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Refractive Indices of Ternary System: Benzene + Toluene + Cyclohexane and its Binary Combination

UMA S. PANDEY*, S.N. PANDEY and MISS KIRANMAYEE
Department of Chemistry
H.D. Jain College (Veer Kunwar Singh University)
Ara-802 301, India

Various mixing rules for the binary and ternary liquid mixtures have been applied for the binary system: benzene + toluene, benzene + cyclohexane and toluene + cyclohexane and ternary system: benzene + toluene + cyclohexane and ternary system: benzene + toluene + cyclohexane for calculating the refractive indices. A comparative study has been made and the theoretical values compared with the experimentally determined values of refractive index. Excellent agreement has been found.

Physico-chemical calculations involving multiphase systems (benzene + toluene + cyclohexane) require the prediction of refractive index of multicomponent liquid systems. The structures of liquids and liquid mixtures can be predicted through refractive indices employing molar refraction and molecular connectivity.

INTRODUCTION

Various theoretical mixing rules for refractive indices of binary liquid mixtures have been proposed. Heller[1] examined the relative merits and interrelations of Lorentz-Lorenz (L-L) Gladstones-Dale (G-D), and Arago-Biot (A-B) relations and propounded a mixing rule for refractive index of binary liquid mixture. For a number of binary liquid mixtures, the validity of these relations were tested recently by Aminabhavi[2, 3] and others[4, 5]. Relative merits of these relations were carefully and thoroughly studied by Pandey *et al.*[6]

All these mixing rules for refractive index were based entirely on pure component properties and rarely applied to multicomponent liquid system[7, 8]. Bertrand and Acree[9, 10] employed the binary data to evaluate the refractive index of multicomponent system, as, such system is made of different binary combinations.

Here the three mixing rules have been extended to ternary liquid system, theoretically predicting the refractive index of ternary system from the values of pure component. A comparative study of these rules has also been made after analysing experimental data for binary and tertiary mixtures. Refractive index studies of three binary (benzene + toluene, benzene + cyclohexane and toluene + cyclohexane) and one ternary (benzene + toluene + cyclohexane) liquid systems have been made.

RESULTS AND DISCUSSION

The mixing rules are based on electromagnetic theory of light, considering the molecules as dipoles or assemblies of diploes induced by an external field.

Various equations for refractive indices of binary liquid mixtures[1-3, 6] have been extended to ternary system after slight mathematical manipulations.

Gladstone-Dale relation for very dilute binary solutions is represented as

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

where n_m, n_1, n_2, n_3 are the refractive indices of mixture and components 1, 2 and 3 respecitvely, W_1, W_2, W_3 the weight fractions of components 1, 2, 3 and ρ_m, ρ_1, ρ_2, ρ_3 the densities of the mixture and respective pure components 1, 2 and 3 respectively in the mixture.

The term $(n_3 - 1/\rho_3)W_3$ is added to binary equation[1-3, 6] to account for contribution of third component.

Lorentz-Lorenz relation involves the density of pure components as well as that of mixture for evaluating the refractive index. Extension of this relation from binary to ternary system requires the addition of third term accounting for the change of refractive index of third component with weight fraction; thus

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

Taking ϕ into consideration, we get

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

The weight fraction w_i of 'i'th component in the mixture may be defined as

$$W_i = \frac{\phi_i \rho_i}{\rho_{ij}} = \frac{M_i}{M_{ij}} x_i$$

providing a media for interrelation of weight fraction (w_i), volume fraction (ϕ_i) and mole fraction (x_i) and, ρ_{ij} being the density of the mixture of components 'i' and 'j'. The volume fraction can also be represented as $\phi_i = C_i/\rho_i$, C_i being the concentration (g/mL). M_i and M_{ij} are the molecular weights of pure components and mixture respectively.

Arago-Biot proposed a relation assuming volume additivity for binary system. This has been extended to ternary system by adding the contribution of third component in the binary equation

$$n_m = \phi_1 n_1 + \phi_2 n_2 + \phi_3 n_3. \qquad (3)$$

All these relations are derived strictly for volume additivity. In the case of volume additivity, most widely used G-D relation is found to be in dentical with Arago-Biot relation.

The present work has been carried out in two parts. Firstly, all the three

relations for refractive indices for binary systems were extended to ternary systems. Secondly, their relative merits and demerits were examined in relation to ternary system and its constituent binaries. The ternary system investigated is: benzene + cyclohexane + toluene whereas the three binary constituents are: benzene + cyclohexane, benzene + toluene and toluene + cyclohexane.

The theoretical values of refractive indices of ternary mixtures, n_m, were obtained from these relations[1-3]. Similarly, the n_m values of three binary liquid mixtures were calculated from the corresponding relations applicable to binary systems[3, 6]

TABLE-1
EXPERIMENTAL DENSITIES OF BINARIES: BENZENE + TOLUENE, BENZENE + CYCLOHEXANE AND TOLUENE + CYCLOHEXANE, AND THE TERNARY MIXTURE: BENZENE + TOLUENE + CYCLOHEXANE DETERMINED AT 25 ± 0.01°C

Benzene + toluene		Benzene + cyclohexane		Toluene + cyclohexane		Benzene + cyclohexane + Toluene		
X_1	ρ_g cc^{-1}	X_1	ρ_g cc^{-1}	X_1	ρ_g cc^{-1}	X_1	X_2	ρ_g cc^{-1}
1	2	3	4	5	6	7	8	9
0.0000	0.86260	0.0000	0.77360	0.0000	0.77360	0.1331	0.2123	0.84349
0.1253	0.86750	0.1323	0.78554	0.1067	0.78429	0.1402	0.2115	0.84502
0.1417	0.86654	0.1898	0.79065	0.1608	0.78865	0.1636	0.2297	0.84307
0.1664	0.86621	0.2577	0.79583	0.2260	0.79316	0.1854	0.2459	0.84170
0.1881	0.86597	0.3241	0.79993	0.2838	0.79759	0.2308	0.2829	0.83668
0.2131	0.86793	0.3875	0.80470	0.3458	0.80495	0.2535	0.3018	0.83609
0.2314	0.86827	0.4498	0.81350	0.4305	0.81020	0.2763	0.3197	0.83250
0.3195	0.86661	0.5700	0.82198	0.4665	0.81243	0.2980	0.3365	0.82993
0.3578	0.86793	0.5095	0.82536	0.5249	0.81718	0.2973	0.3336	0.83111
0.4029	0.86732	0.6280	0.82961	0.5859	0.82407	0.3386	0.3739	0.82942
0.4403	0.86735	0.6938	0.83683	0.6465	0.83351	0.3606	0.3912	0.82733
0.5031	0.86742	0.7406	0.84288	0.7835	0.84189	0.3821	0.4087	0.82550
0.4846	0.87020	0.7952	0.84839	0.7653	0.83828	0.4053	0.4176	0.82329
0.5408	0.86945	0.8464	0.85393	0.8241	0.84382	0.4235	0.4249	0.82389
0.5670	0.86950	0.8984	0.85983	0.8834	0.85151	0.4443	0.4359	0.82318
0.6016	0.87029	0.9519	0.86477	0.9408	0.85815	0.4548	0.4319	0.82277
0.6405	0.87118	1.0000	0.87320			0.4654	0.4219	0.82379
0.7185	0.87156					0.5072	0.3624	0.83035
0.7536	0.87292					0.5272	0.3428	0.83329
0.7892	0.87318					0.5780	0.2966	0.83822
0.8280	0.87351					0.5665	0.3044	0.83749
0.8639	0.87415					0.5864	0.2855	0.83961
0.8941	0.87445					0.6043	0.2678	0.84096
						0.6235	0.2462	0.84241
						0.6432	0.2297	0.84402
						0.6624	0.2116	0.84703
						0.6797	0.1941	0.84337
						0.6959	0.1759	0.84836
						0.7040	0.1650	0.85051

The refractive index data and densities of pure components for binary and ternary mixtures under the present investigations were determined experimentally.

Experimental values of densities determined have been recorded in Table-1. Experimental and theoretical values of n_m of three binaries are enlisted in Tables 2 to 4 along with the corresponding percentage deviations in theoretical n_m values obtained from various relations. Similar calculations were made for the ternary system and results recorded in Table-5.

Table-2 proves perfect coordination among all three mixing rules for the system benzene + toluene. Small deviations of (0.08%) were noticed for L-L, G-D and A-B refractions.

TABLE-2
EXPERIMENTAL AND THEORETICAL VALUES OF REFRACTIVE INDICES OF BINARY SYSTEM—BENZENE + TOLUENE ALONGWITH THEIR PERCENTAGE DEVIATIONS AT 25 ± 0.01°C

X_1	n_m (Expt)	n_m (Theo)			Percentage deviations		
		L-L	G-D	A-B	L-L	G-D	A-B
0.1263	1.4969	1.4964	1.4969	1.4969	0.03	0.00	0.00
0.1417	1.4972	1.4965	1.4970	1.4969	0.04	0.01	0.02
0.1664	1.4974	1.4966	1.4970	1.4970	0.05	0.02	0.02
0.1881	1.4975	1.4967	1.4971	1.4971	0.05	0.02	0.02
0.2131	1.4978	1.4969	1.4972	1.4972	0.04	0.02	0.02
0.2314	1.4980	1.4970	1.4973	1.4973	0.06	0.04	0.04
0.3195	1.4985	1.4975	1.4977	1.4977	0.06	0.05	0.05
0.3578	1.4985	1.4977	1.4978	1.4978	0.05	0.04	0.04
0.4029	1.4986	1.4979	1.4980	1.4980	0.04	0.04	0.04
0.4408	1.4987	1.4981	1.4982	1.4982	0.04	0.03	0.03
0.4931	1.4988	1.4985	1.4985	1.4985	0.02	0.02	0.02
0.4846	1.4989	1.4984	1.4984	1.4984	0.03	0.02	0.02
0.5408	1.4990	1.4987	1.4986	1.4986	0.02	0.03	0.03
0.5670	1.4990	1.4989	1.4988	1.4988	0.00	0.01	0.01
0.6016	1.4991	1.4991	1.4989	1.4989	0.00	0.01	0.01
0.6405	1.4993	1.4993	1.4991	1.4991	0.00	0.01	0.01
0.7185	1.4996	1.4999	1.4995	1.4995	-0.02	0.01	0.01
0.7536	1.4998	1.5001	1.4997	1.4997	-0.02	0.00	0.00
0.7892	1.4999	1.5003	1.4998	1.4998	-0.02	0.00	0.00
0.8280	1.5000	1.5006	1.5001	1.5000	-0.04	0.00	0.00
0.8639	1.5003	1.5008	1.4999	1.5002	-0.03	0.02	0.00
0.8941	1.5005	1.5010	1.5003	1.5003	-0.03	0.01	0.01
		Average percentage deviation			0.05	0.02	0.02

Tables-3 and 4 reveal that for binary systems benzene + cyclohexane and toluene + cyclohexane, all empirical relations L-L, G-D and A-B give very good results. Since volume additivity is true in these binary systems, most widely used G-D becomes identical with A—B.

TABLE-3
EXPERIMENTAL AND THEORETICAL VALUES OF REFRACTIVE INDICES OF BINARY SYSTEM: BENZENE + CYCLOHEXANE ALONG WITH THEIR PERCENTAGE DEVIATIONS AT 25 ± 0.01°C

X_1	n_m (Expt)	n_m (Theo)			Percentage Deviation		
		L-L	G-D	A-B	L-L	G-D	A-B
0.1323	1.4368	1.4355	1.4350	1.4350	0.09	0.12	0.12
0.1893	1.4399	1.4391	1.4387	1.4387	0.05	0.08	0.08
0.2577	1.4434	1.4436	1.4432	1.4432	-0.01	0.01	0.01
0.3241	1.4475	1.4482	1.4479	1.4479	-0.05	-0.02	-0.02
0.3875	1.4519	1.4526	1.4523	1.4523	-0.05	-0.03	-0.03
0.4498	1.4559	1.4569	1.4566	1.4566	-0.07	-0.06	-0.06
0.4700	1.4648	1.4659	1.4656	1.4656	-0.07	-0.05	-0.05
0.5095	1.4591	1.4609	1.4607	1.4606	-0.07	-0.06	-0.05
0.6280	1.4693	1.4702	1.4699	1.4699	-0.06	-0.04	-0.04
0.6938	1.4751	1.4754	1.4751	1.4751	-0.02	0.00	0.00
0.7406	1.4788	1.4792	1.4788	1.4788	-0.02	0.00	0.00
0.7952	1.4837	1.4837	1.4832	1.4832	0.00	0.03	0.03
0.8464	1.4880	1.4881	1.4875	1.4875	0.00	0.03	0.03
0.8984	1.4931	1.4926	1.4920	1.4919	0.03	0.07	0.07
0.9519	1.4981	1.4956	1.4952	1.4917	0.16	0.19	0.26
		Average percentage deviation			0.05	0.05	0.06

TABLE-4
EXPERIMENTAL AND THEORETICAL VALUES OF REFRACTIVE INDICES OF BINARY SYSTEM TOLUENE + CYCLOHEXANE ALONGWITH THEIR PERCENTAGE DEVIATIONS AT 25 ± 0.01°C

X	n_m (Expt)	n_m (Theo)			Percentage deviations		
		L-L	G-D	A-B	L-L	G-D	A-B
0.1067	1.4368	1.4345	1.4341	1.4341	0.16	0.18	0.18
0.1608	1.4400	1.4381	1.4378	1.4378	0.13	0.15	0.15
0.2260	1.4455	1.4424	1.4423	1.4423	0.21	0.21	0.21
0.2838	1.4465	1.4462	1.4463	1.4463	0.02	0.01	0.01
0.3458	1.4510	1.4505	1.4506	1.4506	0.03	0.03	0.03
0.4385	1.4568	1.4561	1.4564	1.4564	0.05	0.03	0.03
0.4665	1.4598	1.4585	1.4589	1.4589	0.09	0.06	0.06
0.5249	1.4627	1.4625	1.4628	1.4628	0.01	-0.01	0.08
0.5859	1.4685	1.4667	1.4672	1.4672	0.12	0.09	0.09
0.6464	1.4713	1.4711	1.4717	1.4717	0.01	-0.03	-0.03
0.6835	1.4808	1.4804	1.4810	1.4810	0.03	-0.01	0.00
0.7653	1.4790	1.4790	1.4796	1.4796	0.00	-0.04	0.04
0.8241	1.4842	1.4831	1.4838	1.4838	0.07	0.03	0.03
0.8834	1.4886	1.4874	1.4881	1.4881	0.08	0.03	0.03
0.9408	1.4925	1.4916	1.4923	1.4923	0.06	0.01	0.02
		Average percentage deviations			0.07	0.06	0.06

For the ternary system (Table-5), the maximum deviations observed in each case were L-L (0.24%), G-D (0.23%), and A-B (0.21%), the minimum deviation being (0.00%) for L-L, G-D and A-B relation. In L-L, G-D and A-B deviations are more prominent at higher concentration of toluene. Values of refractive indices of benzene and toluene are very close whereas benzene and cyclohexane differ much. The explanation for the deviation can be due to presence of cyclohexane component itself.

TABLE-5
EXPERIMENTAL AND THEORETICAL VALUES OF REFRACTIVE INDICES OF TERNARY SYSTEM: BENZENE + TOLUENE + CYCLOHEXANE ALONG WITH THEIR PERCENTAGE DEVIATION AT 25 ± 0.01°C

X_1	X_2	n_m (Expt)	n_m (Theo)			Percentage deviation		
			L-L	G-D	A-B	L-L	G-D	A-B
0.1331	0.2123	1.4843	1.4815	1.4816	1.4916	0.10	0.17	0.17
0.1402	0.2118	1.4850	1.4814	1.4816	1.4816	0.24	0.23	0.23
0.1636	0.2297	1.4835	1.4799	1.4804	1.4804	0.24	0.21	0.21
0.1854	0.2459	1.4824	1.4788	1.4792	1.4792	0.24	0.21	0.21
0.2303	0.2829	1.4785	1.4761	1.4765	1.4766	0.16	0.13	0.13
0.2535	0.3018	1.4775	1.4749	1.4752	1.4752	0.17	0.15	0.15
0.2763	0.3197	1.4752	1.4741	1.4743	1.4743	0.07	0.06	0.06
0.2880	0.3365	1.4730	1.4726	1.4728	1.4728	0.02	0.01	0.01
0.2973	0.3336	1.4715	1.4728	1.4730	1.4730	−0.09	−0.10	−0.10
0.3386	0.3739	1.4710	1.4698	1.4699	1.4699	0.08	0.07	0.07
0.3606	0.3912	1.4692	1.4686	1.4686	1.4686	0.04	0.04	0.04
0.3821	0.4087	1.4686	1.4673	1.4633	1.4673	0.09	0.36	0.09
0.4053	0.4176	1.4672	1.4667	1.4667	1.4667	0.03	0.03	0.03
0.4235	0.4249	1.4668	1.4662	1.4661	1.4658	0.04	0.05	0.06
0.4443	0.4356	1.4655	1.4653	1.4652	1.4649	0.01	0.01	0.04
0.4548	0.4319	1.4650	1.4657	1.4655	1.4655	−0.05	−0.03	−0.03
0.4654	0.4219	1.4663	1.4664	1.4663	1.4663	0.00	0.00	0.00
0.5072	0.3624	1.4710	1.4708	1.4707	1.4707	0.01	0.01	0.01
0.5272	0.3428	1.4727	1.4723	1.4718	1.4722	0.02	0.06	0.02
0.5480	0.2966	1.4762	1.4759	1.4757	1.4757	0.02	0.03	0.03
0.5665	0.3044	1.4760	1.4751	1.4749	1.4749	0.06	0.07	0.07
0.5864	0.2855	1.4772	1.4768	1.4766	1.4766	0.03	0.04	0.04
0.6043	0.2678	1.4780	1.4782	1.4780	1.4780	−0.01	0.00	0.00
0.6235	0.2462	1.4796	1.4800	1.4793	1.4798	−0.03	−0.01	−0.01
0.6432	0.2297	1.4812	1.4813	1.4810	1.4810	0.00	0.01	0.01
0.6624	0.2116	1.4816	1.4827	1.4825	1.4825	−0.07	−0.06	−0.06
0.6797	0.1941	1.4842	1.4842	1.4839	1.4839	0.00	0.12	0.02
0.6969	0.1759	1.4860	1.4857	1.4854	1.4854	0.02	0.04	0.04
0.7040	0.1650	1.4869	1.4866	1.4863	1.4863	0.02	0.04	0.04
			Average percentage deviation			0.07	0.08	0.07

EXPERIMENTAL

Benzene taken was AR grade supplied by Qualigens and toluene and cyclohexane were L.R. of Ranbaxy Chemicals and were further purified by distillation.

The refractive indices were measured with the help of Abbe's Refractometer, thermostatically controlled at 25 ± 0.01°C with the help of ultra cryostat (C 702) of Remi Instruments.

Accuracy in refractive index measurements was found to be ±0.0002 units for Na(D) line.

Densities of the binary and ternary mixtures as well as those of the pure components were determined experimentally using a double stem pyknometer similar to that of Parker and Parker[11] with minor modifications. Uncertainty in density measurements was found to be ±0.04%. The pyknometer was calibrated at 25°C using double distilled water and calibration constants were evaluated by the method of least squares.

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