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Short communication

Excess molar enthalpies of dibromomethane with acetonitrile, furan and acetophenone at 303.15 K

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ABSTRACT

Excess molar enthalpies H^E at 303.15 K using a microcalorimeter have been determined for binary liquid mixtures of dibromomethane (DBM) with acetonitrile, furan and acetophenone over the entire composition range. The excess molar enthalpies values are endothermic for DBM + acetonitrile, and +furan but they are exothermic for the system DBM + acetophenone. The observed values are fitted with the Redlich–Kister equation by means of the least squares method. The excess partial molar enthalpies of the components $H^E_{m,1}$ and $H^E_{m,2}$ have also been evaluated with the help of H^E values. The results indicate the existence of specific interactions between all these components.

1. Introduction

As a part of our continuous efforts to obtain thermodynamic quantities on liquid mixtures of organic compounds [1–5], we report here excess molar enthalpies of dibromomethane (CH_2Br_2) (DBM) with acetonitrile, furan and acetophenone at 303.15 K. Binary systems of CH_2Br_2 with acetonitrile, furan and acetophenone are of considerable interest due to specific interactions between these components in the liquid state. This is caused by the presence of two Br and two H atoms in CH_2Br_2, which can thus act as σ-acceptors towards, and be involved in the hydrogen bond formation with acetonitrile, furan and acetophenone. The latter will act as n-donors. A literature survey revealed that extensive studies on such systems have not been carried out to date. The data obtained for excess molar enthalpies have been interpreted in this paper.

2. Experimental

Dibromomethane (Fluka) has been purified by fractional distillation, only the middle fraction was used for experiments. Acetonitrile (B.D.H.), furan (A.R.) and acetophenone (A.R.) were dried over freshly activated molecular sieves before use. The chemicals have a minimum purity of 99.0 mol% as determined by GLC. The purities of chemicals used, as determined by GLC for the samples of dibromomethane, acetonitrile, furan and acetophenone are found to be 99.8, 99.8, 99.3 and 99.0 mol%, respectively.

2.1. Method

Excess molar enthalpies H^E, were measured in a heat flux microcalorimeter [5] (C-80 model from Setaram, France), whose temperature was controlled to within ±0.001 K. Experimental details are given elsewhere [6]. The solutions were prepared by mass. Mole fractions are accurate to ±0.0001. The reliability of the microcalorimeter was earlier checked by measuring H^E at $T = 298.15$ K for cyclohexane + hexane for which values are accurately known from the literature [7]. The mean deviations of the measured H^E are estimated to be about 1% over most of the mole fraction range.

The purities of the chemicals were also checked by measuring densities using a vibrating tube densimeter (model DMA, Anton-Paar 60/602) [5] operating under static mode. A Haake F3 thermostat and a digital thermometer Anton-Paar DT 100-30 were used to regulate to better than 0.01 K the temperature inside the vibrating tube. Before each measurement the apparatus was calibrated at atmospheric pressure with double distilled and degassed water and 2-pentanone (Fluka, purity 99%). The den-

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Table 1
Excess molar enthalpies of dibromomethane (CH_2Br_2) (1) + acetonitrile (2), +furan (2), and +acetophenone (2) at 303.15 K.

x_1	H^E (J mol^{-1})
Dibromomethane (1) + acetonitrile (2)	
0.1028	89
0.2166	146
0.3067	173
0.4007	179
0.5547	150
0.6564	107
0.7022	89
0.8786	23
Dibromomethane (1) + furan (2)	
0.1499	187
0.2828	232
0.3405	231
0.4247	212
0.6268	166
0.7204	144
0.8358	109
0.9381	55
Dibromomethane (1) + acetophenone (2)	
0.1763	−102
0.3362	−148
0.4052	−162
0.4229	−160
0.5115	−162
0.6248	−151
0.7449	−114
0.8520	−76

sity of 2-pentanone at 298.15 K was in good agreement with the literature value [8]. The densities of purified samples of dibromomethane, acetonitrile, furan and acetophenone were found to be 2.49497, 0.78587, 0.935421 and 1.02766 g/cm^3, which are in good agreement with the literature values [8,9], 2.495, 0.786, 0.936 and 1.028 g/cm^3, respectively.

3. Results and discussions

Excess molar enthalpies, H^E, for various systems are summarized in Table 1. The observed values are fitted with the Redlich–Kister equation by means of the least squares method:

$$H^E\ (\text{J mol}^{-1}) = x_1x_2\sum_{i=0}^{m}A_i(x_1-x_2)^i \tag{1}$$

where x_1 refers to the mole fraction of CH_2Br_2. The least square parameters, along with the standard deviations, σ are reported in Table 2. The standard deviations, σ, are calculated using equation:

$$\sigma = \left[\frac{\sum(H^E - H^E_{\text{calc}})^2}{m-n}\right]^{1/2} \tag{2}$$

Table 2
Least squares coefficients of Eq. (1) for the excess molar enthalpies, and the standard deviations, σ, of dibromomethane (CH_2 Br_2) (1) + acetonitrile (2), +furan (2), and +acetophenone (2) at 303.15 K.

System	A_0	A_1	A_2	σ (J mol^{-1})
Dibromomethane (1) + acetonitrile (2)	650.8	−482.5	−148.8	3.3
Dibromomethane (1) + furan (2)	787.1	−484.7	735	2.7
Dichloromethane (1) + acetophenone (2)	−650.7	71.6	7.7	3.1

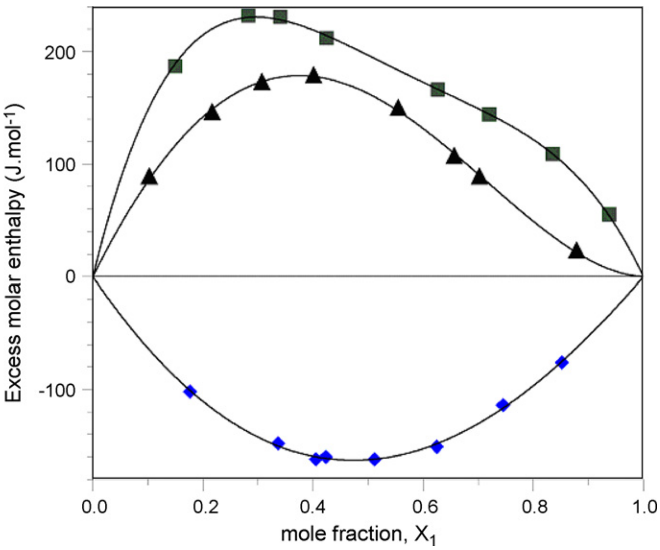

Fig. 1. Excess molar enthalpies of binary liquid mixtures of dibromomethane (1) + acetonitrile (2) (▲), +furan (2) (🟩) and +acetophenone (2) (◆), calculated value with Eq. (1) (—) at 303.15 K.

where H^E is experimental excess enthalpy and H^E_{calc} is calculated excess enthalpy using Eq. (1), m is number of experimental data and n is number of constants characteristic of a system. Graphical presentations of experimental values of data are presented in Fig. 1.

The excess enthalpy results from the disruption of interactions between like molecules and the introduction of new interactions between unlike molecules. The partial excess enthalpies $H^E_{m,1}$, and $H^E_{m,2}$ were calculated from H^E data by using the equation:

$$H^E_{m,1} = \frac{H^E}{x_1} + x_1x_2\left[\frac{\partial(H^E/x_1)}{\partial x_1}\right]_{p,T} \tag{3}$$

$$H^E_{m,2} = \frac{H^E}{x_2} + x_1x_2\left[\frac{\partial(H^E/x_2)}{\partial x_2}\right]_{p,T} \tag{4}$$

The calculation of partial molar enthalpies depends heavily upon the choice of the number of fitting constants in the

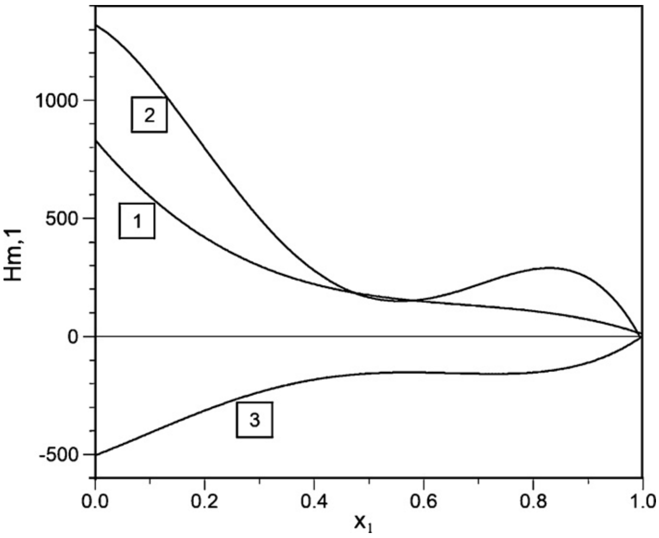

Fig. 2. Partial molar excess enthalpies $H_{m,1}$ of binary liquid mixtures of x_1 dibromomethane + x_2 acetonitrile [1], x_1 dibromomethane + x_2 furan [2] and x_1 dibromomethane + x_2 acetophenone [3].

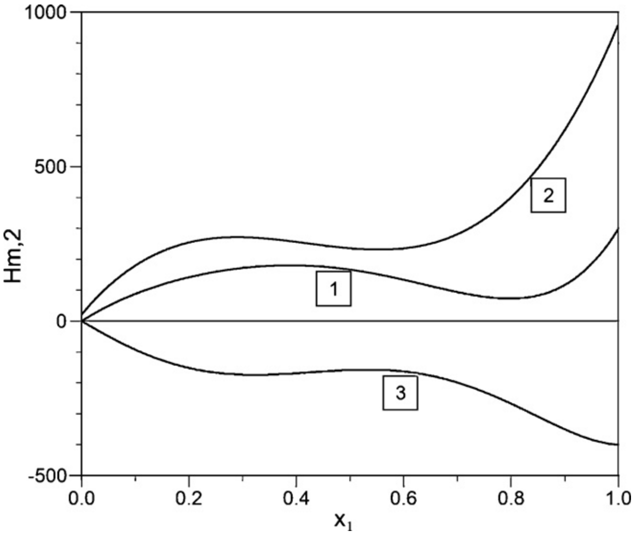

Fig. 3. Partial molar excess enthalpies $H_{m,2}$ of binary liquid mixtures of x_1 dibromomethane + x_2 acetonitrile [1], x_1 dibromomethane + x_2 furan [2], and x_1 dibromomethane + x_2 acetophenone [3].

Redlich–Kister equation [10]. The excess partial molar enthalpies are indicative of the type of effects dominating the overall behaviour of H^E in binary liquid mixtures. The excess partial molar enthalpies calculated from Eqs. (3) and (4) are plotted in Figs. 2 and 3.

The values of H^E are endothermic for CH_2Br_2 + acetonitrile, and +furan but they are exothermic for the system CH_2Br_2 + acetophenone. The magnitude of H^E for the present mixtures is attributed to the net result of positive and negative contribution due to the breaking of bonds or interactions between similar molecules, and from the formation of new bonds such as hydrogen bonds between dissimilar molecules [10].

The enthalpy of mixing of DBM + acetonitrile is positive and small, ≈172 J mol^{-1} at the maximum indicating only slight specific interaction between these components. Acetonitrile is very weak base. Due to this weak basic nature, it is very poor hydrogen bond acceptor. Having high polarity it is capable of dissolving a variety of reactants.

The enthalpy of mixing of DBM + furan is also positive and small, ≈230 J mol^{-1} at the maximum indicating only slight specific interaction between these components. The ethereal oxygen is weak proton acceptor and can interact to form a hydrogen bond with H atom of DBM. However owing to the presence of two double bonds in the furan ring, the oxygen becomes less basic, and therefore the possibility of hydrogen bonding is much reduced, thus shows positive behaviour of H^E.

The values of H^E are exothermic for the system CH_2Br_2 + acetophenone, ≈−160 J mol^{-1} at the minimum thermal effect indicating only slight specific interaction between these components but greater than acetonitrile and furan. This interaction is due to hydrogen bonding between a hydrogen atom of CH_2Br_2 and lone pair electrons on the oxygen atom of acetophenone as is suggested by Tripathi [5] between tetrachloroethane and dimethylsulfoxide.

The above explanation is supported by the values of excess partial enthalpies shown in Figs. 2 and 3. The positive values of $H^E_{m,1}$, and $H^E_{m,2}$ are evidently due to the presence of a positive contribution from the rupture of self-associated dibromomethane and acetonitrile or furan molecules. The negative values of $H^E_{m,1}$ and $H^E_{m,2}$ values are evidently due to the presence of strong hydrogen bonds between H atom of CH_2Br_2 and lone pair electrons on the oxygen atom of acetophenone.

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