Excess Molar Enthalpies of Dibromomethane with Acetonitrile, Furan, Acetophenone and Tetrahydrofuran at *T*=313.15 K

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Abstract: Excess molar enthalpies have been determined for binary liquid mixtures of dibromomethane (CH_2Br_2) (DBM) with acetonitrile, furan, acetophenone and tetrahydrofuran at 313.15 K. The excess molar enthalpies are endothermic for the systems CH_2Br_2 + acetonitrile, and + furan whereas exothermic for the system CH_2Br_2 + acetophenone and + tetrahydrofuran over the whole composition range. The results were fitted with the Redlich- Kister equation by means of the least square method. These results indicate the existence of specific interactions between all these components.

Keywords: Excess molar enthalpy, dibromomethane, tetrahydrofuran.

1. INTRODUCTION

The study of dibromomethane (CH_2Br_2) (DBM) with acetonitrile, furan, acetophenone and tetrahydrofuran is of interest, not only because the compounds are of industrial importance, but also because their interactions are pronounced, making them better solvents and also used in day-to-day life. For example, acetonitrile dissolves a wide range of ionic and nonpolar compounds. Acetophenone is colourless, viscous liquid and is involved in the production of significant resins and fragrances. It is also raw material for the synthesis of some pharmaceuticals.

Furan is colourless, flammable, highly volatile liquid with a boiling point close to room temperature. Due to its aromaticity, furan's behaviour is quite dissimilar to that of the more typical heterocyclic ethers such as tetrahydrofuran. Tetrahydrofuran is a raw material for the manufacture of adipic acid and nylon. It is an industrial solvent for PVC and in varnishes. It is an aprotic solvent and can dissolve a wide range of nonpolar and polar chemical compounds. It can be used to dissolve rubber using gel permeation technology. It dissolves PVC as well and is the main ingredient in PVC adhesives. It liquefies old PVC cement, and is often used industrially to degrease metal parts. Dibromomethane is naturally produced by marine algae and liberated in the oceans and is used as a fumigant for soils, grains and fruits. Also used as a solvent and as an intermediate in the chemical industry.

As a part of our continuing efforts to obtain thermodynamic and physicochemical quantities on organic liquid mixtures [1-5] we report excess enthalpies of dibromomethane (CH_2Br_2) with acetonitrile, furan , acetophenone and tetrahydrofuran at 313.15 K. Binary systems of CH_2Br_2 with all these compounds are of considerable interest due to occurrence of 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, acetophenone and tetrahydrofuran. Latter will act as n-donors. These systems were selected to find out the effect of oxygen atom in aromatic ring (furan), outside the ring (acetophenone), and also to establish the effect of one oxygen (tetrahydrofuran) in the cyclic ether. Dibromomethane has two equivalent proton donors and can thus form different type of complexes with the above-mentioned compounds. A literature survey revealed that extensive studies on such systems have not been carried out to date. The results obtained have also been interpreted in this paper.

2. EXPERIMENTAL

Dibromomethane (Fluka) were further purified by fractional distillation and the constant middle fraction was used for the experiment. Acetonitrile (B.D.H.), furan (A.R.) and acetophenone (A.R.) were dried over freshly activated molecular sieves before use. Tetrahydrofuran (E.Merck) was used without further purification .The chemicals were specified to have a minimum purity of 99.0 mol% as determined by GLC.

2.1. Method

Excess molar enthalpies, H^E, were measured by means of a heat flux micro calorimeter [5] (C-80 model from Setaram, France), whose temperature was

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controlled within ±0.001K. 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 for systems of cyclohexane + hexane at T=298.15 K as given elsewhere [3]. The mean deviations of the H^E are estimated to be about 1% over most of the mole fraction range. The experimental values of this work are estimated to 0.5% at the equimolar composition.

3. RESULTS AND DISCUSSIONS

The experimental excess molar enthalpies, H^E at T=313.15 K for investigated mixtures are summarized in Table **1**. The results were fitted by least squares to the equation:

$$H^E / (\mathrm{J.mol^{-1}}) = x_1\, x_2 \sum_{i=0}^{m} A_i (x_1 - x_2)^i \qquad (1)$$

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

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

where H^E is experimental excess enthalpy and H^E_{calc} calculated excess enthalpy using equation (1), m is number of experimental data & n is number of constants characteristic of a system. Graphical presentation of experimental values of data is presented in Figure **1**.

The excess enthalpy results from the disruption of interactions between like molecules and the introduction of new interactions between unlike molecules [6].

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

The excess enthalpy of DBM + acetonitrile is positive and small, ≈ 167 $\mathrm{J.mol^{-1}}$ at the maximum indicating only slight specific interaction between these components. It means acetonitrile interaction compensates to a great extent the negative effect due to structural contribution, resulting in the overall positive behaviour of H^E.

Table 1: Excess Enthalpies of Dibromomethane (CH_2Br_2) (1) +acetonitrile (2), +furan (2), and +acetophenone (2) and+ tetrahydrofuran at 313.15 K

X_1	$H^E/\mathrm{J.mol^{-1}}$
Dibromomethane (1) + acetonitrile (2)	
0.1129	80
0.2567	160
0.3447	178
0.4558	175
0.5886	144
0.6887	106
0.7445	90
0.9667	22
Dibromomethane (1) +furan (2)	
0.1001	150
0.1388	180
0.2525	233
0.3557	234
0.4347	215
0.5578	201
0.6779	160
0.7575	142
0.8586	114
0.9453	60
Dibromomethane (1) +acetophenone(2)	
0.1884	-110
0.2443	-135
0.3456	-154
0.4993	-165
0.5885	-156
0.6583	-140
0.7567	-116
0.9067 -65	
Dibromomethane (1) + tetrahydrofuran (2)	
0.0987	-470
0.1489	-651
0.2234	-843
0.3211	-1008
0.4567	-1089
0.5576	-1048
0.6719	-919
0.7718	-712
0.8845	-396
0.9513	-176

System type (Pure, Binary, Ternary): Binary
Chemical System(s): Dibromomethane (CH_2 Br_2) (1) + acetonitrile (2), +furan (2), +acetophenone (2) and + tetrahydrofuran (2).
Property: excess molar enthalpy
Experimental Method (10 words or less): micro calorimeter
Combined Expanded Uncertainty (*k* = 2) for the Property: 2σ (H^E) = 1%
State Variables and Constraints: temperature T, mole fraction of dibromomethane x_1, Pressure p = laboratory pressure Standard Uncertainty (*k* = 1) for each Variable and Constraint:
σ(T)=0.001K ; σ(p)=5%; σ(x_1)=0.0001.

Table 2: **Least Squares Coefficients of Eq 1 for the Excess Molar Enthalpies, and the standard deviations, σ,of Dibromomethane (CH_2Br_2) (1) + acetonitrile (2), +furan (2), +acetophenone (2) and+ tetrahydrofuran(2) at 313.15 K**

System	A0	A1	A2	A3	σ/ (J mol^{-1})
Dibromomethane (1) + acetonitrile (2)	663.3	-484.2	-22.4	499.8	2.8
Dibromomethane (1) + furan (2)	820.9	-435.8	769.8		6.2
Dibromomethane (1) +acetophenone (2)	-653	137.9	-106.8	-246.9	3.3
Dibromomethane (1) + tetrahydrofuran (2)	-4330	605.08	-402.8	460.9	3.1

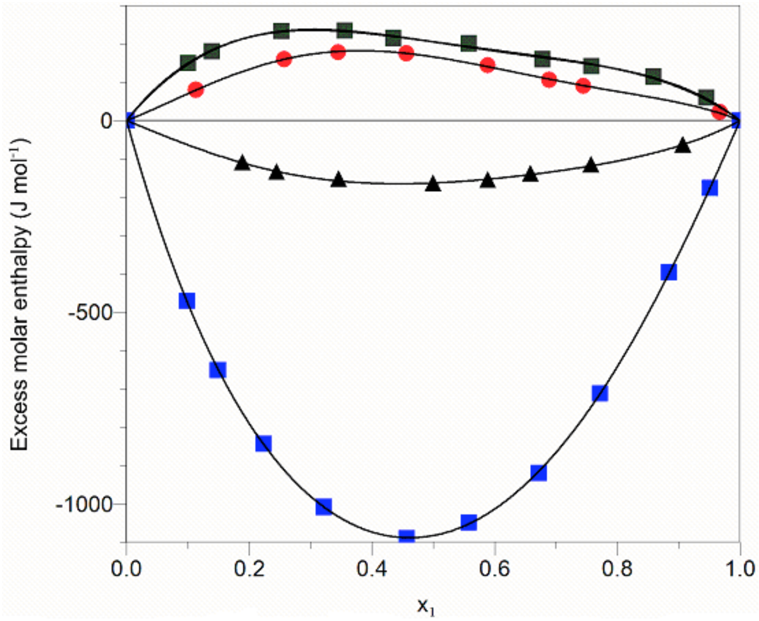

Figure 1: Excess molar enthalpies of binary liquid mixtures of x_1 dibromomethane + x_2 acetonitrile (●), + x_2 furan (🟩), + x_2 acetophenone (▲) and + tetrahydrofuran (◆) at 313.15K.

The enthalpy of mixing of DBM + furan is also positive and small, ≈ 205 J.mol^{-1} at the maximum indicating only slight specific interaction between these components. The etheral oxygen is a 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 resulting in the positive behavior of H^E.

The values of H^E are exothermic for the system CH_2Br_2 + acetophenone, ≈ -163 J.mol^{-1} at the minimum indicating only weak interaction between these components but greater than acetonitrile and furan. This can be explained as due to the formation of weak hydrogen bond between the hydrogen atom of DBM and the π-electrons of the aromatic ring or through O---H interactions. There is, however, also possibility that DBM may form a charge transfer complex with acetophenone, *via* Br atom-π-electron interaction. The high negative values of H^E for the system CH_2Br_2+ tetrahydrofuran (approx.-1082 J.mol^{-1} at the minimum) indicate the presence of strong specific interaction leading to the formation of complexes. This interaction is due to hydrogen bonding between a hydrogen atom of CH_2Br_2 and lone pair electrons on the oxygen atom of tetrahydrofuran as is suggested by Nath and Tripathi [1, 7] between tetrachloroethane and acetone.

4. CONCLUSION

In conclusion, it is pointed out that the present investigation reveals the existence of electron donor acceptor interactions leading to the formation of complexes through hydrogen bonding between the components in the liquid state. Dibromomethane has two equivalent proton donors and can thus form different type of complexes with above- mentioned compounds. The magnitude of H^E for the present mixtures are 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. The values of H^E for the system CH_2Br_2 + acetonitrile, and + furan are positive whereas negative for the system CH_2Br_2 + acetophenone and + tetrahydrofuran. In these systems not only the N----H or O---H or O--Br interactions but interactions between CH_2 groups and Br atoms contribute to excess enthalpy. The high negative values of H^E for the system CH_2Br_2 + tetrahydrofuran indicate the presence of strong specific interaction due to hydrogen bonding between H atom of CH_2Br_2 and lone pair electrons on the oxygen atom of tetrahydrofuran. There is much difference in the values of H^E for the system CH_2Br_2 + tetrahydrofuran and CH_2Br_2 + furan though both has one oxygen atom, this is attributed to the fact that tetrahydrofuran has saturated ring whereas furan unsaturated ring. Saturation of ring in compound makes it more reactive.

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