

## Excess Molar Volumes of Binary Mixtures Containing Bromoform at 25°C

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Excess molar volumes have been calculated at  $25 \pm 0.1^\circ\text{C}$  for binary mixtures of bromoform with (i) ethyl acetate, (ii) carbon tetrachloride, (iii) cyclohexane, (iv) bromobenzene, (v) dimethylformamide, (vi) dimethyl sulphoxide and (vii) methyl ethyl ketone from density data. The excess volume data have been fitted to a polynomial equation. A fair agreement is seen between the calculated and experimental results over the entire composition range of mixtures. The results are discussed in terms of interactions between the components of the mixtures and the nature of the pure components.

Aminabhavi *et al.*<sup>1-9</sup> have extensively studied the interactions in binary liquid mixtures based on excess molar volumes etc. In continuation of these studies, we report herein experimental densities and the calculated excess molar volumes of binary mixtures of bromoform with dimethyl sulphoxide (DMSO), dimethylformamide (DMF), carbon tetrachloride, ethyl acetate, cyclohexane, bromobenzene and methyl ethyl ketone at  $25^\circ\text{C}$ . Bromoform was particularly chosen since its density is higher than those of the other solvents used.

The reagent grade solvents used were purified by fractional distillation. Mixtures were made on volume per cent basis. The densities of pure solvents ( $\rho_1$  and  $\rho_2$ ) and of their mixtures ( $\rho$ ) were measured with a pycnometer at  $25 \pm 0.1^\circ\text{C}$ . Densities of pure components agree closely with the literature data<sup>10</sup> given at  $20^\circ\text{C}$ . Only the mean values of the triplicate measurements are given in Table 1. The agreement between three sets of measurements was within experimental error.

The excess molar volumes were calculated by Eq. (1).

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

Here,  $M_i$  and  $\phi_i$  ( $\equiv x_i v_i / \sum_{i=1}^2 x_i v_i$ ) represent the molecular weights and volume fractions of the  $i$ th component in the mixture respectively; and  $x_i$  and  $v_i$  are the mol fractions and molar volumes ( $M_i/\rho_i$ ),

respectively. The experimental values of  $V^E$  were fitted to a quadratic equation of the type (2)

$$V^E = \phi_1\phi_2[A + B(\phi_2 - \phi_1) + C(\phi_2 - \phi_1)^2] \quad \dots (2)$$

The coefficients  $A$ ,  $B$  and  $C$  were estimated from a least-squares procedure using a DCM microcomputer equipped with machine language. The excess molar volumes and the estimated parameters ( $A$ ,  $B$  and  $C$ ) of Eq. (2) are also included in Table 1.

The quantity,  $V^E/\phi_1\phi_2$ , was back calculated using the values of the estimated parameters, and its dependence on  $\phi_1$  is shown in Fig. 1. In general, a fair agreement is seen between the calculated and experimental excess molar volumes over the entire

Table 1—Densities, Excess Molar Volumes and Computed Coefficients ( $A$ ,  $B$  and  $C$ ) of Eq. (2) for Binary Systems at  $25^\circ\text{C}$

Volume fr. $\phi_1$	Density ( $\rho$ ) ( $\text{g}/\text{cm}^3$ )	$V^E/\phi_1\phi_2$ ( $\text{cm}^3/\text{mol}$ )
<i>Bromoform (1)-dimethyl sulphoxide (2)</i> $A = 17.3973; B = 9.6809; C = 0.0531$		
0.0	1.10004	—
0.1104	1.28879	24.9348
0.2056	1.45414	22.3302
0.3980	1.78439	18.6091
0.5014	1.96369	16.8615
0.6011	2.13745	15.3615
0.6969	2.30322	14.3858
0.7950	2.47025	14.2192
0.8869	2.64874	7.8089
1.0	2.83220	—

<i>Bromoform (1)-dimethylformamide (2)</i> $A = 12.2634; B = 8.1402; C = 8.6983$		
0.0	0.94813	—
0.1606	1.24217	22.5020
0.3004	1.51260	15.5683
0.4997	1.88704	12.6330
0.6487	2.16753	11.0858
0.7434	2.34494	10.6175
0.8389	2.52405	10.2733
1.0	2.83220	—

<i>Bromoform (1)-cyclohexane (2)</i> $A = -21.7500; B = -14.0141; C = -7.3275$		
0.0	0.77585	—
0.1574	1.09849	-35.2344
0.3003	1.39119	-27.6527
0.5000	1.80456	-22.0361
0.6467	2.10475	-18.6083
0.8484	2.51922	-15.3393
1.0	2.83220	—

(Contd)

Table 1—Densities, Excess Molar Volumes and Computed Coefficients (*A*, *B* and *C*) of Eq. (2) for Binary Systems at 25°C—Contd

Volume fr. $\phi_1$	Density ( $\rho$ ) (g/cm <sup>3</sup> )	$V^E/\phi_1\phi_2$ (cm <sup>3</sup> /mol)
<i>Bromoform (1)-bromobenzene (2)</i>		
<i>A</i> = -9.5529; <i>B</i> = -1.7942; <i>C</i> = 1.8143		
0.0	1.49824	—
0.1608	1.70762	-9.8971
0.3020	1.89728	-10.0051
0.5016	2.16803	-9.7003
0.6513	2.36617	-8.6317
0.8402	2.61759	-7.5632
1.0	2.83220	—
<i>Bromoform (1)-methyl ethyl ketone (2)</i>		
<i>A</i> = -1.8354; <i>B</i> = -0.6230; <i>C</i> = 0.8219		
0.0	0.80580	—
0.1582	1.12854	-1.6979
0.3046	1.42964	-2.2790
0.5002	1.82738	-1.8318
0.6495	2.12784	-1.3096
0.8428	2.51718	-1.1449
1.0	2.83220	—
<i>Bromoform (1)-carbon tetrachloride (2)</i>		
<i>A</i> = -4.0260; <i>B</i> = 0.3396; <i>C</i> = 4.2791		
0.0	1.58700	—
0.1110	1.71555	-0.1242
0.2048	1.83346	-2.5032
0.2953	1.95145	-4.1595
0.4228	2.11545	-4.8995
0.5042	2.21869	-4.9655
0.6021	2.33280	-3.4552
0.6982	2.43520	-1.5009
0.7936	2.57291	-3.2283
0.8908	2.69442	-2.9272
1.0	2.83220	—
<i>Bromoform (1)-ethyl acetate (2)</i>		
<i>A</i> = -11.0293; <i>B</i> = -6.8953; <i>C</i> = -2.4805		
0.0	0.89830	—
0.2496	1.39460	-15.1046
0.5008	1.89320	-11.0183
0.7476	2.38070	-8.2230
1.0	2.88460*	—

\*For a different batch of bromoform.

composition range. Mixtures of bromoform with either dimethyl sulphoxide or dimethylformamide give positive  $V^E$  values. The positive values of  $V^E$  and the exothermic heat of mixing for such systems indicate that there may be attractive interaction of the dipole-dipole type<sup>11-13</sup>. Mixtures of bromoform with bromobenzene, ethyl acetate, methyl ethyl ketone, carbon tetrachloride and cyclohexane give negative  $V^E$  values. Generally, negative excess volumes are known for systems in which hydrogen bond formation occurs<sup>13</sup>. It is believed that such volume changes in

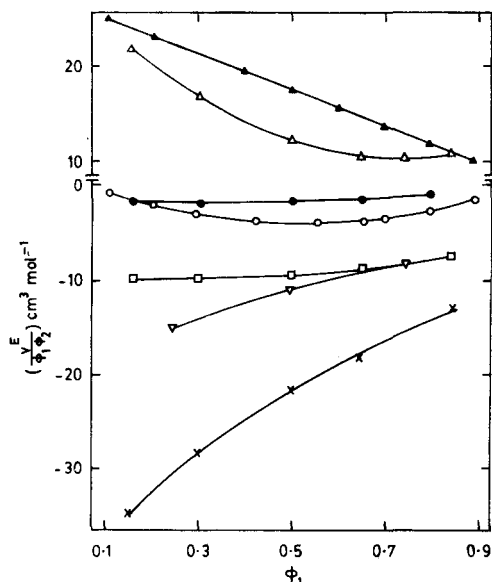


Fig. 1— $V^E/\phi_1\phi_2$  versus volume fraction ( $\phi_1$ ) plots of binary mixtures of bromoform with (1) bromobenzene; (2) carbon tetrachloride; (3) cyclohexane; (4) dimethylformamide; (5) dimethyl sulphoxide; (6) ethyl acetate; and (7) methyl ethyl ketone

nonpolar mixtures are due to contact interactions arising mainly from two effects<sup>14</sup>: (i) a positive contribution from the difference in force fields of the two components because of difference in their chemical nature and (ii) a positive contribution arising from a correlation of molecular orientations in the pure components and their mixtures. If, on the otherhand, a somewhat nonpolar liquid like bromoform is mixed with a polar liquid like ethyl acetate, methyl ethyl ketone, nitrobenzene etc., then one can expect a third contribution arising from dipole-induced dipole interaction<sup>15</sup>. However, whereas  $V^E/\phi_1\phi_2$  versus  $\phi_1$  profile for bromoform-cyclohexane mixture gives a positive slope. Similar profile for mixtures of bromoform-carbon tetrachloride gives a negative slope. The specific interaction here could be of charge transfer type. Carbon tetrachloride and cyclohexane are known to act as electron acceptors for a number of donors<sup>13</sup>. In this case, the bromine atom of the bromoform molecule may act as an electron donor. This attractive interaction is also supported by the observed exothermic heat of mixing of mixtures of chloroform-carbon tetrachloride<sup>13</sup>.

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## NOTES

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