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EXCESS MOLAR ENTHALPIES OF DICHLOROMETHANE +ACETONE OR + DIMETHYL SULFOXIDE OR + TETRAHYDROFURAN OR + 1, 4-DIOXANE AT THE TEMPERATURE 313.15 K

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Abstract
Excess molar enthalpies H^E at T**=** 313.15 K have been determined for dichloromethane (CH_2Cl_2) + acetone $(CH_3)_2CO$ or + dimethyl sulfoxide $(CH_3)_2SO)$ (DMSO) or + tetrahydrofuran (C_4H_8O) or + 1, 4-dioxane ($C_4H_8O_2$). The excess molar enthalpies for all systems are exothermic in nature. The excess partial molar enthalpies of the components $H^E_{m,1}$,and $H^E_{m,2}$ were calculated from H^E data. These results indicate the existence of specific interactions between all these components.

Keywords: Dichloromethane, Acetone, Heat flux calorimeter, Specific interaction, Excess Partial Molar Enthalpies

INTRODUCTION

The study of cyclic ethers such as tetrahydrofuran (THF) and dioxane is of interest, not only because the compounds are of industrial importance, but also because their interactions are more outstanding, actually making them better solvents.

Dichloromethane (methylene chloride) is an organic compound with the formula CH_2Cl_2. This colorless, volatile liquid with a more or less sweet aroma is broadly used as a solvent, even though it is not miscible with water, it is miscible with many organic solvents. 1, 4-Dioxane, often simply called dioxane because the 1, 2 and 1,3 isomers of dioxane are rare, is a heterocyclic organic compound. It is a colorless liquid with a faint sweet odor similar to that of diethyl ether. It is classified as ether.

Tetrahydrofuran (THF) is an organic compound having the formula $(CH_2)_4O$. The compound is classified as heterocyclic compound, specifically cyclic ether. It is a colorless, water-miscible organic liquid with low viscosity. THF has an odor similar to acetone. It is mainly used as a precursor to polymers. Being polar and having a wide liquid range, THF or acetone is a versatile solvent. Dimethyl sulfoxide (DMSO) is an organosulfur compound with the formula $(CH_3)_2SO$. This colorless liquid is an important polar aprotic solvent that dissolves both polar and nonpolar compounds and is miscible in a broad range of organic solvents as well as water. It has a relatively high melting point. DMSO has the remarkable property that a lot of individuals recognize a garlic-like taste in the mouth after contact with the skin.

Binary systems of dichloromethane with acetone, dimethylsulfoxide, tetrahydrofuran and 1, 4-dioxane are of particular interest from the viewpoint of the existence of an electron donor-acceptor interaction leading to the formation of intermolecular complexes between the components in the liquid state. The interaction of $(CH_3)_2CO$, $(CH_3)_2SO)$ (DMSO), (C_4H_8O), and $(C_4H_8O_2)$ can be thought of as being due to the presence of lone-pair electrons on the oxygen atom of these compounds, on account of which it can act as an n-donors toward CH_2Cl_2, which can be involved in the formation of hydrogen bonds with and act as a σ-acceptor toward all above-mentioned compounds. We have reported data on excess volumes, ultrasonic velocities, dielectric constants and excess enthalpies of Chloroalkanes with n-donor compounds in our earlier communications [Nath et. al., 1983, 1984, Chadha et.al, 1995, Tripathi, 1995, 2010). Excess enthalpy data should also reflect the strength of intermolecular forces. A literature survey revealed that extensive studies on such systems have not been carried out. Hence, in the present programme, excess enthalpy measurements have been made for binary liquid mixtures of dichloromethane with acetone, dimethylsulfoxide, tetrahydrofuran and 1,4-dioxane at $T=313.15K$. The results obtained have been reported and interpreted here.

EXPERIMENTAL

Dichloromethane (BDH, AR) shaken with portions of conc. H_2SO_4 until the acid layer remained colourless, then washed with water, aqueous 5% Na_2CO_3, then water again. Pre-dried with $CaCl_2$, and distilled from P_2O_5. Stored away from bright light in a brown bottle with Linde type $4A^0$ molecular sieves. 1, 4-dioxane of UV spectral grade quality were obtained from Sisco research Laboratory, Pvt.Ltd. Bombay, stored over Sodium wire and used. For purifying Tetrahydrofuran, added Sodium wire and benzophenone to a volume of Tetrahydrofuran (pre-dried over calcium hydride or $4A^0$ molecular sieves), heated at reflux/under nitrogen for several hours until the solvent turns deep blue in colour. This indicates the solvent is dry, and it is distilled off the volume desired. Electronic-grade acetone was stored over anhydrous calcium chloride overnight and then fractionally distilled from phosphorus pentoxide. All the chemicals were further purified by fractional distillation and the constant middle fraction was used for the experiment. The chemicals were specified to have a minimum purity of 99.7 mol%. All the compounds were dried over freshly activated molecular sieves $4A^0$ before use.

The purities of chemicals used, as determined by GLC, are more than 99%. The purities of the chemicals were also checked by measuring densities using a vibrating tube densimeter (model DMA, Anton-Paar 60/602)(Patil, Tripathi et al,1990) and have been found as 0.77923,1.3228,0.871,1.02232 and 1.0992 $g.cm^{-3}$ respectively for $(CH_3)_2.CO$, CH_2Cl_2 , C_4H_8O, 1-4-$C_4H_8O_2$ and $(CH_3)_2SO$ at $T=313.15K$ as compared with the corresponding literature values (Riddick et.al., 1970,Lange,1961) 0.77933,1.3234,0.874,1.02230, 1.0998 $g.cm^{-3}$ for the various liquids in the same order.

Method

Excess molar enthalpies, H^E, were measured in a heat flux calorimeter (C-80 model from Setaram, France) (Tripathi, 2010), whose temperature was controlled to within ±0.001K. Experiments have been done by batch method on C-80 micro calorimeter. The calorimeter consists of a reference and experimental vessel. These are surrounded by two symmetrical thermal flux meters composed of thermocouples in series. The whole assembly is kept in an aluminium block and allowed to reach thermal equilibrium. If there is any heat liberated or absorbed in experimental vessel it leads to change in temperature which is allowed and this persists till same temperature is attained in both the vessels by equilibrium. The experimental cell has two chambers separated by a tilting lid. The samples are separately introduced into the vessel. The mixing is performed by inverting the whole calorimeter by 180^0C. The amount of heat, q evolved during an experiment can be calculated by determining the area under the curve obtained during the experiment.

The solutions were prepared by mass. Mole fractions are accurate to ±0.0001. The reliability of the microcalorimeter was checked by measuring H^E at 298.15K for cyclohexane + hexane for which values are accurately known from the literature (Tripathi, 1983). The mean deviations of the measured H^E are estimated to be about 1% over most of the mole fraction range. Excess molar enthalpies, H^E, are estimated to 0.5% at the equimolar composition.

RESULTS AND DISCUSSIONS

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

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

Where, x_1 refers to the mole fraction of CH_2Cl_2. The least square parameters Ai, along with the standard deviation of the fit, σ, are reported in Table 2. The standard deviation of the fit, σ, are calculated using equation

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

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 Figure1.

It is seen from Table 1 that the $(CH_3)_2SO$-CH_2Cl_2 complex is stronger (value of excess enthalpy = -1203 $J.mol^{-1}$ at the minimum) than the acetone- CH_2Cl_2 complex (H^E=-439.5kJ mol^{-1} at the minimum). Structurally, DMSO and acetone are identical but the sulphur atom in the case of DMSO has vacant 3d orbitals which enhance the electron delocalisation on the adjacent carbon atom. Thus the hydrogen atoms on the methyl groups of DMSO are therefore expected to be more acidic than those of acetone. The specific interactions between DMSO and CH_2Cl_2 are expected to be stronger than those between CH_2Cl_2 and acetone which contribute to the stronger complex formation and greater negative value of excess enthalpy of the $(CH_3)_2SO$ - CH_2Cl_2 system.

The enthalpies of mixing of tetrahydrofuran and 1, 4-dioxane is also highly negative. The highly exothermic value of H^E of these systems indicates strong specific interactions involving the heteromolecules. In these systems, two types of interactions are expected. First, the hydrogen bonding between the hydrogen of CH_2Cl_2 and the etherial oxygen. Hydrogen bonded complex formation of chloroform with tetrahydrofuran and dioxane has been reported (Tripathi,2010). In the present systems the interactions are more complicated than those with chloroform, as CH_2Cl_2 (A) has two equivalent proton donors and can thus form AB and A_2 types of complexes with THF (B). In the case of dioxane, it can form AB, A_2B and AB_2 types of complexes.

It may be noted that minimum excess enthalpy (highly negative) for these systems show the trend: THF > 1, 4-dioxane. In the case of binary hydrogen bond forming systems the number of H-bonds formed, the enthalpy of H-bond formation and other specific interactions are the chief contributors to the enthalpy of mixing. As far as hydrogen bond formation is concerned, dioxane can form more numerous H-bonded species than THF owing to the presence of two oxygens. So from the viewpoint of H-bond formation the 1, 4-dioxane system should be more exothermic than the THF system, but the reverse is observed. Wilhelm et al. (1982) studied the heats of mixing of carboxylic acids with THF and 1, 4-dioxane and found the same trend of interaction. This indicates that the interactions other than H-bonding contribute significantly to the enthalpies of mixing of these systems. In these systems not only the O... H and O--C1 interactions (Beath e.al, 1969) but interactions between CH_2 groups and chlorine atoms contribute to the enthalpies of mixing. However, in the case of a cyclic ether or ketone, the interactions of hydrogen and chlorine atoms are so dominant that the presence of a functional group or the position of oxygen does not make any significant difference to the enthalpy of mixing.

The partial excess enthalpies $H^E_{m,1}$,and $H^E_{m,2}$ were calculated from H^E data by using the equation 3 and 4(Mehta et.al.,1997) and are plotted in Figures 2 and 3.

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

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

The values of excess molar enthalpies H^E for all systems are exothermic in nature and through electronic environment around the oxygen atom showed a marked effect on the enthalpy of mixing. The excess enthalpy results from the disruption of interactions between like molecules and the introduction of new interactions between unlike molecules. The negative values of H^E for binary solutions suggest that the interactions between unlike molecules are stronger than like-like interactions in the pure liquids.

Table 1: Excess Molar Enthalpies of dichloromethane (CH_2Cl_2) (1) + acetone (2), or + DMSO (2), or + tetrahydrofuran (2), or + 1,4-dioxane (2) at 313.15 K

X_1	H^E (J.mol^{-1})
CH_2Cl_2 (1) + Acetone (2)	
0.101	-190
0.1987	-321
0.2886	-401
0.3543	-423
0.4565	-447
0.5012	-443
0.6023	-398
0.7686	-275
0.9143	-112
CH_2Cl_2 (1) +DMSO (2)	
0.109	-311
0.2774	-866
0.3455	-1032
0.4222	-1153
0.5015	-1203
0.6543	-1101
0.7312	-956
0.8112	-760
0.9023	-453
CH_2Cl_2 (1) + tetrahydrofuran (2)	
0.1015	-504
0.2023	-908
0.3113	-1198
0.4321	-1348
0.5221	-1356
0.6078	-1266
0.7115	-1054
0.8223	-735
0.9167	-378
CH_2Cl_2 (1) + 1, 4-dioxane (2)	
0.2123	-467
0.3228	-675
0.4432	-761
0.5222	-731
0.6013	-645
0.7112	-467
0.8912	-162

Table 2: Least Squares Coefficients of Eq 1 for the Excess Molar Enthalpies, and the standard deviations ,σ,of CH_2Cl_2 + acetone, + DMSO,+ tetrahydrofuran ,and + 1,4-dioxane at 313.15 K.

System	σ/ (J mol^{-1})	A_0	A_1	A_2	A_3
CH_2Cl_2 (1) + acetone (2)	3.9	-1758	410.8	-19.61	1.546
CH_2Cl_2 (1) + DMSO (2)	1.8	-4812	-338.7	1076	-1439
CH_2Cl_2 (1) + tetrahydrofuran (2)	3.8	-5438	585.7	307.7	-336.3
CH_2Cl_2 (1) +1,4-dioxane (2)	3.0	-2983	1169	1832	-1515

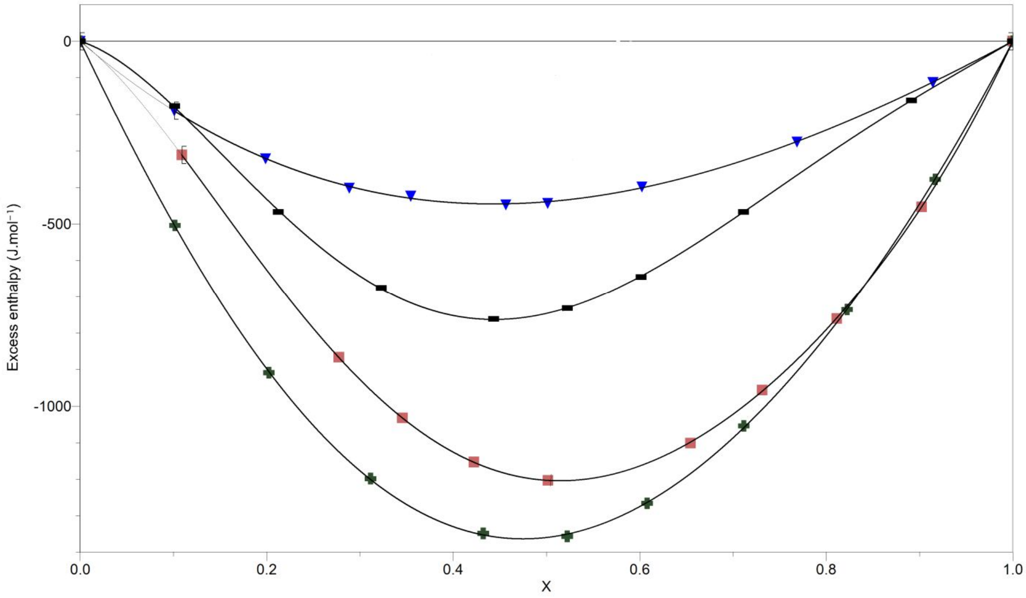

Figure 1: Excess molar enthalpies of binary liquid mixtures of x_1 of Dichloromethane (CH_2Cl_2 (1) + acetone (▼) (2), + dimethylsulfoxide (🟥)(2) ,+tetrahydrofuran(✚) , (2) and + 1, 4-dioxane (▬) (2) at 313.15 K.

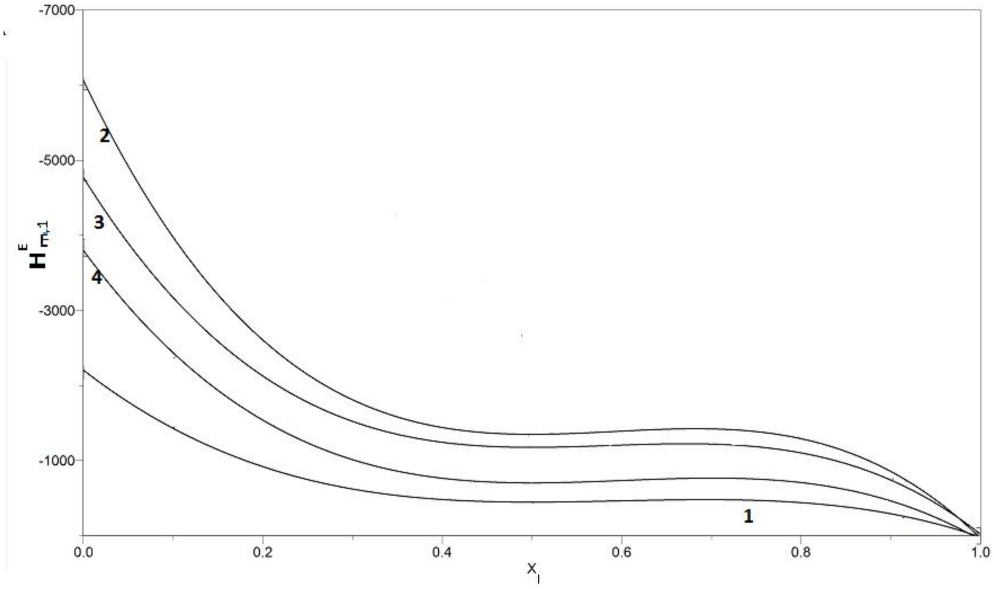

Figure 2: Partial molar Excess enthalpies $Hm,_1$ of binary liquid mixtures of x_1 Dichloromethane (CH_2Cl_2) + x_2 acetone (1), + x_2 DMSO (2) , x_2 tetrahydrofuran (3),+ x_2 1,4-dioxane (4) at 313.15K.

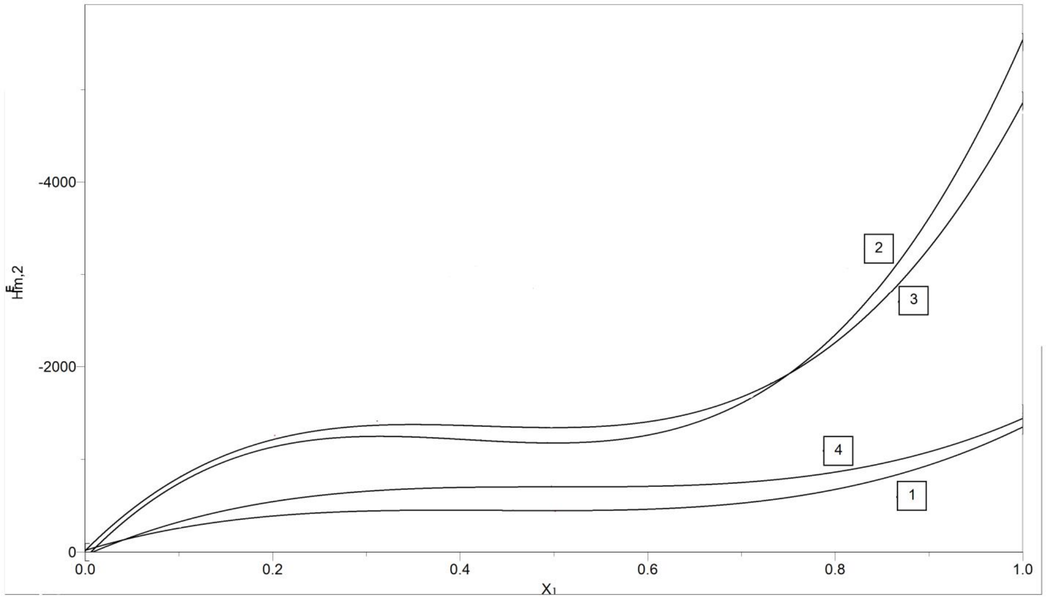

Figure 3: Partial molar Excess enthalpies $Hm,_2$ of binary liquid mixtures of x_1 d Dichloromethane (CH_2Cl_2) + x_2 acetone (1), + x_2DMSO (2) , x_2 tetrahydrofuran (3),+ x_2 1,4-dioxane (4) at 313.15K.

The above justification is supported by the values of excess partial enthalpies shown in Figure 2 and 3. The excess partial molar enthalpy represents 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 obviously due to the occurrence of strong hydrogen bonds between H atom of CH_2Cl_2 & lone pair electrons on the oxygen atom of acetone, dimethylsulfoxide, tetrahydrofuran and 1,4-dioxane as suggested by Tripathi between dibromomethane and acetone (Tripathi,2010).

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