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Excess Molar Enthalpies of Dibromomethane + Cyclohexanone and Dichloromethane + Cyclohexanone or + Pyrrolidin-2-one at *T* =303.15 K

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Abstract: Excess molar enthalpies H^E were measured using a microcalorimeter for binary liquid mixtures of dibromomethane (CH_2Br_2) + cyclohexanone, and dichloromethane (CH_2Cl_2) + cyclohexanone or + pyrrolidin-2-one at $T=$ 303.15 K. The values of H^E are negative for all systems. The excess partial molar enthalpies of the components $H^E_{m,1}$ and $H^E_{m,2}$ were calculated from H^E data. The results were interpreted in terms of specific interactions.

Keywords: Excess molar enthalpies, partial molar enthalpies, dibromomethane, dichloromethane, pyrrolidin-2one.

1. INTRODUCTION

Earlier we have reported dielectric properties and excess enthalpies on binary liquid mixtures of organic compounds [1-5], in the present programme excess molar enthalpies of dibromomethane (DBM) + cyclohexanone, and dichloromethane (DCM) + cyclohexanone, and + pyrrolidin-2-one were measured at 303.15 K. In order to understand the specific interactions between these components in the liquid state, these binary systems have been studied. The cyclic amides are those compounds in which a peptide bond containing N and C are linked by methylene groups forming a ring. An interesting compound is γ-butyrolactam (n=5), pyrrolidin-2-one, it is a highly polar solvent. The unique feature of these compounds have generated more attention because structural part of proteins, peptides, and polypeptides are the amide group.

The interaction of dibromomethane is mainly due to the involvement of two Br and two H atoms, and two Cl and two H atoms in CH_2Cl_2, both DBM and DCM can thus act as σ-acceptors (containing σ-bonds) towards, and must be participated in the hydrogen bond formation with cyclohexanone **(**$C_6H_{10}O$) or pyrrolidin-2-one(C_4H_7NO). Cyclohexanone and pyrrolidin-2-one(C_4H_7NO) will act as nonbonding donors. Hydrogen bonded complex formation of DBM and DCM with compounds containing >CO group have been reported in the literature [6-7]. Extensive studies concerning these systems have not been made in the literature. The effects of the above interactions on H^E have been briefly discussed in this paper.

2. EXPERIMENTAL

Dibromomethane (Fluka), dichloromethane (BDH, AR) and cyclohexanone (AR) were used after fractional distillation and only constant middle fraction was used for this experiment. Pyrrolidin-2-one was purified as earlier [8]. A minimum purity of 99.7 mol% were specified on the chemicals. Freshly activated molecular sieves were used for drying of all chemicals before use.

By means of GLC the purities of chemicals used were determined, and are reported in Table **1**. The chemicals purity were also obtained by measuring densities by using a vibrating tube densimeter (model DMA, Anton-Paar 60/602) [5]. The experimental and literature values of density are compared [9-10] in Table **1**.

Table 1. Densities of Pure Components at *T*= 303.15K

Component	Purity	densityg.cm^{-3}	
	(mol%)	exptl	lit
Dibromomethane	99.8	2.46991	2. 470[a]
Dichloromethane	99.8	1.30684	1.307[a]
Cyclohexanone	99.0	0.93754	0.93761[b]
Pyrrolidin-2-one	99.0	1.1009	1.1020 [b]

[a]values taken from ref. [9], [b]values taken from ref. [10].

2.1. Method

H^E measurements were made in a microcalorimeter (C-80 model from Setaram, France) [5], whose temperature was maintained within ±0.001K. Mole fractions are accurate to ±0.0001. The working of microcalorimeter was tested by measuring excess molar enthalpies at 298.15K for cyclohexane + hexane and compared with the literature values [11]. The mean

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deviations of the measured H^E are estimated to be about 1% over most of the mole fraction range.

3. RESULTS AND DISCUSSIONS

Excess molar enthalpies H^E for various systems are reported in Table **2**. Results obtained were fitted with the Redlich-Kister equation by means of the least squares method:

Table 2: Excess Molar Enthalpies of Dibromomethane (CH_2Br_2) (1) +Cyclohexanone (2), and Dichloromethane(1)+ Cyclohexanone (2), or + Pyrrolidin-2-One (2) at 303.15 K

X_1	H^E/J.mol^{-1}
Dibromomethane (1) + Cycohexanone (2)	
0.0616	-240
0.1958	-630
0.3275	-861
0.4749	-966
0.5562	-960
0.6690	-865
0.7430	-746
0.8471	-509
0.9581	-160
Dichloromethane (1) +cyclohexanone (2)	
0.1232	-476
0.1232	-476
0.2016	-747
0.2853	-987
0.3410	-1114
0.4280	-1256
0.5349	-1320
0.6672	-1209
0.7512	-1022
0.8870	-542
0.9021	-480
Dichloromethane (1) +Pyrrolidin-2-one (2)	
0.0945	-367
0.2423	-847
0.3871	-1145
0.4551	-1214
0.5686	-1211
0.6540	-1114
0.7561	-906
0.8956	-437

Experimental Data Summary

System type (Pure, Binary, Ternary): Binary

Chemical System(s): Dibromomethane(CH_2 Br_2) (1) + cyclohexanone(2),+pyrrolidin-2-one(2),dichloromethane(1),+ cyclohexanone(2),+pyrrolidin-2-one(2).

Property: excess molar enthalpy.

Experimental Method (10 words or less): microcalorimeter.

Combined Expanded Uncertainty (k = 2) for the Property: 2 σ (H^E)=0.002j.mol^{-1}.

State Variables and Constraints: temperature T,mole fraction of dibromomethane x_1 or dichloromethane 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.

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

where x_1 denotes the mole fraction of CH_2Br_2 or CH_2Cl_2. The least square parameters A_0,A_1 A_2, A_3, and the standard deviation of the fit, σ, are reported in Table **3**. Following equation is used to calculate the standard deviation of the fit, σ

$$\sigma = [\Sigma(H^E - H^E_{calc})^2/(m-n)]^{½} \qquad (2)$$

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**.

H^E data were used to calculate the partial excess enthalpies $H^E_{m,1}$,and $H^E_{m,2}$ by using the equations 3 and 4 and are also plotted in Figures **2** and **3**.

$$H^E_{m,1} = H^E/x_1 + x_1 x_2[\partial(H^E/x_1)/\partial x_1]_{p,T} \qquad (3)$$

$$H^E_{m,2} = H^E/x_2 + x_1 x_2[\partial(H^E/x_2)/\partial x_2]_{p,T} \qquad (4)$$

In order to understand the type of effects dominating the overall behavior of H^E the partial excess enthalpies are calculated. The choice of the number of fitting constants in Eq 2 are mainly responsible for the calculation of partial molar enthalpies.

Figure **1** shows that the negative values of the excess molar enthalpies H^E for all binary liquid

Table 3: Least Squares Coefficients of Eq 1 for the Excess Molar Enthalpies, and the Standard Deviations, σ, of Dibromomethane + Cyclohexanone, and +pyrrolidin-2-one, and Dichloromethane+ Cyclohexanone, and + Pyrrolidin-2-one at 303.15 K

System	A_0	A_1	A_2	A_3	σ /(J. mol^{-1})
Dibromomethane (1) + cyclohexanone (2)	-3879	-5.867	-222.5	169.1	0.002
Dichloromethane (1) + cyclohexanone (2)	-5255	-706.9	586.4		0.003
Dichloromethane (1) + pyrrolidin-2-one (2)	-4919	-256.9	647.6		0.004

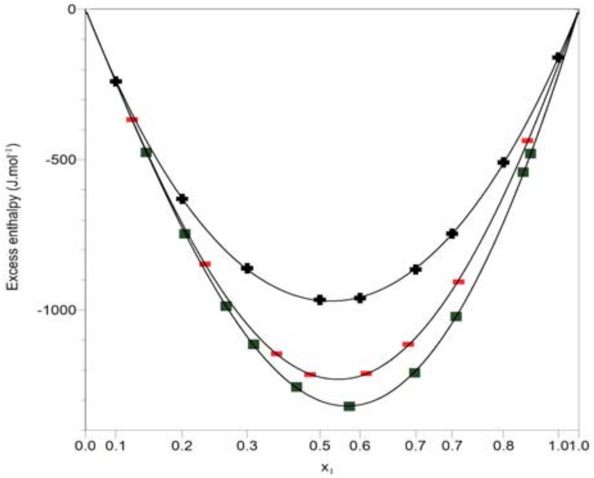

Figure 1: Excess molar enthalpies of binary liquid mixtures of x_1 dibromomethane + x_2 cyclohexanone (✚), and x_1 dichloromethane + $x_2$cyclohexanone (🟥),+ x_2 pyrrolidinone-2-one (🟩), (___) calculated from Eq.1 at 303.15K.

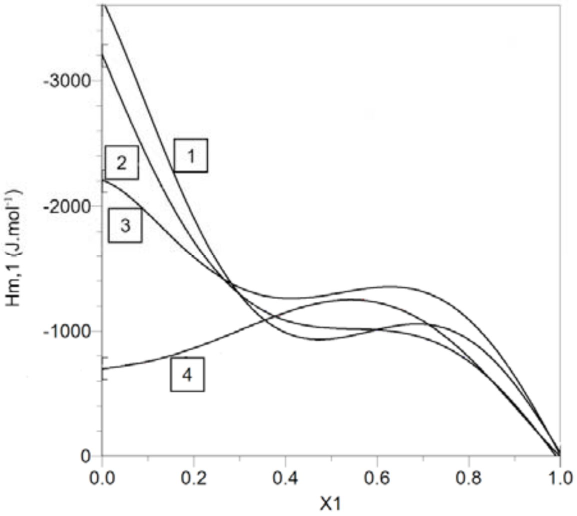

Figure 2: Partial molar Excess enthalpies $H_{m,1}$ of binary liquid mixtures of x_1 dibromomethane + x_2 cyclohexanone (1), + x_2 pyrrolidinone-2-one (2) and x_1 dichloromethane + x_2 cyclohexanone (3),+ x_2 pyrrolidinone-2-one (4) at 303.15K (data for x_1 dibromomethane + x_2 pyrrolidinone-2-one is taken from ref. [4].

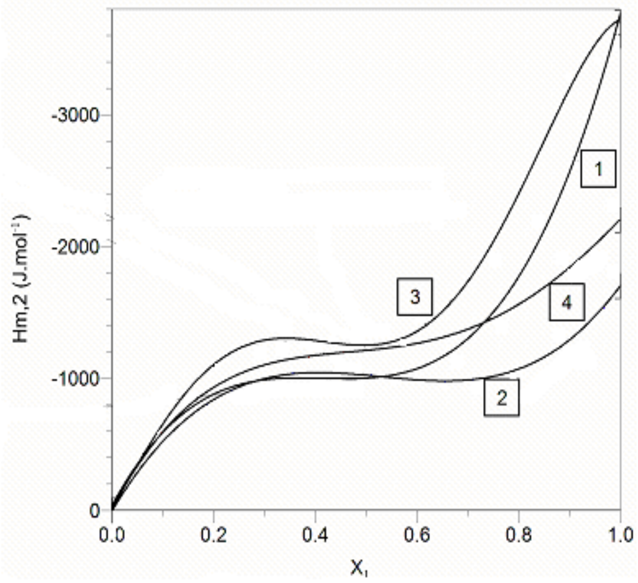

Figure 3: Partial molar Excess enthalpies $H_{m,2}$ of binary liquid mixtures of x_1 dibromomethane + $x_2$cyclohexanone(1), + $x_2$pyrrolidinone-2-one(2) and x_1 dichloromethane + $x_2$cyclohexanone(3),+ $x_2$pyrrolidinone-2-one(4) at 303.15K. (data for x_1 dibromomethane + x_2 pyrrolidinone-2-one is taken from ref. [4].

mixtures and the enthalpies of mixing is greatly effected by the electronic environment of Oxygen atom. As our data shows that the enthalpies of mixing obtained for the system DBM + cyclohexanone or + pyrrolidin-2-one[4] is ≈ -972 J.mol^{-1} and ≈-1030 J.mol $^{-1}$, respectively at the minimum thermal effect. This is an indication of specific interaction between these components. The values of enthalpies of mixing for the system of DCM+cyclohexanone is ≈ -1315 J.mol^{-1} whereas it is ≈-1232 J.mol^{-1} at the minimum thermal effect for DCM +pyrrolidin-2-one.

The excess enthalpy results from the disruption of interactions between like molecules and the introduction of new interactions between unlike molecules. The magnitude of excess enthalpy of mixing for the present mixtures is attributed to the net result of positive and negative contributions due to breaking of bonds or interactions between similar molecules, and from the formation of new bonds such as hydrogen bonds between dissimilar molecules. The negative values of H^E indicate that the interactions between like molecules are weaker in comparision to unlike molecules in the pure liquids. The high exothermicity of all these systems indicate strong specific interactions involving the heteromolecules. The interaction between cyclic ketones and bromo- or chloro- compounds are governed essentially by the saturation of the ring. Pyrrolidin-2-one or cyclohexanone has saturated ring, thus making the interaction stronger. Hydrogenbonded complex formation of chloroform with tetrahydrofuran has been reported in the literature [12]. In these three systems the hydrogen bonding between the hydrogen of DBM or DCM and the keto oxygen can be expected. DBM or DCM (A) contains two equivalent proton donors and can thus form AB or A_2 types of complexes with $C_6H_{10}O$ or pyrrolidin-2-one(B). It is known that the small electronegativity difference between O and Cl or Br is responsible for specific interactions, there is also possibility of interactions of hydrogen of $C_6H_{10}O$ or pyrrolidin-2-one and chlorine or bromine atoms of DCM or DBM. Carboxamides molecules are polar and the oxygen atom is a relatively good electron donor as it has two lone pair of electrons thus good proton acceptor. Pyrrolidin-2-one has a comparatively high dipole moment $11.844.10^{-30}$ C.m at T=298.15K and is self associated in the pure liquid state [8]. The oxygen atom of cyclohexanone is far more negative due to higher electronegativity, than carbon atom. As a result, the O atom tends to attract the electron cloud of the π electron cloud of >C=O, thus >C=O group is unsymmetrical and polar in nature. The magnitude of H^E for CH_2Cl_2+cyclohexanone and+ pyrrolidin-2-one is higher than the value of CH_2Br_2+ cyclohexanone and + pyrrolidin-2-one. It is due to the fact that –I effect (negative inductive effect) of Cl atom is greater than the Br atom. This may be explained as follows:

Whenever an electron-withdrawing atom such as Cl or Br is attached to the end of a carbon chain, the electrons of the C-Cl or C-Br bond are attracted by or displaced towards the more electronegative halogen atom. As a result, the halogen atom acquires a small negative charge and C acquires a small positive charge. Thus carbon-1 having partial positive charge(δ_+) attracts electron density towards it from the adjacent C-C bond. As a result, some positive charge ($\delta\delta_+$) originates on carbon-2 also, In other words, a polarity is induced in the adjacent bonds by means of C-Cl bond. This is called as the inductive effect or the I-effect. In case the substituent is electron with drawing (such as Cl or Br or I) in nature, the effect is called –I-effect. Inductive effect spreads on to the adjacent bonds but decreases as the number of bonds increase. It is negligible after passing three bonds.

Figures **2** and **3** show the values of excess partial enthalpies which supports the above-mentioned predictions.

The values of H^E for the system CH_2Br_2 + pyrrolidin-2-one at T=303.15 K is taken from the literature [4] and excess partial enthalpies are calculated and plotted for this system in Figure **2** and 3. The excess partial molar enthalpy is known to provide the information about the difference between the enthalpy of molecule in solution and the enthalpy in the pure liquid state. 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_2Cl_2 or CH_2Br_2 and lone pair electrons on the oxygen atom of cyclohexanone or pyrrolidin-2-one as suggested by Nath and Tripathi between tetra-chloroethane and acetone [1]. There is also possibility of formation of complex between Cl or Br atom of CH_2Cl_2 or CH_2Br_2 and lone pairs electrons on Oxygen atom of cyclohexanone or pyrrolidin-2-one. In conclusion, it is pointed out that the present investigation reveals the existence of electron donor acceptor interaction of dibromomethane or dichloromethane with cyclohexanone or pyrrolidin-2-one, leading to the formation of complexes in binary liquid mixtures.

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