

# Thermodynamic Properties of Binary Mixtures of Bromoform with Benzene, Toluene, *p*-Xylene, Nitrobenzene, Acetonitrile & Tetrahydrofuran†

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Previously published data on densities and viscosities of binary mixtures of bromoform with benzene, toluene, *p*-xylene, acetonitrile, nitrobenzene and tetrahydrofuran at 298.15, 308.15 and 318.15 K have been used to predict a number of excess thermodynamic quantities such as excess enthalpy, excess entropy, excess Gibbs free energy of flow and excess heat capacity of mixing. A few viscosity models have also been tested to discuss their relative merits.

In continuation of our earlier work<sup>1</sup> on thermodynamic properties of bromoform containing binaries, we now report additional thermodynamic data on the title binaries using density and viscosity results obtained at 298.15, 308.15 and 318.15 K. A few viscosity models have also been tested to discuss their relative merits.

All the solvents used were of either BDH or Fluka AG grade and were purified by standard procedures<sup>2</sup>. The binary mixtures were prepared on volume fraction basis ( $\phi$ ). Densities and viscosities of the binaries were measured as described elsewhere<sup>3</sup>. The temperature was maintained constant within  $\pm 0.01$  K at 298.15 K and  $\pm 0.05$  K at 308.15 and 318.15 K. All computations were done on an HP1000 computer available at CSMRI, Bhavnagar.

The binary contact interaction parameter ( $A_{12}$ ) and density increment  $(\partial\rho/\partial\phi_1)_{P,T}$  were calculated employing Eqs (1) and (2) respectively.

$$A_{12} = (\phi_1\rho_1 + \phi_2\rho_2 - \rho)/\phi_1\phi_2\rho \quad \dots (1)$$

$$(\partial\rho/\partial\phi_1)_{P,T} = \frac{(\rho_1 - \rho_2) - \rho[A_{12}(\phi_2 - \phi_1) + dA_{12}/d\phi_1(\phi_1\phi_2)]}{(1 + A_{12}\phi_1\phi_2)} \quad \dots (2)$$

Details of calculations to compute these parameters have appeared elsewhere<sup>4,5</sup> and the data are presented in Table 1.  $A_{12}$  is negative for binaries of bromoform with benzene, toluene, acetonitrile and tetrahydrofuran and positive for those of *p*-xylene and nitrobenzene. Density increments are positive over the entire range of composition for all the mixtures at 298.15, 308.15 and 318.15 K.

Excess molar Gibbs free energies ( $\Delta G^{*E}$ ) of activation as calculated from Eq. (3) from viscosity data were used to calculate excess enthalpy ( $\Delta H^{*E}$ ) (Eq. 4), excess entropy ( $\Delta S^{*E}$ ) (Eq. 5) and excess heat capacity ( $\Delta C_p^{*E}$ ) of activation (Eq. 6) at equimolar concentrations (i.e.  $x_1 \approx x_2 \approx 0.5$ )

$$\Delta G^{*E} = RT(\ln \eta V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2) \quad \dots (3)$$

$$\Delta H^{*E} = -RT^2 \left\{ \left[ \frac{\partial \ln \eta}{\partial T} \right] - x_1 \left[ \frac{\partial \ln \eta_1}{\partial T} \right] - x_2 \left[ \frac{\partial \ln \eta_2}{\partial T} \right] + \frac{1}{V} \left[ \frac{\partial V}{\partial T} \right] - \frac{x_1}{V_1} \left[ \frac{\partial V_1}{\partial T} \right] - \frac{x_2}{V_2} \left[ \frac{\partial V_2}{\partial T} \right] \right\} \quad \dots (4)$$

$$\Delta S^{*E} = (\Delta H^{*E} - \Delta G^{*E})/T \quad \dots (5)$$

$$\Delta C_p^{*E} = -2RT \left\{ \left[ \frac{\partial \ln \eta}{\partial T} \right] - x_1 \left[ \frac{\partial \ln \eta_1}{\partial T} \right] - x_2 \left[ \frac{\partial \ln \eta_2}{\partial T} \right] + \frac{1}{V} \left[ \frac{dV}{dT} \right] - \frac{x_1}{V_1} \left[ \frac{dV_1}{dT} \right] - \frac{x_2}{V_2} \left[ \frac{dV_2}{dT} \right] - RT^2 \left\{ \left[ \frac{\partial^2 \ln \eta}{\partial T^2} \right] - x_1 \left[ \frac{\partial^2 \ln \eta_1}{\partial T^2} \right] - x_2 \left[ \frac{\partial^2 \ln \eta_2}{\partial T^2} \right] + \frac{1}{V} \left[ \frac{\partial^2 V}{\partial T^2} \right] - \frac{x_1}{V_1} \left[ \frac{\partial^2 V_1}{\partial T^2} \right] - \frac{x_2}{V_2} \left[ \frac{\partial^2 V_2}{\partial T^2} \right] - \left[ \frac{1}{V} \frac{\partial V}{\partial T} \right]^2 + x_1 \left[ \frac{1}{V_1} \frac{\partial V_1}{\partial T} \right]^2 + x_2 \left[ \frac{1}{V_2} \frac{\partial V_2}{\partial T} \right]^2 \right\} \right\} \quad \dots (6)$$

In Eqs (3-6) the term  $RT$  has the conventional meaning;  $V$  is molar volume of the mixture;  $V_1$ ,  $V_2$  and  $x_1$ ,  $x_2$  are respectively the molar volumes and mol fractions of components 1 and 2;  $\eta$ ,  $\eta_1$ , and

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Table 1 – Binary Contact Interaction Parameter and Density Increment of Binaries at 298.15, 308.15 and 318.15 K

| $\phi_1$                             | $A_{12}$ (Eq. 1) at |        |          | $(\partial\rho/\partial\phi_1)_{P,T}$ (Eq. 2) at |        |          |
|--------------------------------------|---------------------|--------|----------|--------------------------------------------------|--------|----------|
|                                      | 298.15              | 308.15 | 318.15 K | 298.15                                           | 308.15 | 318.15 K |
| (I) Bromoform(1)-benzene(2)          |                     |        |          |                                                  |        |          |
| 0.15                                 | -0.017              | -0.028 | -0.034   | 1.983                                            | 1.957  | 1.843    |
| 0.30                                 | -0.016              | -0.016 | -0.035   | 1.960                                            | 1.936  | 1.869    |
| 0.50                                 | -0.019              | -0.025 | -0.023   | 1.935                                            | 1.916  | 1.913    |
| 0.65                                 | -0.009              | -0.019 | -0.021   | 1.945                                            | 1.929  | 1.926    |
| 0.85                                 | 0.000               | -0.003 | -0.033   | 2.041                                            | 2.023  | 1.864    |
| (II) Bromoform(1)-toluene(2)         |                     |        |          |                                                  |        |          |
| 0.15                                 | -0.025              | -0.005 | -0.009   | 1.810                                            | 1.979  | 1.900    |
| 0.30                                 | -0.029              | -0.005 | 0.026    | 1.867                                            | 1.957  | 1.932    |
| 0.50                                 | -0.002              | -0.006 | -0.009   | 1.959                                            | 1.932  | 1.963    |
| 0.65                                 | -0.001              | -0.000 | -0.010   | 1.982                                            | 1.940  | 1.952    |
| 0.85                                 | -0.028              | 0.010  | -0.014   | 1.831                                            | 2.027  | 1.832    |
| (III) Bromoform(1)-p-xylene(2)       |                     |        |          |                                                  |        |          |
| 0.15                                 | 0.013               | 0.008  | 0.007    | 2.006                                            | 1.992  | 1.971    |
| 0.30                                 | 0.011               | 0.007  | 0.003    | 1.995                                            | 1.971  | 1.963    |
| 0.50                                 | 0.010               | 0.008  | 0.004    | 1.979                                            | 1.947  | 1.949    |
| 0.65                                 | 0.009               | 0.010  | 0.002    | 1.976                                            | 1.952  | 1.945    |
| 0.85                                 | 0.014               | 0.020  | 0.005    | 2.006                                            | 2.030  | 1.962    |
| (IV) Bromoform(1)-acetonitrile(2)    |                     |        |          |                                                  |        |          |
| 0.30                                 | -0.011              | -0.013 | -0.013   | 2.070                                            | 2.084  | 2.070    |
| 0.50                                 | -0.017              | -0.022 | -0.020   | 2.062                                            | 2.062  | 2.051    |
| 0.65                                 | -0.019              | -0.027 | -0.024   | 2.048                                            | 2.037  | 2.032    |
| 0.85                                 | -0.023              | -0.028 | -0.025   | 2.015                                            | 2.003  | 2.012    |
| 0.95                                 | -0.027              | -0.035 | -0.028   | 1.993                                            | 1.992  | 2.010    |
| (V) Bromoform(1)-nitrobenzene(2)     |                     |        |          |                                                  |        |          |
| 0.15                                 | 0.012               | 0.017  | 0.013    | 1.618                                            | 1.622  | 1.674    |
| 0.30                                 | 0.014               | 0.016  | 0.013    | 1.626                                            | 1.620  | 1.647    |
| 0.50                                 | 0.010               | 0.012  | 0.006    | 1.629                                            | 1.613  | 1.608    |
| 0.65                                 | 0.008               | 0.011  | -0.003   | 1.623                                            | 1.605  | 1.596    |
| 0.85                                 | 0.005               | 0.009  | 0.010    | 1.589                                            | 1.592  | 1.638    |
| (VI) Bromoform(1)-tetrahydrofuran(2) |                     |        |          |                                                  |        |          |
| 0.15                                 | -0.044              | -0.053 | -0.057   | 1.889                                            | 1.844  | 1.833    |
| 0.30                                 | -0.041              | -0.044 | -0.051   | 1.884                                            | 1.847  | 1.847    |
| 0.50                                 | -0.031              | -0.029 | -0.038   | 1.894                                            | 1.878  | 1.885    |
| 0.65                                 | -0.023              | -0.023 | -0.034   | 1.922                                            | 1.918  | 1.912    |
| 0.85                                 | -0.017              | -0.013 | -0.034   | 1.988                                            | 1.983  | 1.919    |

$\eta_2$  are viscosities of the mixture and of the components 1 and 2, respectively.

The computed results from Eqs (4-6) at equimolar compositions ( $x_1 = x_2 \approx 0.5$ ) are given in Table 2. The values of  $\Delta H^{*E}$  are positive for all the binaries with bromoform(1)-tetrahydrofuran(2) showing the largest and bromoform(1)-benzene(2) showing the smallest  $\Delta H^{*E}$ . The positive sign for the values of  $\Delta H^{*E}$  is a clear evidence for the presence of specific interaction and suggests an endothermic interaction. For all the binaries, the  $\Delta H^{*E}$  values are temperature-dependent. Likewise, the quantity  $\Delta S^{*E}$ , also varies with temperature; however, it does not follow the same pattern as  $\Delta H^{*E}$ . It is intriguing to note that  $\Delta C_p^{*E}$  values do not vary much with temperature. The negative

$\Delta C_p^{*E}$  for bromoform(1)-toluene(2) system is indicative of specific interaction between the components. For other systems  $\Delta C_p^{*E}$  values are positive.

The estimated parameters from a least-squares analysis of McAllister<sup>6</sup>, Auslaender<sup>7</sup> and Heric<sup>8</sup> viscosity models are given in Table 3. McAllister model gives a good agreement between the observed and back calculated values of the viscosities; the average deviation being less than 0.5% for all mixtures. However, the mathematically less complex Auslaender model gives an error of 0.5-1.0%. The Heric theory gives slightly higher average percentage deviation sometimes exceeding 2%.

The other viscosity models, viz. Tamura-Kurata<sup>9</sup>, Hind *et al.*<sup>10</sup> and Grunberg-Nissan<sup>11,12</sup> do not contain adjustable parameters but involve only

Table 2 – Excess Enthalpy, Excess Entropy and Excess Heat Capacity of Activation of Flow for Various Binaries at  $x_1 = x_2 \approx 0.5$ 

| $\Delta H^*E$ (cal/mol) (Eq. 4) at     |         |         | $\Delta S^*E$ (cal/mol) (Eq. 3) at |        |         | $\Delta C_p^*E$ (cal/mol) (Eq. 6) at |        |         |
|----------------------------------------|---------|---------|------------------------------------|--------|---------|--------------------------------------|--------|---------|
| 298.15                                 | 308.15  | 318.15K | 298.15                             | 308.15 | 318.15K | 298.15                               | 308.15 | 318.15K |
| <i>Bromoform(1)-benzene(2)</i>         |         |         |                                    |        |         |                                      |        |         |
| -9.844                                 | 19.437  | 52.649  | -0.200                             | -0.105 | 0.003   | 2.928                                | 3.125  | 3.321   |
| <i>Bromoform(1)-toluene(2)</i>         |         |         |                                    |        |         |                                      |        |         |
| 208.700                                | 192.294 | 172.314 | 0.540                              | 0.487  | 0.422   | -1.640                               | -1.819 | -1.998  |
| <i>Bromoform(1)-p-xylene(2)</i>        |         |         |                                    |        |         |                                      |        |         |
| 36.376                                 | 119.147 | 212.642 | -0.002                             | 0.267  | 0.570   | 8.281                                | 8.815  | 9.350   |
| <i>Bromoform(1)-acetonitrile(2)</i>    |         |         |                                    |        |         |                                      |        |         |
| 138.622                                | 174.050 | 213.216 | -0.138                             | -0.002 | 0.104   | 3.543                                | 3.730  | 3.917   |
| <i>Bromoform(1)-nitrobenzene(2)</i>    |         |         |                                    |        |         |                                      |        |         |
| 39.112                                 | 130.000 | 232.618 | 0.010                              | 0.305  | 0.637   | 9.089                                | 9.675  | 10.262  |
| <i>Bromoform(1)-tetrahydrofuran(2)</i> |         |         |                                    |        |         |                                      |        |         |
| 216.001                                | 263.831 | 316.515 | 0.252                              | 0.408  | 0.578   | 4.783                                | 5.026  | 5.268   |

Table 3 – Computer Fittings of Viscosity Models

| Temp<br>(K)                                 | McAllister |            | Auslaender |          |          | Heric          |                |                |
|---------------------------------------------|------------|------------|------------|----------|----------|----------------|----------------|----------------|
|                                             | $\nu_{12}$ | $\nu_{21}$ | $B_{12}$   | $A_{21}$ | $B_{21}$ | $A \cdot 10^2$ | $B \cdot 10^2$ | $C \cdot 10^2$ |
| <i>(I) Bromoform(1)-benzene(2)</i>          |            |            |            |          |          |                |                |                |
| 298.15                                      | 1.44       | 1.19       | -1.24      | -1.62    | -0.81    | -19.34         | 12.18          | -13.88         |
| 308.15                                      | 1.28       | 1.02       | 0.09       | 0.16     | 7.68     | -18.67         | 15.41          | -6.63          |
| 318.15                                      | 1.15       | 0.89       | 0.70       | 1.03     | 1.13     | -17.39         | 14.36          | -7.69          |
| <i>(II) Bromoform(1)-toluene(2)</i>         |            |            |            |          |          |                |                |                |
| 298.15                                      | 1.46       | 1.05       | -4.98      | -6.92    | -0.21    | -10.83         | 13.43          | 12.37          |
| 308.15                                      | 1.25       | 0.90       | 0.74       | 1.20     | 1.08     | -12.24         | 11.23          | -1.33          |
| 318.15                                      | 1.12       | 0.80       | 0.20       | 0.41     | 3.15     | -12.35         | 10.11          | 1.58           |
| <i>(III) Bromoform(1)-p-xylene(2)</i>       |            |            |            |          |          |                |                |                |
| 298.15                                      | 1.46       | 1.02       | -1.45      | -2.06    | -0.66    | -5.70          | 11.18          | 6.41           |
| 308.15                                      | 1.26       | 0.88       | 1.03       | 1.70     | 0.76     | -8.08          | 11.44          | -0.44          |
| 318.15                                      | 1.10       | 0.79       | 2.58       | 4.11     | 0.32     | -9.35          | 7.81           | 1.63           |
| <i>(IV) Bromoform(1)-acetonitrile(2)</i>    |            |            |            |          |          |                |                |                |
| 298.15                                      | 1.52       | 1.41       | 1.07       | 1.50     | 0.47     | -17.07         | 37.13          | -13.24         |
| 308.15                                      | 1.21       | 1.44       | -0.74      | -0.65    | -1.32    | -17.48         | 14.93          | 22.44          |
| 318.15                                      | 1.13       | 1.16       | 0.48       | 0.65     | 1.34     | -15.72         | 25.28          | -16.47         |
| <i>(V) Bromoform(1)-nitrobenzene(2)</i>     |            |            |            |          |          |                |                |                |
| 298.15                                      | 2.12       | 1.97       | 6.81       | 2.41     | -1.94    | -32.87         | 23.08          | -7.91          |
| 308.15                                      | 1.78       | 1.67       | 1.65       | 0.92     | -1.16    | -27.13         | 15.74          | 6.50           |
| 318.15                                      | 1.56       | 1.45       | 1.34       | 0.99     | -0.46    | -23.14         | 14.15          | -5.05          |
| <i>(VI) Bromoform(1)-tetrahydrofuran(2)</i> |            |            |            |          |          |                |                |                |
| 298.15                                      | 1.61       | 1.35       | 0.50       | 0.59     | 1.24     | 12.29          | 11.67          | -10.51         |
| 308.15                                      | 1.39       | 1.16       | 0.49       | 0.58     | 1.32     | 7.91           | 11.06          | -9.48          |
| 318.15                                      | 1.23       | 1.03       | 0.59       | 0.69     | 1.11     | 4.43           | 10.10          | -8.22          |

one parameter to be evaluated. For mixtures of bromoform with benzene or toluene  $T_{12}$  (Tamura-Kurata parameter) and  $H_{12}$  (Hind *et al.* parameter) decrease with increase in the concentration of bromoform; the reverse is true for the remaining mixtures. With rise in temperature both  $T_{12}$  and  $H_{12}$  decrease. This observation is in agreement with the earlier data<sup>13</sup>. The Grunberg-Nissan parameter ( $G_{12}$ ) increases with increase in bromoform concentration of the mixture. Both positive and negative  $G_{12}$  values are observed for the mixtures of bromoform with acetonitrile and tetrahydrofuran, while for the remaining mixtures  $G_{12}$  values are always negative. The binaries of bromoform with toluene, *p*-xylene and nitrobenzene show identical pattern in  $G_{12}$  values.

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