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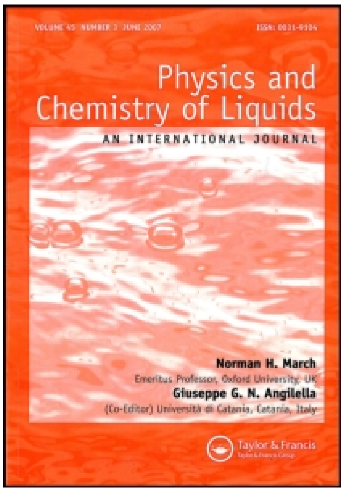

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Prediction of Refractive Index of Quaternary Liquid Mixtures

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Refractive index data for three quaternary liquid mixtures have been analysed after extending the mixing rules for index of refraction available in literature. Relative merits and interrelations of various important mixing rules for these quaternary liquid mixtures have been discussed in detail. Surprisingly the extended equations yield fairly good agreement between theoretical and experimental values of refractive indices.

Key Words: Lorentz–Lorenz relation, polarizability.

INTRODUCTION

A knowledge of refractive index of quaternary liquid mixtures is often desirable in many applications of multiphase systems. The only experimental measurement of refractive index available on quaternary liquid mixtures, as far as our knowledge is concerned, is due to Heric and Brewer.[1] In the year 1965, Heller[2] for the first time examined and scrutinized the relative merits and interrelations of important mixing rules for refractive index of binary liquid mixtures. He also proposed a new mixing rule while performing the test of various mixing rules for binary liquid mixtures. The most widely used relations for the refractive index of binary liquid mixtures are those due to Lorentz–Lorenz (L–L), Gladstone–Dale (G–D), Wiener (W), Heller (H), Argo–Biot (A–B), Eykman (Ek)[3] and Oster (O)[4]. Various drawbacks of most of the mixing rules are pointed out recently[5,6] and binary mixture data of density and refractive index were analysed to test their validity.

Although nobody has tested the validity of Eykman's (Ek)[3] and Oster (O)[4] relations discussed earlier along with other mixing relations for the binary liquid mixture. Recently this work has been carried out by Pandey *et al.*[7], concluding that (L–L), (G–D), (W), (A–B), (H) relations performed considerably well whereas Eykman's and Oster's relations are found to show maximum deviation in comparison to others but deviations are not out of the experimental precision.

No such attempt has been made, so far, on predicting the values of refractive index of multicomponent liquid mixtures from the data of the pure components. An attempt in this direction has been made recently by Bertrand *et al.*[8,9] who developed an equation for the estimation of physical properties of multicomponent systems from the properties of the various binary combinations of the components and applied it for computing the refractive index of some multicomponent liquid mixtures. However, mixing rules of refraction for quaternary liquid systems are not available and theoretical predictions of refractive indices from the data of the pure components could not be made.

In the present paper an attempt has been made to extend the existing binary mixing rules for the refractive index to quaternary liquid systems. The validity of these proposed relations has been tested using the only available experimental density and refractive index data of Herric and Brewer[1] on quaternary liquid mixtures.

THEORETICAL

All the theoretical mixing rules tested earlier[2,5,6,7] for predicting the refractive indices of binary liquid mixtures have been extended for quaternary systems after some slight mathematical manipulations. Most of the mixing rules are fundamentally based on the electromagnetic theory of light with the restriction that molecules may be considered as dipoles or assemblies of dipole induced by an external field. The important mixing rules used for the present analysis are formulated here.

The Lorentz–Lorenz relation has the widest applicability in predicting the refractive indices of mixture from refractive index and density of the pure components. The extension of the (L–L) relation for quaternary system with the knowledge of binary system requires addition of two terms which account for the change in polarizability, $P = n^2 -$

$1/n^2 + 2$, with the volume fraction for third and fourth components which can be represented as,

$$\left[\frac{n_m^2-1}{n_m^2+2}\right] = \left[\frac{n_1^2-1}{n_1^2+2}\right]\phi_1 + \left[\frac{n_2^2-1}{n_2^2+2}\right]\phi_2 + \left[\frac{n_3^2-1}{n_3^2+2}\right]\phi_3 + \left[\frac{n_4^2-1}{n_4^2+2}\right]\phi_4 \tag{a}$$

The above equation may be represented in the form of specific refraction i.e.

$$\left[\frac{n_m^2-1}{n_m^2+2}\right]\frac{1}{\rho_m} = \left[\frac{n_1^2-1}{n_1^2+2}\right]\frac{W_1}{\rho_1} + \left[\frac{n_2^2-1}{n_2^2+2}\right]\frac{W_2}{\rho_2} + \left[\frac{n_3^2-1}{n_3^2+2}\right]\frac{W_3}{\rho_3} + \left[\frac{n_4^2-1}{n_4^2+2}\right]\frac{W_4}{\rho_4} \tag{1}$$

Here n_m, n_1, n_2, n_3 and n_4, are the refractive indices of mixture and pure components 1, 2, 3 and 4 respectively. W_1, W_2, W_3 and W_4 and ρ_1, ρ_2, ρ_3 and ρ_4 are the respective weight fractions and densities of the pure components in the mixture. The weight fraction, (W_1), of the ith component in the mixture may be defined as,

$$W_i = \frac{\phi_i \rho_i}{\rho_{ij}} = \frac{M_i}{M_{ij}} X_i \tag{b}$$

where the volume fraction, $(\phi_i) = C_i/\rho_i$.

The Gladstone-Dale relation has wide applicability in predicting the refractive index of binary mixtures successfully, especially in the case of dilute solution and where $n_1 \approx n_2 \approx n_3 \approx n_4$ i.e. the difference between the refractive index of pure component must be small for the better performance of this relation. For quaternary liquid mixtures, this relation takes the form

$$(n_m - 1) = \phi_1(n_1 - 1) + \phi_2(n_2 - 1) + \phi_3(n_3 - 1) + \phi_4(n_4 - 1) \tag{c}$$

The above relation may be expressed in the terms of specific refraction whch is used for the computational purpose, i.e.

$$\left[\frac{n_m-1}{\rho_m}\right] = \left[\frac{n_1-1}{\rho_1}\right]W_1 + \left[\frac{n_2-1}{\rho_2}\right]W_2 + \left[\frac{n_3-1}{\rho_3}\right]W_3 + \left[\frac{n_4-1}{\rho_4}\right]W_4 \tag{2}$$

Wiener's relation was applied to isotropic body of spherically symmetrical shape assuming volume additivity. Wiener's relation for quaternary system has been obtained by substituting $[1 - (\phi_2 + \phi_3 + \phi_4)]$ in place of ϕ_1 in L–L relation. With slight rearrangement, one gets

$$\left[\frac{n_m^2-1}{n_m^2+2}-\frac{n_1^2-1}{n_1^2+2}\right]=\phi_2\left[\frac{n_2^2-1}{n_2^2+2}-\frac{n_1^2-1}{n_1^2+2}\right]+\phi_3\left[\frac{n_3^2-1}{n_3^2+2}-\frac{n_1^2-1}{n_1^2+2}\right]+\phi_4\left[\frac{n_4^2-1}{n_4^2+2}-\frac{n_1^2-1}{n_1^2+2}\right] \tag{d}$$

On solving the above equation and assuming $n_1 \neq 1$, one gets the final expression

$$\left[\frac{n_m^2-n_1^2}{n_m^2+2n_1^2}\right]=\phi_2\left[\frac{n_2^2-n_1^2}{n_2^2+2n_1^2}\right]+\phi_3\left[\frac{n_3^2-n_1^2}{n_3^2+2n_1^2}\right]+\phi_4\left[\frac{n_4^2-n_1^2}{n_4^2+2n_1^2}\right] \tag{3}$$

On the basis of the above fact, it can be concluded that Wiener's relation is a relatively simple formulation of L–L relation. Wiener's relation as well as the L–L relation give identical results only if the solution process is accompanied by neither contraction nor expansion i.e. ideal. Heller's relation is simply limiting form of the Wiener's equation inasmuch as it applies only to dilute solutions. Heller's relation for quaternary system can be obtained by assuming $n_m \approx n_1$ and substituting $n_2/n_1 = m_1$, $n_3/n_1 = m_2$, $n_4/n_1 = m_3$ in Wiener's relation for quaternary system, i.e.

$$\left[\frac{(n_m^2+1)(n_m-1)}{n_m^2+2n_1^2}\right]=\phi_2\left[\frac{n_2^2/n_1^2-1}{n_2^2/n_1^2+2}\right]+\phi_3\left[\frac{n_3^2/n_1^2-1}{n_3^2/n_1^2+2}\right]+\phi_4\left[\frac{n_4^2/n_1^2-1}{n_4^2/n_1^2+2}\right] \tag{e}$$

After some rearrangement and using the approximation, one finds

$$\left[\frac{n_m-n_1}{n_1}\right]=\frac{3}{2}\left[\phi_2\left(\frac{m_1^2-1}{m_1^2+2}\right)+\phi_3\left(\frac{m_2^2-1}{m_2^2+2}\right)+\phi_4\left(\frac{m_4^2-1}{m_4^2+2}\right)\right] \tag{4}$$

The fundamental basis of the above equation lies on the light scattering equation of Debye.[10] Wiener's and Heller's relation can be distinguished with other relations mainly due to the absence of ϕ_1 in the formulation. They can, therefore, be strictly valid only in the case of volume additivity i.e.

$$\phi_1 = V_1^0/(V_1^0+V_2^0+V_3^0+V_4^0) \tag{f}$$

$$\phi_2 = V_2^0/(V_1^0+V_2^0+V_3^0+V_4^0) \tag{g}$$

$$\phi_3 = V_3^0/(V_1^0+V_2^0+V_3^0+V_4^0) \tag{h}$$

$$\phi_4 = V_4^0/(V_1^0+V_2^0+V_3^0+V_4^0) \tag{i}$$

where superscript zero refers to the volume of the components before mixing.

Argo-Biot (A-B) relation for quaternary system can be obtained by adding the contribution of the third and fourth components in the binary equation. According to this relation, the refractive index of the mixture will be given by

$$n_m = \phi_1 n_1 + \phi_2 n_2 + \phi_3 n_3 + \phi_4 n_4 \tag{5}$$

A-B relation is nothing but it is the volume fraction average of the refractive indices of the pure components which ultimately provides the refractive index of the mixture.

An assumption of volume additivity is the major drawback behind all the relations where volume additivity is involved. In the case of volume additivity, most widely used G-D relation is found to be identical with A-B relation and becomes the limiting case of the Heller's equation.

Eykman's relation can be successfully used to evaluate the refractive index of mixtures from refractive index and density of the pure components. Eykman's relation has great experimental verification and their extension for quaternary system needed the addition of two terms to explain their contribution for refraction. The specific refraction equation of L-L relation is very close to Eykman's relation which may be represented as

$$\begin{aligned}\left[\frac{n_m^2 - 1}{n_m + 0.4}\right]\left(\frac{M_1X_1 + M_2X_2 + M_3X_3 + M_4X_4}{\rho_m}\right) &= \left[\frac{n_1^2 - 1}{n_1 + 0.4}\right]\frac{M_1X_1}{\rho_1} + \left[\frac{n_2^2 - 1}{n_2 + 0.4}\right]\frac{M_2X_2}{\rho_2} + \left[\frac{n_3^2 - 1}{n_3 + 0.4}\right]\frac{M_3X_3}{\rho_3} \\ &\quad + \left[\frac{n_4^2 - 1}{n_4 + 0.4}\right]\frac{M_4X_4}{\rho_4}\end{aligned} \tag{6}$$

where X_1, X_2, X_3 and X_4 are the mole fractions of their respective components while M_1, M_2, M_3 and M_4 are the molecular weights of components 1, 2, 3 and 4. All other notations have their usual significance.

Oster[4] compiled a review in which he has discussed the application of light scattering in chemistry and proposed an equation for prediction of refraction in binary system. Oster's relation is considerably good for predicting the refractive indices of mixtures which is quite similar to Eykman's relation. It can be represented by adding two extra terms in their binary equation to explain their contribution for quaternary system, i.e.

$$\left[\frac{(n_m^2-1)(2n_m^2+1)}{n_m^2}\right]\left(\frac{M_1X_1+M_2X_2+M_3X_3+M_4X_4}{\rho_m}\right)$$
$$=\left[\frac{n_1^2-1)(2n_1^2+1)}{n_1^2}\right]\frac{M_1X_1}{\rho_1}+\left[\frac{(n_2^2-1)(2n_2^2+1)}{n_2^2}\right]\frac{M_2X_2}{\rho_2}$$
$$+\left[\frac{(n_3^2-1)(2n_3^2+1)}{n_3^2}\right]\frac{M_3X_3}{\rho_3}+\left[\frac{(n_4^2-1)(2n_4^2+1)}{n_4^2}\right]\frac{M_4X_4}{\rho_4} \tag{7}$$

RESULTS AND DISCUSSION

The validity of all the seven theoretical mixing rules (1–7) has been tested using the refractive index and density of pure components. The values of the density for pure as well as mixtures have been taken from the work of Heric and Brewer[1] through the experimental values of the refractivity intercept (R_F), using the relation i.e.

$$\rho = 2R_F - 2n_D \tag{8}$$

where R_F and n_D denote the refractivity intercept and refractive index of the mixture respectively. The refractive index of mixtures has been computed using relations (1–7) and compared with the experimental refractive indices of mixture. The average percentage deviations from the experimental values of refractive indices of the mixture have been recorded in Table 2 while their percentage deviations from the experimental values have been recorded in Table 1 for the three quaternary liquid mixtures, namely *n*-hexadecane + *n*-tetradecane + *n*-hexane + 2-bromobutane (1), *n*-hexadecane + *n*-tetradecane + 4-methylcyclohexanone + *n*-hexane (2), and *n*-hexadecane + carbon tetrachloride + benzene + *n*-hexane (3), containing aliphatic, aromatic and alicyclic liquids having significant difference in their molecular size.

n-Hexadecane + *n*-Tetradecane + *n*-Hexane + 2-Bromobutane (1)

Wiener's relation which is a relatively simple formulation of L–L relation, provides better performance having -174.9×10^{-4} per cent deviation from the experimental values and this relation is followed by Gladstone–Dale (G–D), Argo–Biot (A–B), Lorentz–Lorenz (L–L), Heller (H), Oster (O) and Eykman relation. Eykman's relation has been

Table 1 Percentage deviations for quaternary liquid mixtures using various theoretical mixing rules refraction 298.15°K.

Volume fractions			10^4 × Percentage deviations						
ϕ_1	ϕ_2	ϕ_3	L–L relation	G.D. relation	Wiener's relation	Heller's relation	Argo–Biot's relation	Eykman's relation	Oster's relation
			n-Hexadecane + *n*-Tetradecane + *n*-Hexane + 2-Bromobutane						
0.6854	0.1091	0.1041	24.162	−63.037	−53.172	−2189.171	−79.089	−9183.861	−6957.138
0.4164	0.3944	0.0852	9200.048	7981.994	−143.768	−3821.345	−164.509	−1900.815	1839.263
0.1245	0.5764	0.1451	−32.137	−147.761	−207.168	−5888.058	−238.466	−838.730	−7100.118
0.3325	0.3261	0.1809	25.772	−108.796	−107.201	−4703.816	−146.572	−10362.545	−9053.945
0.4437	0.1712	0.1934	31.647	−119.368	−153.701	−3930.916	−196.344	−10697.054	−9593.918
0.1779	0.4291	0.1861	−30.914	−174.732	−240.089	−5552.952	279.319	−9021.033	−8104.881
0.2547	0.2660	0.1842	−33.498	−203.421	−424.977	−4638.562	−465.779	−8095.556	−7316.949
0.3862	0.1012	0.4091	360.696	−181.068	545.489	−5918.689	480.054	−20753.263	−18360.823
0.2472	0.2644	0.2893	136.903	−36.586	69.042	−5680.126	14.500	−12600.000	−11244.335
0.2477	0.2574	0.2505	113.208	−67.083	−123.393	−5252.851	−173.6422	−10517.193	−9423.322
0.2903	0.1785	0.2004	−92.380	−265.886	−427.634	−4302.963	−471.892	−1067.657	−7355.332
0.1750	0.3092	0.3059	−17.636	−181.587	−14.007	−4286.680	−69.529	−12417.087	−11088.640
0.1852	0.2928	0.1896	−41.739	−216.672	−456.272	−4905.278	497.843	−7285.908	−6592.215
0.0929	0.3811	0.4323	305.391	141.243	503.555	−8103.715	443.071	−18660.159	−16523.243
0.0922	0.3797	0.0914	−208.866	−355.139	−841.405	−4397.651	−864.334	−4026.422	−3714.388
0.2567	0.1759	0.2866	79.305	−123.045	−204.625	−5320.084	−260.501	−10649.438	−9553.073
0.3289	0.0852	0.1056	−135.974	−290.764	−734.056	−2605.824	−761.067	−4632.754	−4248.287
0.1677	0.2690	0.2693	−2.022	−196.980	−302.042	−5759.777	−354.699	−9429.141	−8484.042
0.1677	0.1850	0.4502	209.084	−2.631	118.628	−7449.806	52.865	−15543.619	−13822.137
0.1655	0.1878	0.1748	−16.863	−210.746	−618.732	−4136.066	−659.086	−3096.723	−4418.532
0.1225	0.1323	0.1428	−58.208	−232.665	−627.140	−3289.719	−1266.005	−2784.480	−2612.009
0.0833	0.0954	0.1045	−50.067	−188.566	−513.039	−2348.963	−540.120	−1379.000	−1343.978
0.0834	0.0843	0.7380	327.611	172.694	367.886	−10786.355	317.135	−18665.689	−16476.365
0.0482	0.0537	0.8475	287.044	191.018	388.852	−12194.513	355.203	−4862.552	−13382.830

(*continued over page*)

Table 1 (*continued*)

Volume fractions			10^4 × Percentage deviations						
ϕ_1	ϕ_2	ϕ_3	L–L relation	G.D. relation	Wiener's relation	Heller's relation	Argo–Biot's relation	Eykman's relation	Oster's relation
			n-Hexadecane + *n*-Tetradecane + 4-Methylcyclohexnone + *n*-Hexanone						
0.6916	0.1057	0.0887	−13.292	−117.123	−129.495	−1667.221	−159.173	3327.156	102.833
0.0572	0.8289	0.0603	−33.367	−78.106	−66.570	−1732.390	−81.033	468.833	−8.135
0.3921	0.4145	0.0932	144.621	32.203	−118.775	−1841.015	−144.538	793.924	225.907
0.3887	0.3961	0.1021	42.427	−69.205	−152.552	−2013.358	−181.172	541.574	170.631
0.5858	0.1466	0.1297	50.707	−83.173	−160.238	−1990.294	−195.632	792.113	310.173
0.0906	0.7036	0.1002	−57.955	−139.192	−97.820	−2247.399	−123.280	2199.066	65.070
0.3987	0.1102	0.3860	99.529	−97.444	−620.370	−1309.818	−652.990	2084.479	1308.896
0.1486	0.5767	0.1438	−40.884	−155.076	−178.282	−2420.814	−210.455	622.154	4417.380
0.4605	0.1757	0.1853	36.031	−119.573	−135.996	−2445.925	−180.574	1182.246	579.715
0.3042	0.3273	0.1822	−7.380	−153.564	−103.158	−2725.167	−148.112	1069.680	507.130
0.3077	0.1990	0.3024	42.558	−134.209	−174.841	−2403.873	−224.604	1809.908	1087.990
0.1793	0.4448	0.1755	−105.283	−210.566	−66.327	−3056.235	−112.504	938.949	−70903.339
0.2674	0.2754	0.2576	−5.535	−176.525	−181.305	−2742.049	−231.034	1501.146	835.861
0.1379	0.1477	0.5901	−121.367	−302.752	−813.395	−342.930	−342.930	2337.549	1612.399
0.1944	0.1775	0.4684	61.422	−128.025	−309.198	−1658.974	−356.079	2306.644	1532.714
0.2729	0.2877	0.1789	−145.748	−272.069	170.643	−3470.546	114.042	1114.403	516.183
0.2836	0.1982	0.2790	40.044	−136.249	−1.679	−2977.336	−59.268	1803.576	1078.953
0.2439	0.2540	0.2416	−48.251	−208.471	66.576	−3377.315	7.397	1529.984	854.758
0.1759	0.2614	0.2672	−17.339	−189.209	135.678	−3756.238	71.122	1690.395	997.731
0.1821	0.2962	0.1761	155.032	−9.199	404.754	−4475.760	339.011	1475.661	841.187
0.1884	0.1802	0.3059	−26.445	−204.990	212.233	−3910.562	141.573	1923.698	1192.493
0.1684	0.1611	0.3304	54.252	−130.745	309.171	−3937.924	235.795	2072.477	1337.962
0.0928	0.4041	0.0934	174.965	50.728	712.141	−5434.679	618.371	1040.648	525.200
0.0904	0.1109	0.3982	47.255	−136.280	533.223	−4339.320	450.357	1924.467	1282.204
0.1827	0.1697	0.1740	118.042	−40.365	646.939	−5921.831	572.230	1548.380	922.841
0.0927	0.0920	0.3972	31.581	−152.161	558.994	−4555.126	474.385	1867.444	606.888
0.1429	0.1335	0.1299	154.815	7.502	723.607	−7650.728	652.337	1254.190	6456.3602
0.0889	0.0827	0.0992	230.860	104.710	700.984	−9663.357	641.983	907.429	565.7542

n-Hexadecane + Carbontetrachloride + Benzene + *n*-Hexane

0.7871	0.0645	0.0460	145.408	−54.080	−297.315	−694.790	−345.729	1479.720	832.185
0.6720	0.0899	0.0928	426.212	60.637	−591.215	−750.972	−670.094	3199.174	2110.664
0.4223	0.1961	0.1849	734.838	114.899	−1057.668	35.615	−1187.510	8566.828	6382.057
0.3766	0.4005	0.1002	1149.291	617.977	−874.240	1151.443	−958.171	8735.754	6967.694
0.3592	0.1019	0.4000	606.549	−172.642	−1744.917	2839.303	−1899.473	1763.939	4335.451
0.3800	0.1200	0.0931	442.560	−8.161	−24.400	−4740.304	−159.523	6247.052	4635.738
0.2994	0.3044	0.1952	1149.144	466.102	−924.915	872.562	−1061.755	11957.691	9379.837
0.2925	0.1981	0.1806	809.052	133.131	−664.319	−1498.411	−831.254	9894.370	7531.049
0.2463	0.2257	0.2691	1002.327	221.699	−994.454	645.786	−1171.067	11788.750	8911.365
0.2489	0.1813	0.2953	910.158	93.271	−1111.125	450.022	−1299.740	10470.181	7613.369
0.2484	0.2832	0.1841	967.436	271.098	−765.132	−432.227	−925.345	12123.615	9517.591
0.1391	0.1436	0.5818	919.343	167.649	−1042.129	6501.518	−1204.404	2060.201	6311.311
0.1088	0.0925	0.6885	813.444	121.125	−1017.778	8158.749	−1163.533	661.224	3335.393
0.1716	0.1835	0.4562	1082.519	193.069	−1174.984	3997.620	−1357.965	8176.426	8176.878
0.1710	0.4581	0.1862	1313.456	673.241	−578.291	2178.911	−707.589	14293.862	11548.111
0.0472	0.0681	0.7873	686.259	132.060	−584.433	10072.979	−711.736	1051.914	1549.707
0.1774	0.2800	0.2534	1085.184	208.477	−745.105	538.071	−928.913	13497.288	10509.122
0.1648	0.1872	0.3290	1058.287	170.646	−967.741	501.159	−1181.836	10988.929	8019.813
0.0828	0.3847	0.4119	1317.467	705.652	−305.908	6278.734	−437.279	3478.775	14376.443
0.1670	0.3344	0.1800	1070.697	351.519	−647.767	−573.018	−818.990	13742.285	10956.563
0.1631	0.2012	0.1729	727.620	7.641	−561.458	−3406.112	−753.732	10351.031	7972.392
0.0783	0.6957	0.0995	1055.299	636.637	−150.146	3467.917	−235.014	10885.724	−7273.470
0.1255	0.1604	0.1556	688.553	−7.176	−443.051	−5157.645	−634.691	8489.855	6454.930
0.1012	0.3965	0.1210	987.902	321.835	−363.287	−1714.559	−531.767	14228.043	11601.099
0.0922	0.1146	0.0962	799.647	248.601	−93.204	−7983.097	−245.193	5998.929	4601.7149
0.0564	0.0744	0.0726	−69.424	−398.716	−0.771	−9941.664	−120.935	2622.778	1838.9053

Table 2 Average percentage deviations for quaternary liquid mixtures using various theoretical mixing rules of refraction at 298.15°K.

System	10^4 × Standard average percentage deviations						
	L-L relation	G.D. relation	Wiener's relation	Heller's relation	Argo-Biot relation	Eykman's relation	Oster's relation
1. *n*-Hexadecane + *n*-Tetradecane + *n*-Hexane + 2-Bromobutane	432.5	228.4	−174.9	−5310.9	−242.7	−8997.5283	−6166.8981
2. *n*-Hexadecane + *n*-Tetradecane + 4-Methylcyclohexanone + *n*-Hexane	36.7	−101.19	94.09	−3376.74	44.06	1504.5776	−1464.4019
3. *n*-Hexadecane + Carbontetrachloride + Benzene + *n*-Hexane	839.6	206.78	−681.76	415.28	−828.59	8471.2157	6470.9968

found to predict maximum deviation of 0.89 per cent but this is not out of experimental precision. L–L and A–B relations predict good agreement due to minimum change of volume on mixing. The better performance of G–D relation is due to the close similarity of the refractive indices of their pure components.

n-Hexadecane + *n*-Tetradecane + 4-Methylcyclohexanone + *n*-Hexane (2)

Lorentz–Lorenz L–L relation provides very good agreement when the volume additivity is not considered during mixing. L–L relation performs well than all other relations over a small and moderate concentration range. The small negative deviations are accounted due to the volume dilation without one having to assume a change in molecular polarizability on mixing of the components. This relation is followed by Argo–Biot (A–B), Wiener's (W), Gladstone–Dale (G–D), Oster (O), Heller (H) and Eykman relations, Eykman relation has been found to exhibit deviation of 0.15 per cent.

n-Hexadecane + Carbontetrachloride + Benzene + *n*-Hexane (3)

Gladstone–Dale relation predicts better performance which has been observed only under two conditions: firstly due to similar values of refractive indices i.e. $n_1 \approx n_2 \approx n_3 \approx n_4$ and secondly due to the dilutation of solution. In fact this relation formulated for volume additivity is a limiting case of Heller's equation. Gladstone–Dale relation is followed by Heller (H), Wiener's (W), Lorentz-Lorenz (L–L), Oster (O) and Eykman's relations yielding a maximum deviation of 0.84 per cent.

On basis of the above discussion, it can be concluded that all the theoretical mixing rules (1–7) are correlated with each other by a simple quantitative manner and perform well only at lower concentrations. On the basis of the analysis given above it is clear that such cases of apparently better performance of equations, other than (1), (2) and (3), are purely fortuitous and this is due to compensation of major deviations of opposite sign effective over limited range of concentration. Thus Eqs (1), (2) and (3) are safest to use at low concentrations irrespective of whether volume additivity applies or volume expansion occurs on mixing. To conclude, it can be stated that L–L relation alone appears to be the most reliable equation over a wide range of concentration. Deviations can be minimized to some extent by considering the change of volume, V^E, of the liquid with refractivity during mixing because excess volume is well recognized as a thermodynamic property predicting the different types of interactions in liquid mixture.

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