

Thermodynamic & Optical Studies on Binary Liquid Mixtures

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Excess molar volume (V^E) and excess molar refractivity (R^E) have been calculated at $20 \pm 0.01^\circ\text{C}$ from density and refractive index data on three binary mixtures of bromobenzene with cyclohexane, carbon tetrachloride and ethyl acetate. The validity of the existing mixing rules in the prediction of excess molar refractivity is discussed. The data are also used to predict density and refractive index increments of the mixtures. Results are discussed in terms of thermodynamic interactions between the mixing components.

As a part of our earlier work on interactions in binary solvent mixtures¹⁻³, we now report data on density and refractive index for three binary mixtures of bromobenzene with cyclohexane, carbon tetrachloride and ethyl acetate at 293.1K. These data have been used to calculate the excess molar volume (V^E) and excess molar refraction (R^E) of mixing. The latter quantity has been calculated using the existing mixing rules discussed elsewhere⁴. The results are discussed in terms of thermodynamic interactions with respect to the nature of mixing components.

Materials and Methods

The solvents used were of spectral grade and were found to be free from any impurity as revealed by gas chromatography. The purity of the solvents were further checked by measuring their densities and refractive indices and comparing these with the literature values. Agreement between the two sets of values was within ± 0.0005 units.

Solvent mixtures were made by weight in special air-tight stoppered bottles; the volume fractions were calculated from the weights and densities of pure components⁵. The possible error in the calculation of volume fraction (ϕ) was estimated to be less than 0.0001. All the physical properties were studied on the same day on which mixtures were prepared.

Densities were measured with a precision density meter, model DMA 02C (Anton Paar K.G., Austria) adopting the procedure described earlier⁶. Refractive indices of pure solvents and solvent mixtures were measured with a Bausch and Lomb precision refractometer equipped with mercury and sodium light sources. The precision of the instrument as

quoted by the manufacturer is ± 0.00003 units. The initial calibration of the instrument was made at 293.1K using the standard glass test piece provided by the manufacturer. Samples were applied to the prism surfaces of the refractometer and readings were taken by using sodium (589 nm) and the mercury green (546 nm) and blue (436 nm) lines. Experimental densities and refractive indices are given in Table 1.

Results and Discussion

The experimentally measured densities were used to predict the excess molar volume using¹ Eq (1)

$$V^E (\text{cm}^3/\text{mol}) = \frac{M_1 \phi_1 + M_2 \phi_2}{\rho} - \frac{M_1 \phi_1}{\rho_1} - \frac{M_2 \phi_2}{\rho_2} \dots (1)$$

where ρ_1 , ρ_2 and ρ are the densities of components 1, 2 and their mixtures respectively; M_1 and M_2 are the molecular weights of components 1 and 2, and ϕ_1 and ϕ_2 their volume fractions, respectively.

Excess molar refraction was calculated using Eq. (2)

$$R^E (\text{cm}^3/\text{mol}) = R - R_1 \phi_1 - R_2 \phi_2 \dots (2)$$

where R_1 , R_2 and R are respectively the molar refractions of components 1, 2 and their mixtures. A large number of refractive index mixture rules have been proposed in the literature⁴. However, the Lorentz-Lorenz^{7,8} rule is usually preferred because it is supported by a plausible theory; other rules such as Eykman⁹, Gladstone-Dale¹⁰, Newton¹¹ and Oster¹² are at least as good as the Lorentz-Lorenz rule. The Eykman rule is often superior from the experimental viewpoint¹³. In this paper one of our goals is to

Table 1—Densities and Refractive Indices of Binary Mixtures

Volume fraction (ϕ_1)	Density (g/cm ³)	Refractive index for		
		589 nm	546 nm	436 nm
(I) Bromobenzene (1)-cyclohexane (2)				
1.0	1.49132	1.55891	1.56373	1.58422
0.9	1.42122	1.54580	1.55010	1.56943
0.8	1.35118	1.53193	1.53587	1.55380
0.7	1.27835	1.51804	1.52188	1.53850
0.6	1.20780	1.50451	1.50809	1.52344
0.5	1.13591	1.49092	1.49420	1.50813
0.4	1.06268	1.47742	1.48041	1.49348
0.3	0.99320	1.46430	1.46734	1.47880
0.2	0.92222	1.45304	1.45392	1.46402
0.1	0.85093	1.43820	1.44051	1.44931
0.0	0.77880	1.42627	1.42810	1.43580

(II) Bromobenzene (1)-ethyl acetate (2)				
1.0	1.49131	1.55891	1.56363	1.58421
0.9	1.43780	1.54070	1.54519	1.56420
0.8	1.38109	1.52229	1.52643	1.54408
0.7	1.32104	1.50182	1.51670	1.52352
0.6	1.26440	1.48518	1.48871	1.50550
0.5	1.20534	1.46670	1.46983	1.48330
0.4	1.14491	1.44792	1.45081	1.46281
0.3	1.08484	1.42928	1.43181	1.44240
0.2	1.02724	1.40969	1.41190	1.42101
0.1	0.96534	1.39172	1.39360	1.40140
0.0	0.90072	1.37230	1.37377	1.38033

(III) Bromobenzene (1)-carbon tetrachloride (2)				
1.0	1.49131	1.55891	1.56355	1.58416
0.9	1.50442	1.55010	1.55462	1.57420
0.8	1.51577	1.54091	1.54533	1.56460
0.7	1.52728	1.53193	1.53601	1.55368
0.6	1.53650	1.52192	1.52582	1.54231
0.5	1.54853	1.51222	1.51580	1.53133
0.4	1.55426	1.50143	1.50469	1.51888
0.3	1.56791	1.49148	1.49455	1.50777
0.2	1.57692	1.48113	1.48400	1.49612
0.1	1.58544	1.47112	1.47370	1.48460
0.0	1.59430	1.46002	1.46241	1.47222

present an experimental argument supporting the superiority of the mixing rules. Expressing Eq. (2) in terms of mixing rules we get for Lorentz-Lorenz relation (3);

$$R_{(LL)}^E = \left(\frac{n^2 - 1}{n^2 + 2} \right) (V_m) - V_1 \left(\frac{n_1^2 - 1}{n_1^2 + 2} \right) \phi_1 - V_2 \left(\frac{n_2^2 - 1}{n_2^2 + 2} \right) \phi_2 \quad \dots (3)$$

for Gladstone-Dale relation (4);

$$R_{(GD)}^E = (n - 1) \cdot (V_m) - V_1 (n_1 - 1) \phi_1 - V_2 (n_2 - 1) \phi_2 \quad \dots (4)$$

for Eykman relation (5);

$$R_{(EYK)}^E = \left(\frac{n^2 - 1}{n + 0.4} \right) (V_m) - V_1 \left(\frac{n_1^2 - 1}{n_1 + 0.4} \right) \phi_1 - V_2 \left(\frac{n_2^2 - 1}{n_2 + 0.4} \right) \phi_2 \quad \dots (5)$$

for Oster relation (6);

$$R_{(OST)}^E = \left[\frac{(n^2 - 1)(2n^2 + 1)}{n^2} \right] (V_m) - V_1 \left[\frac{(n_1^2 - 1)(2n_1^2 + 1)}{n_1^2} \right] \phi_1 - V_2 \left[\frac{(n_2^2 - 1)(2n_2^2 + 1)}{n_2^2} \right] \phi_2 \quad \dots (6)$$

for Newton relation (7);

$$R_{(NWT)}^E = (n^2 - 1)(V_m) - V_1 (n_1^2 - 1) \phi_1 - V_2 (n_2^2 - 1) \phi_2 \quad \dots (7)$$

where $V_m = [(M_1 \phi_1 + M_2 \phi_2) / \rho]$ and $V_1 = (M_1 / \rho_1)$ and $V_2 = (M_2 / \rho_2)$ are the molar volumes of mixture, components 1 and 2 respectively.

The excess quantities as calculated from Eq. (1) and Eqs (3-7) are fitted to a polynomial of the type (8)

$$X^E = a + b(\phi_2 - \phi_1) + c(\phi_2 - \phi_1)^2 \quad \dots (8)$$

to evaluate the coefficients a , b and c from least-squares fitting of the data. Here X^E refers to either V^E or R^E .

The values of the computed coefficients for R^E are compiled in Table 2 together with the error analysis.

Density and refractive index increments have been^{2,3} calculated from Eqs. (9) and (10), respectively

$$\left(\frac{\partial \rho}{\partial \phi_1} \right)_{P,T} = \frac{(\rho_1 - \rho_2) - \rho \cdot D}{(1 + A_{12} \phi_1 \phi_2)} \quad \dots (9)$$

Table 2—Least-squares Fittings of Eq. (8) and Statistical Errors^(a) for Excess Molar Refraction

λ (nm)	Coefficients Eq. (8)	$R^E(\text{LL})$ Eq. (3)	$R^E(\text{GD})$ Eq. (4)	$R^E(\text{EYK})$ Eq. (5)	$R^E(\text{OST})$ Eq. (6)	$R^E(\text{NWT})$ Eq. (7)
(I) Bromobenzene(1)-cyclohexane(2)						
589	a	-0.024	-0.038	0.081	0.415	-0.092
	b	-0.233	-1.001	-1.704	-11.929	-4.474
	c	0.278	1.109	1.536	11.156	4.791
	$10^4 \sigma$	4.10	5.22	3.00	10.82	8.00
546	a	0.010	0.023	0.025	0.148	0.081
	b	-0.401	-1.374	-1.521	-11.314	-5.627
	c	0.359	1.294	1.423	10.826	5.405
	$10^4 \sigma$	4.20	5.41	2.98	10.10	6.00
436	a	0.012	0.030	0.033	0.198	0.106
	b	-0.337	-1.394	-1.501	-12.056	-6.094
	c	0.287	1.298	1.383	11.464	5.822
	$10^4 \sigma$	4.51	6.41	3.11	10.00	7.98
(II) Bromobenzene(1)-ethyl acetate(2)						
589	a	0.067	0.165	-0.165	-0.732	0.476
	b	0.628	-0.178	0.078	-7.190	-3.710
	c	-0.790	-0.165	0.022	7.607	2.689
	$10^4 \sigma$	4.91	6.10	3.62	9.42	8.48
546	a	0.023	-0.069	-0.158	-0.731	0.267
	b	0.610	-0.245	0.089	-7.436	-4.668
	c	-0.704	0.045	0.007	7.889	4.043
	$10^4 \sigma$	4.12	5.14	3.19	10.11	9.22
436	a	-0.076	-0.133	-0.178	-0.876	-0.350
	b	0.710	-0.254	0.284	-7.586	-5.260
	c	-0.683	0.302	-0.216	7.951	5.392
	$10^4 \sigma$	4.66	5.86	3.42	10.01	8.96
(III) Bromobenzene(1)-carbon tetrachloride(2)						
589	a	-0.029	-0.039	-0.057	-0.201	-0.063
	b	-0.183	-0.634	-0.709	-5.325	-2.612
	c	0.213	0.673	0.048	5.524	2.673
	$10^4 \sigma$	4.91	5.86	3.98	8.78	7.69
546	a	-0.019	-0.018	-0.032	-0.063	0.002
	b	-0.202	-0.692	-0.774	-5.775	-2.836
	c	0.221	0.708	0.803	5.819	2.825
	$10^4 \sigma$	4.88	6.10	3.48	9.68	8.99
436	a	-0.017	-0.013	0.007	0.163	0.022
	b	-0.198	-0.773	0.881	-6.872	-3.326
	c	0.213	0.780	0.886	6.665	3.282
	$10^4 \sigma$	4.44	6.08	3.07	10.08	8.80

^(a) standard error $\sigma = \{\Sigma[\text{exptl-calc}]^2/\text{number of observations}\}^{1/2}$

$$\left(\frac{\partial n}{\partial \phi_1}\right)_{P,T} = \frac{(n^2 + 2)^2 \{[(P_1 - P_2) + B_{12}(\phi_2 - \phi_1) + dB_{12}/d\phi_1(\phi_1\phi_2)] - P \cdot D\}}{6n(1 + A_{12}\phi_1\phi_2)} \quad \dots (10)$$

where

$$D = [A_{12}(\phi_2 - \phi_1) + \frac{dA_{12}}{d\phi_1}(\phi_1\phi_2)] \quad \dots (11)$$

The procedure to evaluate these quantities has already been outlined earlier^{2,14}.

Dependence of refractive index on volume fraction is shown in Fig. 1. As expected, refractive index is higher for mercury blue line than that for the green wavelength. The lowest refractive indices are

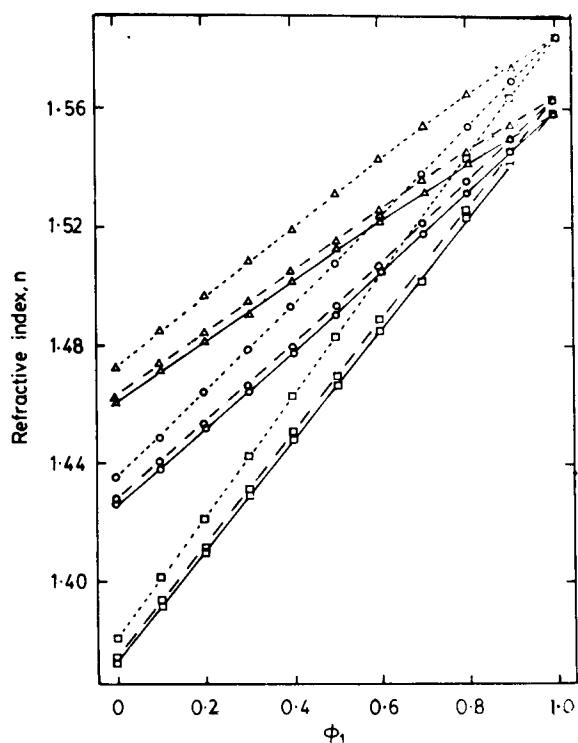


Fig. 1—Refractive index versus volume fraction for bromobenzene(1)-carbon tetrachloride(2) (Δ), bromobenzene(1)-cyclohexane(2) ($\circ$), and bromobenzene(1)-ethyl acetate(2) ($\square$), [--- 436 nm; - - 546 nm and — 589 nm]

observed for sodium line. As is evident from Fig. 1, the plots of the three systems slightly deviate from linearity.

The computed density and refractive index increments, evaluated from Eqs (9) and (10), are plotted as a function of ϕ_1 in Fig. 2. Smaller values of refractive index increments are observed for bromobenzene (1)-carbon tetrachloride (2) system as compared to bromobenzene (1)-cyclohexane (2) and bromobenzene (1)-ethyl acetate (2) systems. Refractive index increments exhibit the same trend as that of refractive index, i.e. the increment is higher for mercury blue line than that for green line. However, sodium yellow line exhibits highest refractive index increments. The density increment is negative and small for bromobenzene (1)-cyclohexane (2) system; but for the remaining two systems it is positive and also large.

The curves for density and refractive index increments (Fig. 2) exhibit widely differing behaviours. for bromobenzene (1)-carbon tetrachloride (2) system, refractive index increment at 589 and 546 nm shows a sigmoid behaviour; but at 436 nm, almost a rectilinear behaviour exists. Even the density increment for this system has a flattened sigmoid shape.

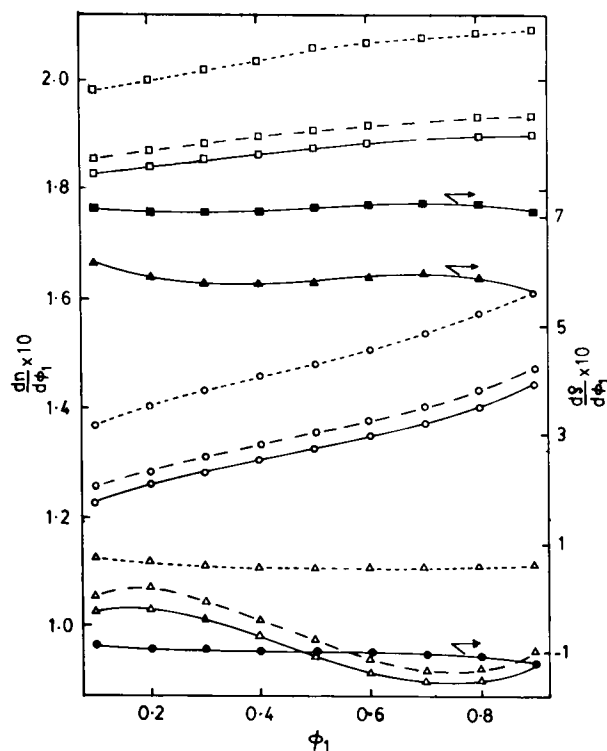


Fig. 2—Refractive index increment (left scale) and density increment (right scale) versus volume fraction. [Symbols for refractive index increment are the same as in Fig. 1] Symbols for density increment: bromobenzene(1)-cyclohexane(2) ($\bullet$); bromobenzene(1)-carbon tetrachloride(2) ($\blacktriangle$); and bromobenzene(1)-ethyl acetate(2) ($\blacksquare$)

for all the systems, the shape of refractive index increment curve for the mercury blue line is different from those for the curves at 589 and 546 nm, for which identical behaviour is seen.

Excess molar volumes as calculated from Eq. (1) are plotted in Fig. 3 as a function of ϕ_1 . For mixtures of bromobenzene with either carbon tetrachloride or cyclohexane, the excess molar volume is negative. Due to the presence of vacant 3d-orbitals in bromine atom of bromobenzene it acts as an electron acceptor towards both carbon tetrachloride or cyclohexane which act as electron donors. This suggests that weak donor-acceptor type complexes with attractive interactions are formed in solution thereby giving negative V^E values. On the otherhand, in the case of bromobenzene (1)-ethyl acetate (2) mixture, V^E curve shows both negative and positive values. Such systems are very rare in literature. Ethyl acetate, being highly polar, its polarity seems to be affected by the addition of bromobenzene. Presence of methyl and ethyl groups in ethyl acetate may be the cause of this anomaly. In the mixture, when methyl group comes closer to bromine atom of bromobenzene an attractive force exists between bro-

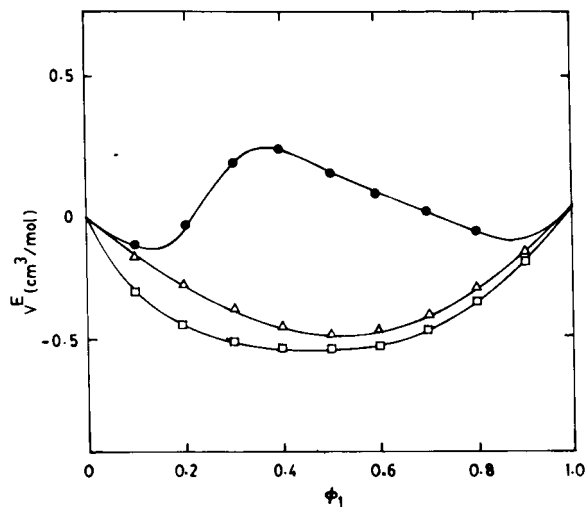


Fig. 3—Excess molar volume versus volume fraction. [bromobenzene(1)-ethyl acetate(2) (●); bromobenzene(1)-cyclohexane(2) (□); and bromobenzene(1)-carbon tetrachloride(2) (△)]

mine and oxygen atom of ethyl acetate. On the otherhand, when the carboxylate moiety comes close to bromine atom then the Br---O type weak bond formed may be broken giving positive V^E . This happens around $\phi_1 = 0.25$ to 0.65 and above $\phi_1 = 0.65$, negative V^E is observed.

From the results of Table 2 it is seen that the standard error (σ) involved in fitting Eykman relation (Eq. 5) is very small as compared to those of the other relations, viz. Eqs (3), (4), (6) and (7). However, the errors for $R^E(LL)$ are also significantly smaller but somewhat larger than those for Eykman; for Oster's mixing rule the error involved is large. The errors for Gladstone-Dale and Newton relations are more or less the same although in major-

ity of cases small deviations are observed for Newton's relation. This analysis indicates that Eykman relation gives the best results, whereas Lorentz-Lorenz and Gladstone-Dale relations are quite satisfactory. Newton's relation is better than Oster's relation but not comparable in its performance to either Eykman, Lorentz-Lorenz or Gladstone-Dale relations. Although Lorentz-Lorenz relation has a sound theoretical foundation than that of Eykman, the latter seems to fit the data much satisfactorily.

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