their relative merits and demerits were examined in relation to the two ternary systems. The ternary systems under the present investigation are toluene + cyclohexane+carbon tetrachloride-(I) and benzene+cyclohexane+toluene-(II).

The experimentally determined values of the refractive index of pure components have been utilized for the evaluation of theoretical values of refractive index of ternary systems using all the five aforesaid relations.

Tables 2 and 3 enlist experimental and theoretical values of refractive indices for both the ternary systems with their percentage deviations from various mixing rules.

From results represented in Tables 2 and 3 it is evident that for the ternary system (I) the maximum percentage deviations observed in each case were (3.62), (1.17), (2.01), (0.86) and (0.72) and their minimum percentage deviations were 0.70, 0.42, 0.59, 0.27 and 0.41 for L-L, G-D, W, H and A-B relation respectively, while for the ternary system(II) the maximum percentage deviations were found to be 0.24, 0.36, −1.56, −2.17 and 0.23 and the minimum percentage deviations were 0.00 for L-L, G-D and A-B relations except Weiner and Heller relations for which the minimum percentage deviations are (−0.54) and (−0.72) respectively. These relations yield their average percentage deviation of 0.54, 0.54, 0.86, 1.31 and 1.89 respectively for the system I and 0.07, 0.08, 1.03, 1.47 and 0.07 percent respectively for the system II from their experimental values.

In the system I the values of refractive indices of carbon tetrachloride and cyclohexane are very close, whereas toluene and cyclohexane differ much. The possible explanation for the deviations in this system is due to the presence of cyclohexane itself. But in the case of ternary system II deviations obtained in L-L, G-D and A-B relations are more prominent at higher concentration of toluene whereas deviations in case of W and H relations are more effective at higher concentration of cyclohexane. Since small negative deviation are having to assume a change in molecular polarisability, *i.e.* $P = (n^2 - 1)/(n^2 + 2)$ on mixing off the components Heller's relation is based on the approximation $(m^2 - 1/m^2 + 2) = (\frac{2}{3}m)(m - 1)$, *i.e.* $n_1 = n_2$ which is not true. The values of refractive indices of benzene and toluene are very close whereas benzene and cyclohexane differ much. Here the deviations are assumed due to the presence of cyclohexane component itself.

It can be concluded that all the five relations which are interrelated in simple quantitative manner, provide good agreement at ion concentration. It was observed particularly that L-L relation, G-D relation and A-B relation provide satisfactory performance followed by W and H relations.

TABLE 2

EXPERIMENTAL AND THEORETICAL VALUES OF REFRACTIVE INDICES OF TERNARY SYSTEM (TOLUENE + CYCLOHEXANE + CCl_4) WITH THEIR PERCENTAGE DEVIATION FROM VARIOUS MIXING RULES AT 298.15°K

S. No.	X_1	X_2	m (Expt.)	m (Theo.)					Percentage deviation				
				A-B	H	L-L	G-D	W	A-B	H	L-L	G-D	W
1.	0.1131	0.2041	1.4629	1.4523	1.4528	1.4526	1.4527	1.4535	0.7245	0.6891	0.7026	0.6916	0.6420
2.	0.1269	0.2244	1.4632	1.4529	1.4529	1.4102	1.4505	1.4482	0.6971	0.7019	3.6195	0.8618	1.0207
3.	0.1535	0.3004	1.4610	1.4516	1.4514	1.4501	1.4504	1.4523	0.6434	0.6540	0.7440	0.5624	0.5933
4.	0.1734	0.2534	1.4629	1.4536	1.4535	1.4514	1.4519	1.4529	0.6357	0.6391	0.7799	0.7492	0.6778
5.	0.1912	0.2818	1.4630	1.4537	1.4538	1.4499	1.4506	1.4467	0.6356	0.6240	0.8939	0.8465	1.1074
6.	0.2126	0.3031	1.4633	1.4539	1.4905	1.4510	1.4516	1.4462	0.6355	0.8620	0.8375	0.7972	1.1670
7.	0.2318	0.3260	1.4633	1.4540	1.4544	1.4451	1.4465	1.4457	0.6287	0.6032	1.2419	1.1465	1.1982
8.	0.2518	0.3444	1.4627	1.4542	1.4543	1.4496	1.4565	1.4451	0.5742	0.5701	0.8892	0.4214	1.1969
9.	0.2737	0.3617	1.4629	1.4546	1.4548	1.4479	1.4490	1.4448	0.5673	0.5493	1.0225	0.9447	1.2349
10.	0.2970	0.3856	1.4625	1.4548	1.4552	1.4454	1.4469	1.4443	0.5264	0.4954	1.1677	1.0644	1.2439
11.	0.3134	0.4080	1.4625	1.4547	1.4550	1.4468	1.4481	1.4436	0.5333	0.5066	1.0696	0.9784	1.2865
12.	0.3360	0.4277	1.4622	1.4550	1.4553	1.4483	1.4490	1.4431	0.4924	0.4703	0.9699	0.9165	1.3199
13.	0.3573	0.4405	1.4626	1.4555	1.4557	1.4483	1.4496	1.4429	0.4854	0.4704	0.9496	0.8994	1.2997
14.	0.3764	0.4496	1.4632	1.4559	1.4563	1.4468	1.4484	1.4428	0.4989	0.4673	0.9745	0.8876	1.9676
15.	0.3955	0.4609	1.4628	1.4563	1.4567	1.4472	1.4488	1.4425	0.4443	0 4575	1.1150	1.0099	1.3925
16.	0.4172	0.4688	1.4629	1.4569	1.4574	1.4476	1.4492	1.4424	0.4101	0.4111	1.0606	0.9544	1.3821
17.	0.4178	0.4536	1.4638	1.4578	1.4576	1.45I3	1.4525	1.4428	0.4098	0.3754	1.0401	0.9309	1.3966
18.	0.4926	0.3494	1.4708	1.4637	1.4641	1.4547	1.4563	1.4463	0.4827	0.4527	1.0925	0.5857	1.6641
19.	0.5386	0.2956	1.4735	1.4672	1.4675	1.4610	1.4622	1.4480	0.4275	0.2746	0 8440	0.7632	1.7250
20.	0.6228	0.2279	1.4801	1.4727	1.4730	1.4667	1.4679	1.4505	0.4999	0.4769	0.9011	0.8232	1.9998
21.	0.6551	0.1944	1.4815	1.4752	1.4754	1.4691	1.4703	1.4516	0.4252	0.4113	0.8306	0.7545	2.0143
					Average percentage deviation				0.5418	0.5379	1.083	0.8566	1.3109
					Standard error				0.5409	0.5511	1.2304	0.8717	1.3689

TABLE 3

EXPERIMENTAL AND THEORETICAL VALUES OF REFRACTIVE INDICES OF TERNARY SYSTEM BENZENE + TOLUNE + CYCLOHEXANE ALONG WITH THE PERCENTAGE DEVIATIONS

S. No.	X_1	X_2	η_m(Expt.)	n_m(Theo)					Percentage deviations				
				L-L	G-D	W	H	A-B	L-L	G-D	W	H	A-B
	1	2	3	4	5	6	7	8	9	10	11	12	13
1.	0.1331	0.2123	1.4842	1.4815	1.4816	1.4935	1.4949	1.4816	0.18	0.17	−0.62	−0.72	0 17
2.	0.1402	0.2115	1.4850	1.4814	1.4816	1.4935	1.4963	1.4816	0.24	0.23	−0.57	−0.76	0.23
3.	0.1636	0.2297	1.4835	1.4799	1.4804	1.4930	1.4963	1.4804	0.24	0.21	=0.64	−0.86	0.21
4.	0.1854	0.2459	1.4824	1.4788	1.4792	1.4926	1.4964	1.4792	0.24	0.21	−0.69	−0.94	0.21
5.	0.2303	0.2829	1.4785	1.4761	1.4765	1.4917	1.4964	1.4766	0.16	0.13	−0.89	−1.20	0.13
6.	0.2535	0.3018	1.4775	1.4749	1.4752	1.4913	1 4965	1.4752	0.17	0.15	−0.93	−1.28	0.15
7.	0.2763	0.3197	1.4752	1.4741	1.4743	1.4909	1.4966	1.4743	0.07	0.06	−1.06	−1.45	0.06
8.	0.2980	0.3365	1.4730	1.4726	1.4728	1.4904	1.4966	1.4728	0.02	0.01	−1.18	−1.60	0.01
9.	0.2973	0.3336	1.4715	1.4728	1.4730	1.4905	1.4966	1.4730	−0.09	−0.10	−1.29	−1.70	−0.10
10.	0.3386	0.3739	1.4710	1.4698	1.4699	1.4894	1.4966	1.4699	0.08	0.07	−1.25	−1.74	0.07
11.	0.3606	0.3912	1.4692	1.4686	1.4686	1.4890	1.4966	1.4686	0.04	0.04	−1.34	−1.86	0.04
12.	0.3821	0.4087	1.4686	1.4673	1.4633	1.4885	1.1966	1.4673	0.09	0.36	−1.35	−1.90	0.09
13.	0.4053	0.4176	1.4672	1.4667	1.4667	1.4883	1.4967	1.4667	0.03	0.03	−1.44	−2.01	0.03
14.	0.4235	0.4249	1.4668	1.4662	1.4661	1.4881	1.4967	1.4658	0.04	0.05	−1.45	−2.04	0.06
15.	0.4443	0.4356	1.4655	1.4653	1.4652	1.4878	1.4968	1.4649	0.01	0.01	−1.52	−2.13	0.04

TABLE 3 (Contd.)

	1	2	3	4	5	6	7	8	9	10	11	12	13
16.	0.4548	0.4319	1.4650	1.4657	1.4655	1.4879	1.4968	1.4655	−0.05	−0.03	−1.56	−2.17	−0.03
17.	0.4654	0.2219	1.4663	1.4664	1.4663	1.4881	1.4969	1.4663	0.00	0.00	−1.48	−2.08	0.00
18.	0.5072	0.3624	1.4710	1.4708	1.4707	1.4897	1.4970	1.4707	0.01	0.01	−1.27	−1.76	0.01
19.	0.5272	0.3428	1.4727	1.4723	1.4718	1.4902	1.4973	1.4722	0.02	0.06	−1.19	−1.67	0.02
20.	0.5780	0.2966	1.4762	1.4759	1.4757	1.4914	1.4975	1.4757	0.02	0.03	−1.03	−1.44	0.03
21.	0.5665	0.3044	1.4760	1.4751	1.4749	1.4911	1.4978	1.4749	0.06	0.07	−1.02	−1.48	0.07
22.	0.5864	0.2855	1.4772	1.4768	1.4766	1.4917	1.4977	1.4766	0.03	0.04	−0.98	−1.39	0.04
23.	0.6043	0.2678	1.4780	1.4782	1.4780	1.4922	1.4979	1.4780	−0.01	0.00	−0.96	−1.34	0.00
24.	0.6235	0.2462	1.4796	1.4800	1.4798	1.4928	1.4980	1.4798	−0.03	−0.01	−0.89	−1.24	−0.01
25.	0.6432	0.2297	1.4812	1.4813	1.4810	1.4932	1.4982	1.4810	0.00	0.01	−0.81	−1.14	0.01
26.	0.6624	0.2116	1.4816	1.4827	1.4825	1.4937	1.4983	1.4825	0.07	−0.06	−0.81	−1.12	−0.06
27.	0.6797	0.1941	1.4842	1.4842	1.4839	1.4942	1.4985	1.4839	0.00	0.12	−0.67	−0.96	0.02
28.	0.6969	0.1759	1 4860	1.4857	1.4854	1.4947	1.4986	1.4854	0.02	0.04	−0.58	−0.85	0.04
29.	0.7040	0.1650	1.4869	1.4866	1.4863	1.4950	1.4988	1.4863	0.02	0.04	−0.54	−0.80	0.04
						Average percentage deviation			0.07	0.08	−1.03	−1.47	0.07

At relatively higher concentration of cyclohexane, all the relations deviate a little more.

ACKNOWLEDGEMENT

One of the authors (Mrs.) V. Vyas is thankful to the UGC (New Delhi) for the award of Research Associateship.

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(*Received*: 22 January 1990; *Accepted*: 30 October 1990) AJC-238