Refractive Indices and Molar Refractions of Liquid Mixtures

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Refractive indices of mixtures of 1,2-dibromomethane with cyclohexane, benzene, methylbenzene, 1,2-dimethylbenzene, 1,3-dimethylbenzene, and 1,4-dimethylbenzene were measured at 303.15 K as a function of composition. Molar refractions of the mixtures were calculated from refractive index measurements at 303.15 K.

Excess volumes of the above mentioned mixtures were reported earlier by us (*1*). Recently, we (*2*, *3*) reported surface tensions and viscosities of these mixtures. We, in order to look further, measured refractive indices of these mixtures and calculated molar refractions. Deviations from additive law for molar refractions may be caused by association in mixtures but are not always good evidence of association particularly for weak complexes.

Table I. Refractive Indices of Pure Components

Compound	n_D Exptl	n_D Lit. (*6*)
Cyclohexane	1.4214	1.4210
Benzene	1.4948	1.4948
Methylbenzene	1.4916	1.4913
1,2-Dimethylbenzene	1.5005	1.5003
1,3-Dimethylbenzene	1.4922	1.4919
1,4-Dimethylbenzene	1.4908	1.4905
1,2-Dibromobenzene	1.5332	1.5329

Experimental and Results

Cyclohexane, benzene, methylbenzene, 1,2-dimethylbenzene, 1,3-dimethylbenzene, 1,4-dimethylbenzene (all B.D.H.), and 1,2-dibromoethane (Reidel) were purified as described earlier (*4*). The purities of the samples were checked by density measurements, which agreed to within 0.000 02 g cm^{-3} with the corresponding literature values (*5*–*7*).

Refractive indices were measured using an Abbe refractometer. The refractometer was thermostated by circulating water through it from a thermostat. The temperature was maintained constant at 303.15 ± 0.1 K. The refractive indices of pure components are recorded in Table I at 303.15 K along with the corresponding literature values (*6*).

The mixtures of varying mole fractions were prepared for the systems of 1,2-dibromoethane + cyclohexane, + benzene, + methylbenzene, + 1,2-dimethylbenzene, + 1,3-dimethylbenzene, and + 1,4-dimethylbenzene and refractive indices were measured at 303.15 K. The refractive indices of the mixtures are recorded in Table II and have been plotted in Figures 1 and

Table II. Refractive Indices and Molar Refractions of Mixtures at 303.15 K

x	n	R_{12}, cm^3	x	n	R_{12}, cm^3	x	n	R_{12}, cm^3
			x1,2-Dibromoethane + (1 − x)Cyclohexane					
0.0000	1.4214	27.81	0.4539	1.4648	27.64	0.8321	1.5111	27.11
0.1226	1.4327	27.53	0.5594	1.4771	27.37	0.9172	1.5223	27.18
0.2380	1.4424	27.18	0.6528	1.4880	27.20	1.0000	1.5332	27.09
0.3471	1.4552	27.47	0.7448	1.4993				
			x1,1-Dibromoethane + (1 − x)Benzene					
0.0000	1.4948	26.20	0.4681	1.5102	26.50	0.7791	1.5254	26.74
0.1138	1.4981	26.34	0.5631	1.5150	26.54	0.8905	1.5322	26.93
0.2069	1.5023	26.38	0.6740	1.5186	26.62	1.0000	1.5332	27.09
0.3387	1.5056	26.46						
			x1,2-Dibromoethane + (1 − x)Methylbenzene					
0.0000	1.4916	31.15	0.4506	1.5072	29.21	0.8299	1.5241	27.93
0.1033	1.4980	30.86	0.5540	1.5112	28.72	0.9149	1.5290	27.34
0.2378	1.4988	30.15	0.6494	1.5148	28.30	1.0000	1.5332	27.09
0.3468	1.5027	29.73	0.7391	1.5187	27.98			
			x1,2-Dibromoethane + (1 − x)1,2-Dimethylbenzene					
0.0000	1.5005	35.87	0.4817	1.5128	31.64	0.8474	1.5261	28.33
0.1362	1.5020	34.16	0.5860	1.5161	30.74	0.9239	1.5304	27.65
0.2596	1.5061	33.53	0.6787	1.5202	29.98	1.0000	1.5332	27.09
0.3639	1.5076	32.71	0.7679	1.5220	29.18			
			x1,2-Dibromoethane + (1 − x)1,3-Methylbenzene					
0.0000	1.49222	35.99	0.4886	1.5077	31.63	0.8522	1.5241	28.39
0.1184	1.4971	34.72	0.5884	1.5115	30.62	0.9230	1.5287	27.50
0.2566	1.5002	34.16	0.6845	1.5154	29.79	1.0000	1.5332	27.09
0.3771	1.5035	32.60	0.8105	1.5186	28.87			
			x1,2-Dibromoethane + (1 − x)1,4-Dimethylbenzene					
0.0000	1.4908	36.07	0.4919	1.5068	31.62	0.8548	1.5240	28.35
0.1363	1.4961	34.05	0.5889	1.5109	30.65	0.9215	1.5277	27.50
0.2622	1.4933	33.66	0.6801	1.5136	29.81	1.0000	1.5532	27.09
0.4044	1.5033	32.44	0.7704	1.5188	29.17			

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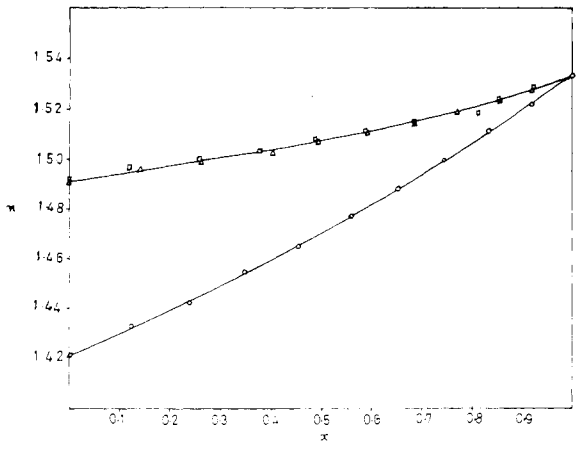

Figure 1. Plots of refractive index against mole fraction x: O, x1,2-dibromoethane + (1 − x)cyclohexane; □, x1,2-dibromoethane + (1 − x)1,3-dimethylbenzene; Δ, x1,2-dibromoethane + (1 − x)1,4-dimethylbenzene.

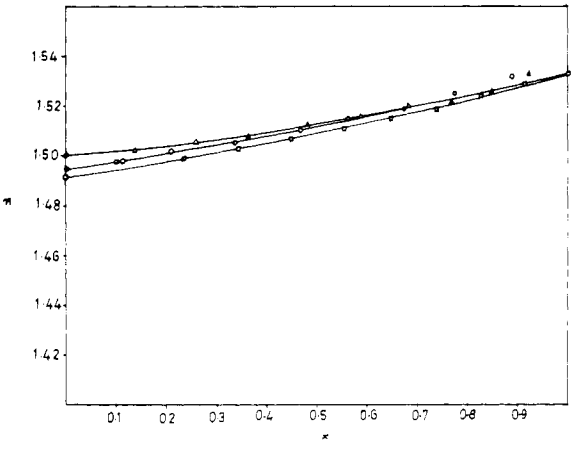

Figure 2. Plots of refractive index against mole fraction x: O, x1,2-dibromoethane + (1 − x)benzene; □, x1,2-dibromoethane + (1 − x)methylbenzene; Δ, x1,2-dibromoethane + (1 − x)1,2-dimethylbenzene.

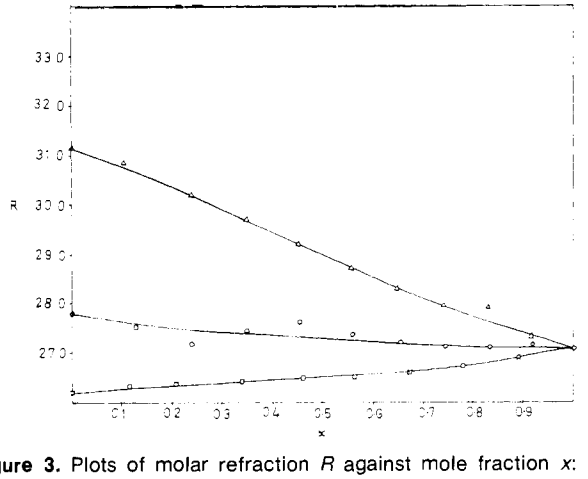

Figure 3. Plots of molar refraction R against mole fraction x: O, x1,2-dibromoethane + (1 − x)cyclohexane; □, x1,2-dibromoethane + (1 − x)benzene; Δ, x1,2-dibromoethane + (1 − x)methylbenzene.

2. The lines in the figures are drawn to make the best fit of the experimental points.

The refractive indices were measured with sodium light and the results are reproducible to within 0.0002. The measured refractive indices of the pure components are in agreement to within 0.0004 with the corresponding literature values (*6*).

It is evident from Figures 1 and 2 that refractive index plots against composition show slight deviations from linearity. Molar

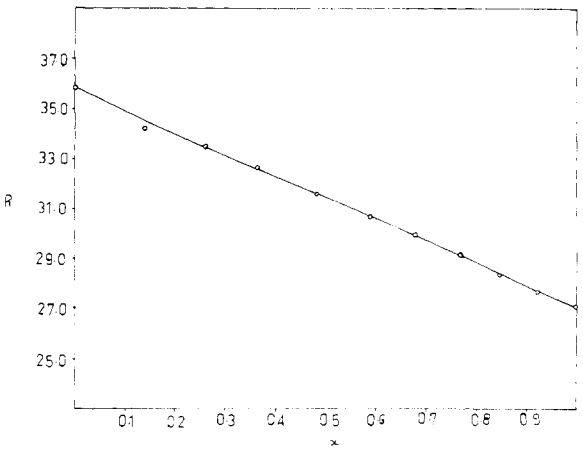

Figure 4. Plots of molar refraction R against mole fraction x of x1,2-dibromoethane + (1 − x)1,2-dimethylbenzene.

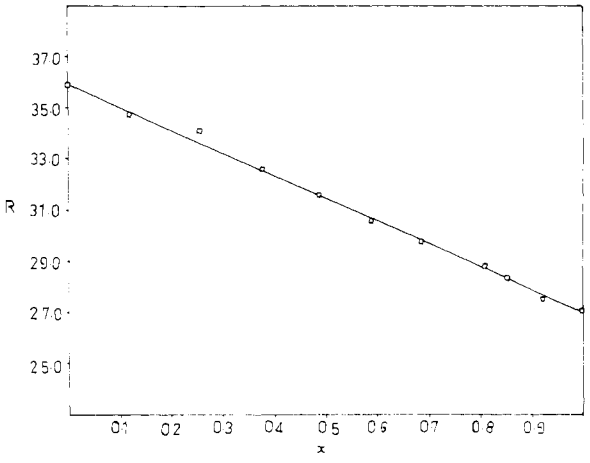

Figure 5. Plots of molar refraction R against mole fraction x of x1,2-dibromoethane + (1 − x)1,3-dimethylbenzene.

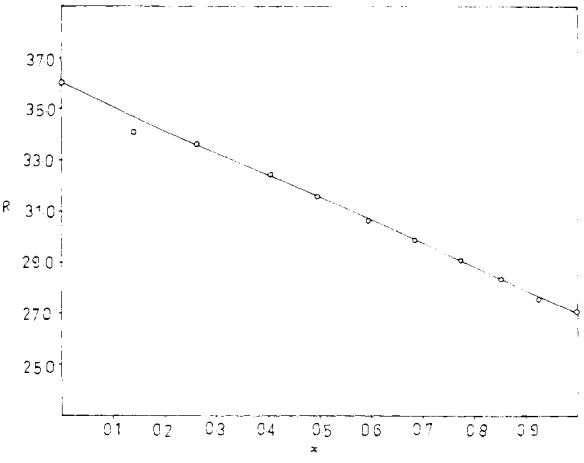

Figure 6. Plots of molar refraction R against mole fraction x of x1,2-dibromoethane + (1 − x)1,4-dimethylbenzene.

refraction is related to refractive index by the relation:

$$R = (n^2 - 1)/(n^2 + 2)M/d \qquad (1)$$

Molar refraction for a mixture is given by the relation:

$$R_{12} = (n_{mix}^2 - 1)/(n_{mix}^2 + 2)\,(x_1M_1 + x_2M_2)/d_{mix} \qquad (2)$$

where n_{mix} and d_{mix} are the refractive index and density of the mixture, x_1 and x_2 are the mole fractions, and M_1 and M_2 are molecular weights. The values of densities of the mixtures were taken from excess volume measurements (*1*). Molar refraction

values are recorded in Table II and have been plotted in Figures 3–6.

The lines in the figures are drawn to make the best fit of the calculated values. From Figures 3 to 6 it is evident that the plots of molar refraction against composition are not linear. There is a slight scatter of points from linear behavior.

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Literature Cited

(1) Dhillon, M. S., Chugh, H. S., *J. Chem. Thermodyn.*, **7**, 359 (1975).
(2) Dhillon, M. S., Chugh, H. S., *Thermochim. Acta*, **16**, 185 (1976).
(3) Dhillon, M. S., Chugh, H. S., *Thermochim. Acta*, **16**, 345 (1976).
(4) Dhillon, M. S., *J. Chem. Thermodyn.*, **6**, 915 (1974).
(5) Lange, N. A., "Handbook of Chemistry", McGraw-Hill, New York, N.Y., 1972.
(6) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds", Elsevier, New York, N.Y., 1964.
(7) Weast, R. C., Ed., "Handbook of Chemistry and Physics", The Chemical Rubber Co., Cleveland, Ohio, 1972.

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Vapor–Liquid Equilibria of the Binary and Ternary Systems Containing *n*-Hexane (1)–Benzene (2)–*tert*-Butyl Alcohol (3) at 760 mmHg Pressure

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Vapor–liquid equilibrium data at 760 mmHg pressure are reported for the binary systems *n*-hexane–*tert*-butyl alcohol and benzene–*tert*-butyl alcohol and for the ternary system *n*-hexane–benzene–*tert*-butyl alcohol. The binary and ternary vapor–liquid equilibrium data were tested by Herington's method and the Li and Lu method, respectively, for the thermodynamic consistency. While the binary data were correlated through the Wilson, NRTL, and Andiappan–McLean equations the ternary data were correlated through the Wilson and NRTL equations.

In continuation of the research program made by the authors to study the effect of alcohols on the separation of *n*-hexane–benzene mixtures, this is the fifth (*2–5*) and the last in the series dealing with the vapor–liquid equilibrium of the binary and ternary systems containing *n*-hexane–benzene and *tert*-butyl alcohol at 760 mmHg pressure. Of the three possible binary systems the vapor–liquid equilibrium data for the system *n*-hexane–benzene are available in literature (*9, 11, 14*). These authors also measured the data on this system. The vapor–liquid equilibrium data for the other binaries, *n*-hexane–*tert*-butyl alcohol and benzene–*tert*-butyl alcohol and the ternary *n*-hexane–benzene–*tert*-butyl alcohol are reported in this communication.

Experimental Section

"Analar" grade benzene supplied by B.D.H., India, and Guaranteed Reagent grade *n*-hexane, Japan make, were used after drying with sodium and distillation.

Laboratory grade *tert*-butyl alcohol supplied by B.D.H., India, was treated with burnt lime for about 2 days. Then it was distilled and the fraction boiling at 82.2–82.4 °C was collected for use. The physical properties of the liquids together with the literature values (*15*) are reported in Table I.

The experimental procedure for measuring the equilibrium data was the same as described in the previous communications (*2, 3*).

Density was used as the means of analyzing the binary mixtures while density and refractive index were used for analyzing the ternary mixtures. For the ternary system, curves of constant density and refractive index as functions of compositions were drawn. From these curves the composition of each unknown mixture was established. These curves are shown in Figure 1.

Table I. Physical Properties of Pure Components

Component	Density g cm^{-3} (35 °C) Obsd	Density g cm^{-3} (35 °C) Lit.	Refractive index (35 °C) Obsd	Refractive index (35 °C) Lit.	Bp, °C Obsd	Bp, °C Lit.
n-Hexane	0.6460	0.6470	1.3680	1.3670	68.70	68.70
Benzene	0.8630	0.8633	1.4915	1.4915	80.10	80.10
tert-Butyl alcohol	0.7703	0.7709	1.3800	1.3823 (25 °C)	82.30	82.41

Table II. Vapor–Pressure Constants of Pure Components

Component	C_1	C_2	C_3	C_4	C_5	C_6
n-Hexane	113.283	−7151.50	0.0	0.019 95	0.0	−17.00
Benzene	133.313	−8026.29	0.0	0.023 93	0.0	−20.29
tert-Butyl alcohol	12.3567	−3858.00	−43.15	0.00	0.0	0.0