Excess molar enthalpies of dichloromethane +acetonitrile or + furan or +2-methylfuran or + acetophenone at the temperature 303.15 K

Abstract

Excess enthalpies, H^E, at the temperature 303.15 K have been determined for dichloromethane (CH_2Cl_2) (DCM)+ acetonitrile (CH_3CN) or + furan (C_4H_4O) or + 2-methylfuran (C_5H_6O) or + acetophenone ($C_6H_5C(O)CH_3$). The values of H^E for the systems for CH_2Cl_2 +acetonitrile or + C_4H_4O are of positive sign while negative sign obtained for the systems CH_2Cl_2 +2-methylfuran or + $C_6H_5C(O)CH_3$. The values of H^E of the different systems have been fitted with the help of smoothing equation using the least squares method. The obtained H^E data represent the presence of specific interactions.

Keywords: CH_2Cl_2, Acetonitrile, Microcalorimeter, Hydrogen bonding, liquid state

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Introduction

Cyclic ethers e.g. furan or 2-methylfuran is of interest because the compound is of industrial significance, and its interactions are more outstanding, thus creating them better solvents. CH_2Cl_2 is an organic compound, which is colorless, hot-tempered liquid and also used as a solvent, although immiscible with water but miscible with lots of organic solvents.

Mixtures of CH_2Cl_2 with acetonitrile (CH_3CN) or + furan (C_4H_4O) or + 2-methylfuran (C_5H_6O) or + acetophenone ($C_6H_5C(O)CH_3$) are of meticulous significance from the opinion of the occurrence of an electron transfer interaction which results in the formation of adducts between the components . The interaction of CH_3CN, C_4H_4O, C_5H_6O and $C_6H_5C(O)CH_3$, due to the occurrence of two nonbonding electrons on the O or N atom of these compounds, it can act as an n-donors toward CH2Cl2, which can be engaged in the creation of

H-bonds with and perform as a σ- acceptor with all aforementioned compounds. We have already 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).

A literature investigation disclosed that wide-ranging studies on such type of systems have not been made. The values of H^E data are used to detect the strength of intermolecular forces such as hydrogen bonding and charge-transfer complex formation between the components in the liquid state. Hence, in the current programme, H^E measurements have been carried out for mixtures of of CH_2Cl_2 with acetonitrile (CH_3CN) or + furan (C_4H_4O) or + 2-methylfuran (C_5H_6O) or + acetophenone ($C_6H_5C(O)CH_3$) at the temperature $T=303.15K$. The experimental data obtained have been reported and discussed in the present programme.

Experimental

Dichloromethane (BDH, AR) was shaken with of conc. H_2SO_4 to obtain acid layer colourless, then rinsed with H_2O, after that washed with aq. 5% sodium carbonate and then with H_2O again. The compound is predried with Calcium Chloride, and distilled over P_2O_5. Purified dichloromethane was stored away from light in a ambered bottle having $4A^0$ molecular sieves.

All chemicals were subjected to fractional distillation for purification and a fixed central portion was utilized for the experiment. The specified minimum purity of chemicals were 99.5 mol%. Before using the chemicals, activated molecular sieves $4A^0$ were used for drying purpose.

The purities of chemicals used, as obtained by Gas Liquid Chromatography, are about 99%. Density measurements were made by means of a vibrating tube densimeter (Patil et.al,1990) and found to be in excellent concord with the available literature data(Riddick and Bunger,1970).

Method

A Micro calorimeter (Model no.C-80 received from Setaram, France) was used for determination of H^E data, the temperature was maintained in the range of ±0.001K. Weight of compounds were taken for Solutions preparation . Mole fractions prepared was accurate to ±0.0001. The trustworthiness of the instrument was compared with the help of H^E data for hexane and cyclohexane at 25^0C as reported earlier(Tripathi

AD,2018). The deviation in the HE measurement was 0.5% at mole fraction, x1 =0.5 while it is about 1% deviations of the H ^{E} at other mole fractions.

Results and discussion:

The H^E data obtained in the present study , for all systems are reported in Table 1 and the data were put into to the following smoothing equation:

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

In this case x_1 refers to the mole fraction of CH_2Cl_2. The parameters Ao,A$_1$,A$_2$ and A$_3$, and the values of σ, are given in Table 2 . The values of deviation of the fitting , σ , are calculated by means of equation as given below(eq.2)

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

In the above equation, H^E represents measured values and H$^E_{calc}$ for calculated excess enthalpy by using eq. (1), m* for no. of data obtained & n* refers no. of constants for a particular system. A plot of obtained experimental values of H^E data against mole fractions (x1) are given in Fig. 1.

Interactions between like molecules and the commencement of new interactions between unlike molecules, are the explanation for the values of H^E obtained . The values of H^E are endothermic for CH_2Cl_2 + CH_3CN or + C_4H_4O while exothermic for the system CH_2Cl_2 + C_5H_6O, and + $C_6H_5C(O)CH_3$.

The H^E values of DCM + CH_3CN is +ve and small, (H^E=152.2J mol^{-1} at x1=0.5) Which indicates little interaction of two components. It clearly suggests that CH_2Cl_2 + CH_3CN interaction reimburses to a great extent the -ve behavior of excess enthalpy due to structural involvement, which results on the whole positive values of H^E.

The excess enthalpy of DCM + C_4H_4O is also +ve and small (value of excess enthalpy = 223.8 J.Mol^{-1} at x1=0.5) which indicates only slight interaction between these each component. The "O" of furan is a weak hydrogen acceptor and may intermingle for forming a hydrogen bond with hydrogen atom of DCM. on the other hand , due to the occurrence of two double bonds present in the C_4H_4O ring , the O acquires less basicity, thus the chance of H- bonding is reduced to a great extent , which results in the positive values of excess enthalpy for this system.

The –ve values of H^E for CH_2Cl_2 + $C_6H_5C(O)CH_3$(H^E= -176 J mol^{-1} at x1=0.5) clearly indicates that there is only partial or weak interaction between these compounds but it is higher as compared to CH_3CN or C_4H_4O .This may also be attributed to be due to the creation of partial or weak hydrogen bond from the H atom of DCM and the π-electrons of the furan ring or via Oxygen—Hydrogen interactions. There is, however, also chance that DCM may also create a charge transfer complex with $C_6H_5C(O)CH_3$, throgh Cl atom π-electron interface. It is seen from Fig.1, that the values of H^E for the system CH_2Cl_2+2-methylfuran is more negative (H^E=-217J mol^{-1} at the minimum) than CH_2Cl_2 +acetophenone system.

The specific interactions between CH_2Cl_2 and C_5H_6O are expected to be stronger than those between CH_2Cl_2 and CH_3CN or C_4H_4O which add to the stronger complex formation and greater negative value of excess enthalpy of this system. The higher negative values for the system CH_2Cl_2 and C_5H_6O than those CH_2Cl_2 and C_4H_4O can be explained due to an increase in the basic character of the ethereal O atom owing to the occurrence of CH3 group, situated at the α-carbon atom, which is an electron -donor .

Due to presence of heteromolecules, highly negative value of H^E of these systems is obtained and this is clear indication of specific interactions. In these systems, two types of interactions are expected. First, there is creation of hydrogen bonding between the Hydrogen of CH_2Cl_2 and the oxygen of furan or methylfuran.

$CHCl_3$ with $(CH_2)_4O$ and dioxane forms a hydrogen bonded complex as given   in the literature(Wilhelm A E.et.al,1982).

In the case of binarysystems the number of H-bonds created, the enthalpy of H-bond creation and other type of interactions are the main donor to the value of H^E. This point outs that the interactions other than H-bonding contribute to the value of H^E of different systems. Thus in the present case not only the Oxygen. Hydrogen and Oxygen—Chlorine interactions (Beath LA. Williamson AG.1969) are involved, but other type of interactions add to the value of H^E . However, in the case of a ethereal groups present in a cycle , the interactions of H and Cl atoms are so governing that the occurrence of a functional group or the position of O atom is not important for making any noteworthy difference to the value of H^E .

Table1. H^E values of dichloromethane (CH_2Cl_2) (1) + CH_3CN (2), or + C_4H_4O (2), or + C_5H_6O (2), or + acetophenone (2) at 303.15 K

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X_1 H^E $(J.mol^{-1})$

CH_2Cl_2 (1) + acetonitrile (2)

X_1	H^E
0.1028	78
02166	132
0.3067	164
0.4007	168
0.5547	140
0 6564	101
0.7022	85
0.8786	31
0.9444	16

CH_2Cl_2 (1) + furan (2)

X_1	H^E
0.0876	82
0.1499	141
0.2828	221
0.3405	232
0.4247	236
0.5098	224
0.5786	199
0.6268	181
0.7204	137
0.8358	95
0.9381	43

CH_2Cl_2 (1) +2-methylfuran   (2)

0.1022	-67
0.1789	-114
0.2567	-154
0.3021	-184
0.3789	-198
0.459	-212
0.5034	-221
0.5643	-216
0.6189	-211
0.7023	-201
0.8222	-169
0.8876	-138
0.9233	-109
0.9678	-56

$CH_2Cl_2\ (1) +$ acetophenone (2)
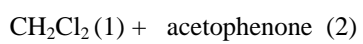
0.1763	-110
0.3362	-165
0.4052	-176
0.4229	-175
0.5115	-175
0.6248	-161
0.7449	-142
0.8520	-95
0.9467	-43
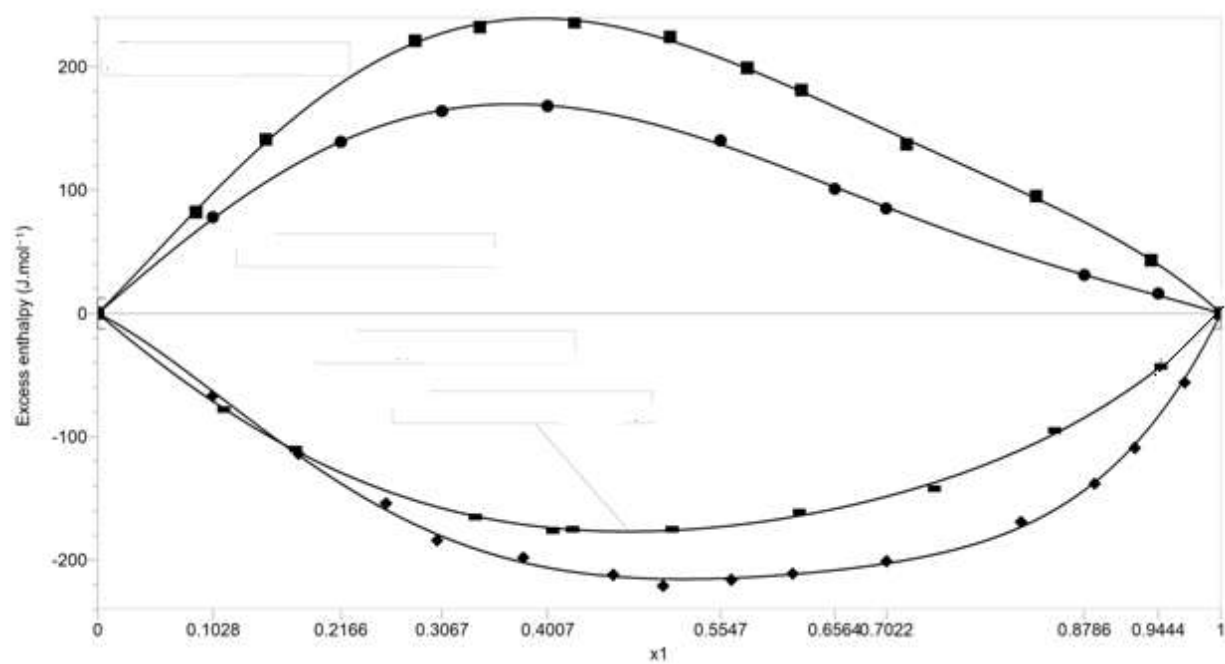
Fig. 1: H^E values of binary mixtures of x1 of Dichloromethane $(CH_2Cl_2$

$(1) + CH_3CN$ ( ) (2), + furan ( )(2) ,+2-methylfuran( ) , (2)and + acetophenone ( ) (2) at the temperature 303.15 K.

Table 2. Least Squares Coefficients of Eq 1 for the Excess Molar Enthalpies, and the standard deviations , σ,of $CH_2Cl_2(1) + CH_3CN$ (2), or + C_4H_4O (2), or + C_5H_6O (2), or + $C_6H_5C(O)CH_3$ (2) at 303.15 K

System		A_0	A_1	A_2	A_3	$\sigma/ (J\ mol^{-1})$
CH_2Cl_2	(1) + + acetonitrile (2)	608.8	-494.2	-76.92	235.5	1.9
CH_2Cl_2	(1) + furan (2)	895.3	-528.1	-18.81	481.4	2.4
CH_2Cl_2	(1) + 2-methylfuran (2)	-868.1	-44.37	-295.1	-643.7	3.7
CH_2Cl_2	(1) + acetophenone (2)	-705.7	65.44	-134.9	-135.4	2.6

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