Excess Molar Enthalpies of Mixtures of Acetylene Tetrachloride with Dimethylsulfoxide, Acetone, Acetonitrile and N-Dibutyl Ether at 303.15 K

Atri D. Tripathi* and Shalini Choudhary

Department of Chemistry, College of Engineering, Teerthankar Mahaveer University, Moradabad 244001, India

Abstract: The Excess molar enthalpies have been determined for binary liquid mixtures of acetylene tetrachloride ($CHCl_2CHCl_2$) (ATC) with dimethylsulfoxide, acetone, acetonitrile and n-dibutyl ether at the temperature 303.15 K by microcalorimetry.

The excess molar enthalpies are negative for all the mixtures over the whole composition range. The results were fitted with the Redlich-Kister equation by means of the least square method. The values of H^E decrease in the order: Dimethylsulphoxide > acetone>acetonitrile > dibutyl ether. The same decreasing trend was observed for calculated hydrogen bond energies of these systems. These results indicate the existence of specific interactions between all these components.

Keywords: Excess molar enthalpy, acetylene tetrachloride, acetone, microcalorimetry, hydrogen bonding.

INTRODUCTION

As a part of our ongoing efforts to obtaining thermodynamic and physicochemical quantities on organic liquid mixtures [1-6] we report here excess enthalpies of acetylene tetrachloride ($CHCl_2CHCl_2$) (ATC) with dimethylsulfoxide, acetone, acetonitrile and n-dibutyl ether at 303.15 K. Binary systems of $CHCl_2CHCl_2$ with all these compounds are of considerable interest due to occurrence of specific interactions between these components in the liquid state. This is due to the occurrence of four Cl atoms and two H atoms in $CHCl_2CHCl_2$, which can therefore take action as σ-acceptors towards, and be concerned in the hydrogen bond construction with dimethylsulfoxide, acetone, acetonitrile and n-dibutyl ether. Latter compounds will operate as n-donors. $CHCl_2CHCl_2$ has two alike proton donors and can therefore form dissimilar type of complexes with the latter compounds. With the help of an NMR study McClellan and Nicksic [7] concluded that $CHCl_2CHCl_2$ is self-associated in the liquid state, while Tripathi [3], from the dielectric property measurement showed that it formed a 1: 1 complex with acetone. A literature survey exposed that broad studies on such systems have not been conceded out to date. The experimental data have also been interpreted in this paper.

The study of acetylene tetrachloride ($CHCl_2CHCl_2$) (ATC) with dimethylsulfoxide, acetone, acetonitrile and n-dibutyl ether 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.

ATC is a chlorinated derivative of ethane. It contains the maximum solvent power of any chlorinated hydrocarbon. As a refrigerant, it is marketed under the name R-130. It was extensively used as a solvent and as an intermediate in the business production of trichloroethylene, tetrachloroethylene, and 1, 2-dichloroethylene. However, ATC is no longer used much in the United States due to concerns about its toxicity. Dimethyl sulfoxide (DMSO) is an organosulfur compound with the formula $(CH_3)_2SO$. This dull liquid is a significant polar aprotic solvent that dissolves both polar and nonpolar compounds and is miscible in an extensive range of organic solvents as well as water. Acetone (systematically named propanone) is the organic compound with the formula $(CH_3)_2CO$. It is a dreary, mobile, burnable liquid, and is the simplest ketone.

Acetone is mixed with water and acts as an essential solvent in its own right, typically for cleaning purposes in the laboratory. Acetone is formed and disposed of in the human body through normal katabolic or anabolic mechanism. It is normally available in blood and urine. Acetonitrile is the chemical compound with the formula CH_3CN. This colorless liquid is the simplest organic nitrile (hydrogen cyanide is a simpler nitrile, but the cyanide anion is not classed as organic). It is created as a consequence of acrylonitrile manufacture and used as a polar aprotic

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*Address correspondence to this author at the Department of Chemistry, College of Engineering, Teerthankar Mahaveer University, Moradabad 244001, India; Tel: +919458444596; E-mail: atrideo@rediffmail.com

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solvent in organic synthesis and in the purification of butadiene. In the laboratory, it is used as a medium-polarity solvent that is miscible with water and range of organic solvents, but not saturated hydrocarbons. It has a convenient liquid range and a high dielectric constant of 38.8. With a dipole moment of 3.92 D, acetonitrile dissolves a wide range of ionic and non-polar compounds and is useful as a mobile phase in HPLC and LC-MS. The N-C-C skeleton is linear with a short C-N distance of 1.16 Å. Dibutyl ether is a chemical compound belonging to the ether family with the molecular formula of $C_8H_{18}O$. It is colorless, volatile, and flammable liquid and has peculiar ethereal smell.

Liquid dibutyl ether is lighter than water. Alternatively, the vapor is heavier than air. It is not soluble in water, but it is soluble in acetone and many other organic solvents. Due to this property, dibutyl ether is used as solvent in different chemical reactions.

2. EXPERIMENTAL

Acetylene tetrachloride ($CHCl_2CHCl_2$), dimethylsulfoxide and acetone (all Analar grade) were fractionally distilled and only the middle portion of compound was used for taking measurements. Acetonitrile (B.D.H.) and acetone (A.R.) were dried over recently activated molecular sieves 4A before use. Minimum purity of chemicals were 99.0 mol% as determined by GLC.

2.1. Method

A heat flux micro calorimeter [5] (C-80 model supplied from Setaram, France) was used for taking measurements on excess molar enthalpies, H^E, the temperature was restricted within ±0.001K. Preparation of the solutions was done by mass. Accuracy of mole fractions is ±0.0001. The trustworthiness of the instrument was earlier checked by measuring H^E for systems of cyclohexane + hexane at T=298.15 K as given elsewhere [1]. At equimolar composition i.e.at x_1=0.5, the deviation of present work is 0.5% whereas about 1% in the mean deviations of the excess enthalpy is estimated.

3. RESULTS AND DISCUSSIONS

The experimental data for excess enthalpies, H^E at the temperature T=303.15 K for the all binary mixtures are given in Table **1**. The obtained results were fitted by least squares to the equation:

Table 1: Excess Enthalpies of Acetylene Tetrachloride ($CHCl_2CHCl_2$) (1) + Dimethylsulphoxide (2)+Acetone (2), + Acetonitrile (2), and + Dibutylether (2) at 303.15 K

X_1	$H^E/(J.mol^{-1})$
$CHCl_2CHCl_2$ (1)	**+dimethylsulphoxide (2)**
0.0762	-676
0.1234	-1071
0.1945	-1751
0.4111	-3086
0.4445	-3189
0.5887	-3187
0.7112	-2738
0.8557	-1659
0.9555	-615
$CHCl_2CHCl_2$ (1)	**+ acetone (2)**
0.0678	-415
0.1123	-698
0.2314	-1367
0.2556	-1478
0.3567	-1875
0.4515	-2092
0.5818	-2119
0.7012	-1899
0.7995	-1523
0.8999	-919
0.9223	-748
$CHCl_2CHCl_2$ (1)	**+ acetonitrile (2)**
0.0654	-267
0.0978	-389
0.1098	-432
0.1567	-587
0.2113	-776
0.2578	-899
0.2888	-992
0.4104	-1234
0.4987	-1324
0.5253	-1323
0.6238	-1276
0.7176	-1104
0.7987	-843
0.8446	-689
0.9805	-98
$CHCl_2$ $CHCl_2$ (1)	**+ dibutyl ether (2)**
0.1042	-421
0.2143	-714
0.2596	-811
0.3224	-925
0.3654	-969
0.4478	-1013
0.578	-967
0.6234	-911
0.7082	-772
0.8456	-434
0.9387	-171

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

where x_1 refers to the mole fraction of $CHCl_2CHCl_2$. The fitting constants and the standard deviations, σ, are summarized in Table **2**. Following equation has been used for the calculation of the standard deviations, σ,

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

where H^E refers the experimental values of excess enthalpy and H^E_{calc} calculated excess enthalpy which can be obtained by means of equation (1), experimental data is denoted by m whereas n is number of constants characteristic of a binary system. Graphical presentation of H^E *vs.* mole fraction (x_1) is plotted in Figure **1**.

The values of excess enthalpy outcome from the distraction of interactions between similar molecules and the introduction of new connections between dissimilar molecules [8].

All the binary systems show negative values of H^E. The extent of H^E for the current mixtures are ascribed to the net effect of +ve and -ve donations due to the rupture of bonds or interactions between like molecules, and also due to the possibility of new bond creation e.g. hydrogen bonds between the unlike molecules. The negative values of excess enthalpy

Table 2: Least Squares Coefficients of Eq 1 for the Excess Molar Enthalpies, and the Standard Deviations, σ, of Acetylene Tetrachloride ($CH_2Cl_2CH_2Cl_2$) (1) + Dimethylsulphoxide (2)+Acetone (2), + Acetonitrile (2), and +Dibutylether (2) at 303.15 K

System	A0	A1	A2	A3	σ/ (J mol^1)
$CH_2Cl_2CH_2Cl_2$ (1) + DMSO (2)	-13039.9	-1060	2039	-2235	19.42
$CH_2Cl_2CH_2Cl_2$ (1) + acetone (2)	-8530	-1126,	-94.42	-1517	7.80
$CH_2Cl_2CH_2Cl_2$ (1) +acetonitrile (2)	-5294	-836.7	933	681	7.04
$CH_2Cl_2CH_2Cl_2$ (1) +dibutylether (2)	-4043	516.5	395.8	472.5	6.28

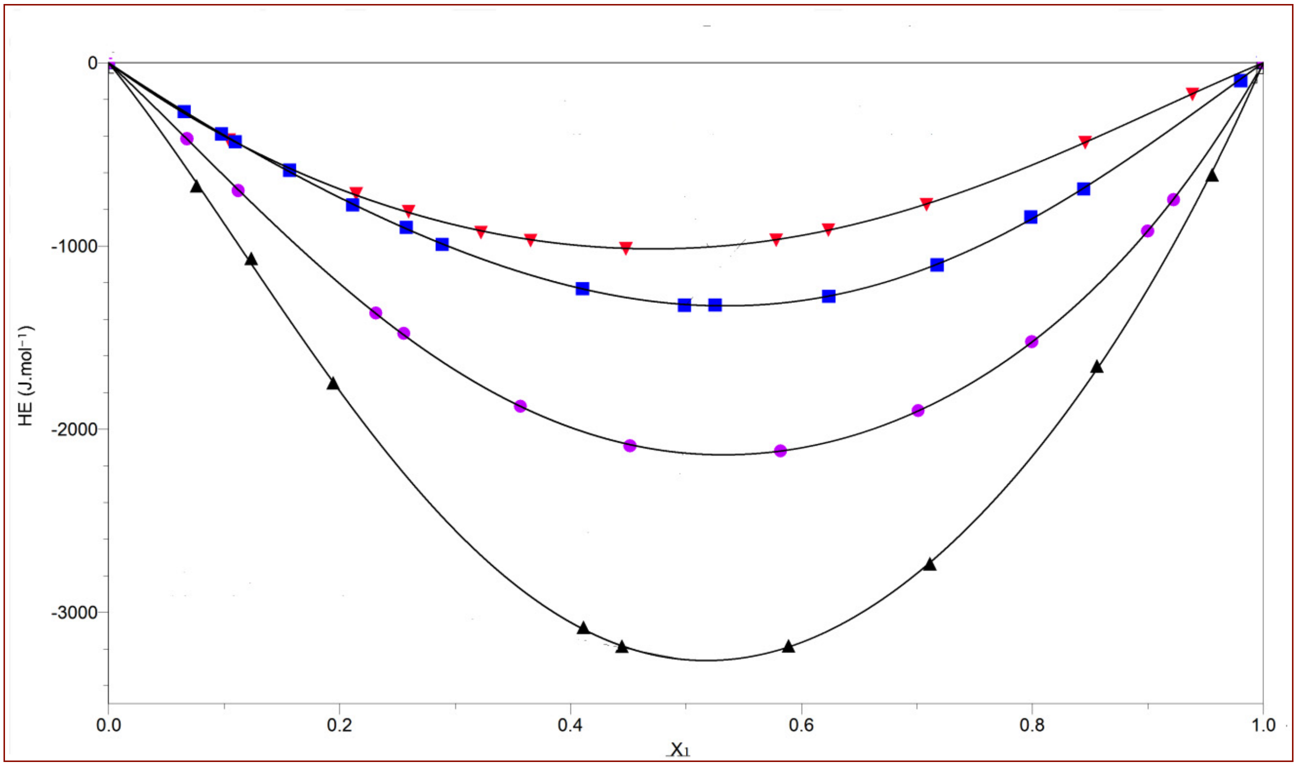

Figure 1: Excess molar enthalpies of binary liquid mixtures of x_1 of Acetylene tetrachloride ($CH_2Cl_2CH_2Cl_2$) (1) + ▼ dimethylsulphoxide (2) (▲) +acetone (2) ●, + acetonitrile (2) ◆, and +dibutylether (2) at 303.15 K.

showed a distinct dependence on the functional group following the order sulpho > keto > nitrile > ether. Such type of the particular interactions is likely to be hydrogen bond creation between the hydrogen of ATC and other donor compounds. The values of H^E obtained are due to the product of the strength of hydrogen bonding and the number of such bonds which are created in the mixture. From the dielectric properties data of acetone and ATC mixtures, Tripathi [3] predicted that a 1: 1 complex forms between the two, while McClellan and Nicksic [7] studied the DMSO + tetrachloroethane system by NMR and concluded a 1: 1 type of complex formation between these two components. The specific interactions between acetone and DMSO with ATC are much stronger than those in the other two systems and, therefore, an AB_2 type of complex creation is not predictable in acetonitrile- ATC and butyl ether-ATC mixtures. It is thus logical to suppose that all four systems form effectively 1: 1 complexes in the binary mixtures. The partial molar enthalpies of dibutylether, acetone, DMSO, acetonitrile in Acetylene Tetrachloride are something like the hydrogen bond energies of the complexes [9]. However, ATC is some extent self-associated and dibutylether, acetone, DMSO, and acetonitrile have tough specific interactions. Three types of interactions are believed to be present when we mix any of these compounds with acetylene tetrachloride: (1) Other molecules dissociate self association of ATC molecules (2) ATC breaks specific interactions of the second compound (3) There is possibility of strong H-bond formation between acetylene tetrachloride and other donor compound.

In this case (1) and (2) interactions are endothermic whereas the 3rd one is an exothermic reaction. Thus it may be concluded that the enthalpy of mixing is thus the total of two +ve contributions (endothermic) and one –ve(exothermic reactions). The enthalpies of H-bonded complexes (ΔHc) are therefore obtained as

$$\Delta Hc = \Delta H_1, - \Delta H_2, - \Delta H_3,$$

where ΔH_1, ΔH_2, and ΔH_3 are the partial molar enthalpy of the proton acceptor in acetylene tetrachloride, the partial molar enthalpy of the proton acceptor in a non-polar solvent and the partial molar enthalpy of ATC in a non-polar solvent, respectively. The ΔH_1, ΔH_2, and ΔH_3 values were obtained by extrapolating the $\Delta H/x_1$, x_2 versus x_1 curve to zero mole fraction. The data on the enthalpies of mixing used to obtain the ΔH_2, and ΔH_3, values were taken from the literature [10-13]. The enthalpies of complex formation therefore obtained are given in Table **3**. The strength of hydrogen bonded complexes between different proton acceptor groups increases in the order S=O > *C=O* > *C≡N* > *C-O-C.*

Dibutyl ether has oxygen which is a weak proton-acceptor and creates a delicate complex with ATC. Acetonitrile is also a weaker proton acceptor than acetone and thus creates a weaker complex with ATC, whereas acetone forms a stronger complex. This observation is same as given in the literature [10, 14].

The acetone-acetylene tetrachloride complex is weaker than the complex DMSO-ATC by about 2.0 kJ mol^{-1}. If we compare the structure of DMSO and acetone, they are similar. The only difference is that DMSO has S atom whereas acetone O atom. There is a vacant 3d orbital which is present in sulphur atom of DMSO in its electronic configuration, thus facilitating the electron delocalization on the nearby carbon atom. Thus the three hydrogen atoms on the methyl groups of

Table 3: The Enthalpies of Complex Formation (ΔHc) of ATC with Dimethylsulphoxide (2) +Acetone (2), + Acetonitrile (2), and +Dibutylether (2) at 303.15 K

System	ΔH_1	ΔH_2	ΔH_3	ΔHc
ATC + DMSO	-13.0			-25.0
ATC + acetone	-9.0			-23.0
ATC +acetonitrile	-3.5			-20.8
ATC +dibutylether	-2.8	-		- 8.7
Dibutylether + hexane		0.9	-	
ATC + hexane			5.0	
Acetonitrile + hexane		12.3		
Acetone + hexane		9.0		
Dimethy lbenzene + DMSO		7.0		

DMSO are believed to be more acidic than those of acetone [15]. The complex formation between DMSO and ATC are therefore believed to be stronger than those between ATC – acetone, which add to the higher negative values of excess enthalpy in the DMSO-ATC system.

The values of H^E are exothermic for the system ATC-dibutyl ether, ≈ -1025 $J.mol^{-1}$ at the minimum indicating only weak interaction between these components. This is due to the creation of weak hydrogen bond between the hydrogen atom of ATC and the donor O of ether or through O---H interactions. The values of excess enthalpy for Acetonitrile-ATC are more negative suggesting stronger complex formation with ATC in the liquid state. The high negative values of dimethylsulfoxide (≈ -3300 $J.mol^{-1}$) at the minimum point toward the presence of strong specific interaction leading to the creation of complexes. This can be believed to be due to presence of strong hydrogen bonding between lone pair electrons which are present on the oxygen atom and a hydrogen atom of acetylene tetrachloride as is suggested by Tripathi [1] between dibromomethane and acetone.

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