

Excess Molar Enthalpies of acetylene tetrachloride with cyclohexanone, pyrrolidin-2-one, methyl ethyl ketone, and acetophenone at the temperature 303.15K

Abstract

The excess molar enthalpies, H^E , of mixtures of acetylene tetrachloride with cyclohexanone ($(CH_2)_5CO$), pyrrolidin-2one (C_4H_7NO), methyl ethyl ketone ($CH_3C(O)CH_2CH_3$), and acetophenone ($C_6H_5C(O)CH_3$) at the temperature 303.15K, have been measured throughout the whole composition range by means of a microcalorimeter at the temperature $T=303.15$ K. The excess molar enthalpies, H_m^E , are -ve for all the mixtures. The values of H^E for n-donor compounds raise in the order: acetophenone > methyl ethyl ketone > pyrrolidin-2one > cyclohexanone. The values of H^E are used to calculate the excess partial molar enthalpies of the particular component at the same temperature..

Key Words: Microcalorimeter, $C_6H_5C(O)CH_3$, acetylene tetrachloride, tetrahydrofuran, C_4H_7NO and excess partial enthalpy

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Introduction

Binary systems of acetylene tetrachloride (ATC) ($CHCl_2 CHCl_2$) with n-donor compounds are of great interest from the perspective of the presence of an electron releasing and accepting groups interaction which leads to the creation of intermolecular complexes between the components. The specific interaction can be thought of as being due to the existence of two Hydrogen atoms with four Chlorine atoms in $CHCl_2 CHCl_2$, which would thus be able to act as σ -acceptors toward and be engaged with the creation of hydrogen bonds with cyclohexanone ($C_6H_{10}O$), pyrrolidin-2one (C_4H_7NO), methyl ethyl ketone ($CH_3COC_2H_5$), and acetophenone ($C_6H_5COCH_3$). Then again, the existence of non-bonding electrons on the O atoms of latter compounds, can prove itself as n-donors toward $CHCl_2 CHCl_2$. A writing review uncovered that far and wide examinations on such frameworks have not been completed to date. Recently we have reported data on excess molar enthalpies H^E of mixtures of $CHCl_2 CHCl_2$ with C_4H_4O or C_5H_6O or $(CH_2)_4O$ or $C_4H_8O_2$ over the entire composition range at the temperature $T=308.15$ K (Tripathi AD.2018) and the results obtained have been discussed from the perspective of molecular interaction between the components. In the current program experimental data on

the H^E values of acetylene tetrachloride, with cyclohexanone, pyrrolidin-2-one, methyl ethyl ketone, and acetophenone have been taken with the help of microcalorimeter at the temperature 303.15 K. The values obtained for H^E are used to get the excess partial molar enthalpies. The outcomes, accordingly got have been reported and deciphered in this paper.

Experimental Section

Acetylene tetrachloride(AR), and and methyl ethyl ketone were collected from Sisco Research Laboratories, Pvt. Ltd., Bombay, India. Both compounds were agitated with K_2CO_3 solution, isolated, and afterward it was kept for drying above anhydrous K_2CO_3 , and it was distilled fractionally. Cyclohexanone is of AR quality and lowest specific purity of 99.5%, HPLC High quality chemicals were also sourced from Sisco Research Laboratories, Ltd., Mumbai, India. Cyclohexanone was applied over anhydrous sodium sulfate to eliminate traces of water and the purest form of the mixture collected in the fractional column and was used for the experiments. The arrangements were placed in a dry box that completely prohibited contact between materials and air humidity. All estimates were made on fresh samples to avoid any dissociation upon standing.

Pyrrolidin-2-one (Fluka) (E. Merck) and acetophenone were taken as such. All compounds were dried over recently activated molecular sieves. Purities of chemicals utilized are $> 99.6\%$ as decided by Gas Liquid Chromatography.

With the help of Gas Liquid Chromatography, chemicals purities have been obtained, and are collected in Table 1. These purities have also been obtained by determining the density values with the help of a vibrating tube densimeter (Tripathi et.al.2018) using under static mode. A thermostat (Haake F3) and a digital thermometer (Anton-Paar DT) were also used for regulating $0.01K$ the temperature. Prior to each determination the apparatus was calibrated at normal pressure with deionised water and $C_5H_{10}O$ (Fluka, purity 99%). The density value of $C_5H_{10}O$ at 298.15K was in good concord with the literature value (Riddick JA, Bunger WB.1970).

The results obtained experimentally were compared with the theoretical results of densities are given (Riddick JA, Bunger WB.1970, Timmermans,1950) in Table 1.

Table 1. Values of different Densities for Pure Components at T= 30°C

Compound	Mol% Purity	Density(g.cm ⁻³)	
		Experimental	Literature
Acetylene tetrachloride	99.6%	1.578 57	1.578 60 ^a
Cyclohexanone	99.7%	0.93754	0.93761 ^a
pyrrolidin-2one	99.8%	1.1009	1.1020 ^a
Methyl ethyl ketone	99.9%	0.794 49	0.794 53 ^a
Acetophenone	99.7%	1.02766	1.028 ^b

^avalues taken from ref. (Timmermans,1950), ^bvalues taken from ref. (Riddick JA, Bunger WB.1970).

Experimental

A Micro calorimeter (C-80 model manufactured from Setaram, France) was utilized for determination of excess molar enthalpies, H^E , the temperature was adjusted within ± 0.001 K. solutions preparation was done by mass. Accuracy of mole fractions is ± 0.0001 . The trustworthiness of the instrument was earlier checked by measuring H^E for binary systems of C₆H₁₂ + C₆H₁₄ at 25 °C as given elsewhere (Tripathi AD, 2018). At mole fraction, $x_1=0.5$, the deviation is 0.5% whereas it is approximately about 1% in case of the deviations (mean) of the H^E is estimated.

Result and Discussion

The values of H^E , for different systems are collected in Table 2 and data were put into to the following equation:

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

In this case x_1 represents to the mole fraction of ATC. The different parameters, and the standard deviations, σ , are collected in Table 3. The values of, σ , have been obtained using equation

$$\sigma = [\sum (H^E - H_{cal}^E)^2 / (m - n)]^{1/2} \quad (2)$$

where H^E is experimental values of excess enthalpy and H_{cal}^E refers to calculated excess enthalpy with the help of equation (1), m represents number of data measured experimentally & n is number of constants which are distinctive of a binary system. A plot of measured values of H^E data Vs mole fractions (x_1) are plotted in **Fig. 1**.

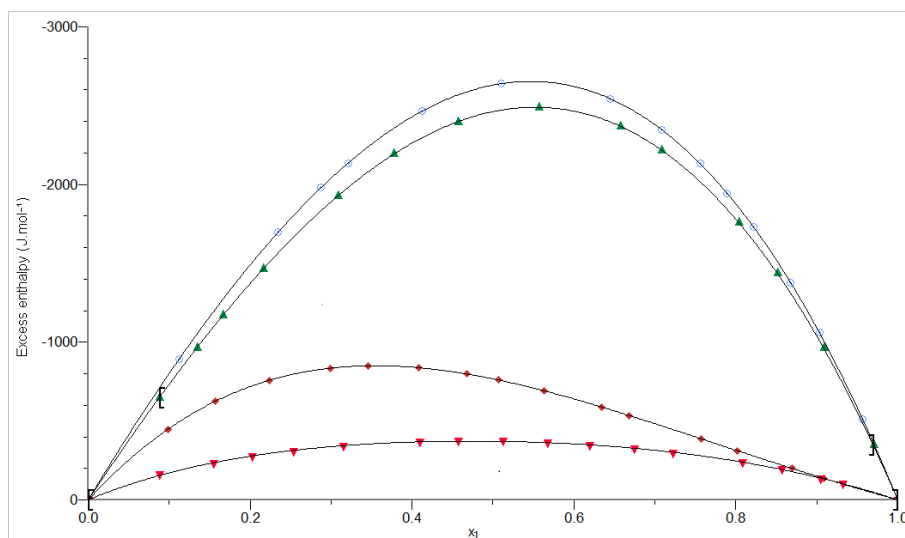






Fig.1 Excess molar enthalpies of binary liquid mixtures of X_1 of Acetylene tetrachloride($\text{CHCl}_2.\text{CHCl}_2(1)$) with Cyclohexanone .

$(\text{C}_6\text{H}_{10}\text{O}(2))$ (), + 2-pyrrolidinone () (2) ,+methyl ethyl ketone(), (2) and + acetophenone () (2) at 303.15 K. The smoothed curves are based on the parameters A_0, A_1, A_2 and A_3 given in Table 2.

Interference of interactions between resembling molecules and the beginning of fresh interactions between dissimilar molecules, are the main reason for the values of H^E obtained . The values of partial excess enthalpies $H_{m,1}^E$, and $H_{m,2}^E$ have been obtained with the help of experimental H^E data by using equations 3 and 4 and are represented graphically in Figures 2 and 3.

$$H_{m,1}^E = \frac{H^E}{x_1} + x_1 x_2 \left[\frac{\delta \left(\frac{H^E}{x_1} \right)}{\delta x_1} \right] p, T \quad (3)$$

$$H_{m,1}^E = \frac{H^E}{x_2} + x_1 x_2 \left[\frac{\delta \left(\frac{H^E}{x_2} \right)}{\delta x_2} \right] p, T \quad (4)$$

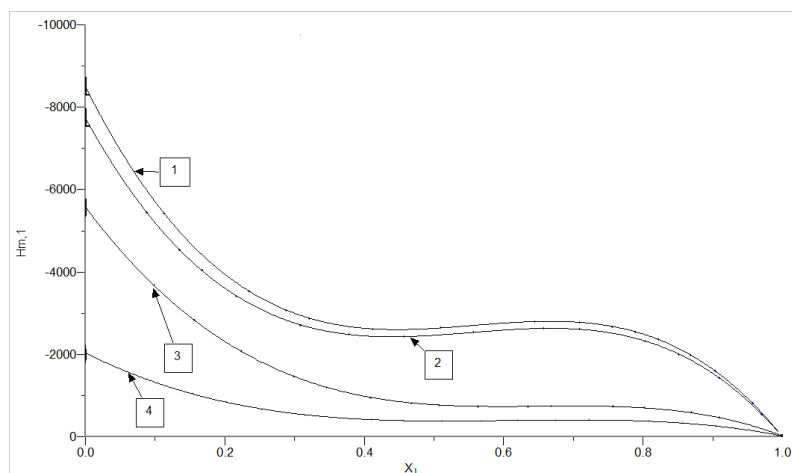


Fig 2. Partial molar excess enthalpies $H_{m,1}$ of binary liquid mixtures of x_1 acetylene tetrachloride+ x_2 cyclohexanone [1], x_1 acetylene tetrachloride + x_2 pyrrolidin-2-one [2], x_1 acetylene tetrachloride + x_2 methyl ethyl ketone [3] and x_1 acetylene tetrachloride + x_2 acetophenone at 303.15 K.

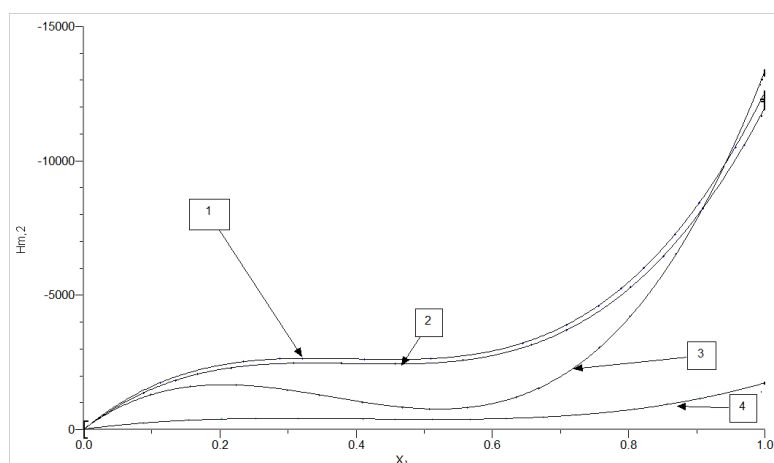


Fig 3. Partial molar excess enthalpies $H_{m,2}$ of binary liquid mixtures of x_1 acetylene tetrachloride+ x_2 cyclohexanone [1], x_1 acetylene tetrachloride + x_2 pyrrolidin-2-one [2], x_1 acetylene tetrachloride + x_2 methyl ethyl ketone [3] and x_1 acetylene tetrachloride + x_2 acetophenone at 303.15 K.

The values of $H_{m,1}^E$, and $H_{m,2}^E$ depends greatly upon the selection of the quantity of fitting constants in the Redlich–Kister equation (Mehta SK, Chauhan RK, Tripathi AD .1997). The values of $H_{m,1}^E$, and $H_{m,2}^E$ are pinpointing of the type of consequences dominating on the whole performance of H^E in the concerned liquid mixtures. The $-ve$ values of H^E for binary solutions suggest that the interactions between dissimilar molecules are more effective than like-like interactions in the pure liquids. The net result of $+ve$ and $-ve$ involvement caused the extent of H^E for the current mixtures because of the breaking of bonds or interactions between like-like molecules, and from the creation of new bonds like hydrogen bonds between unlike molecules (Mehta SK, Chauhan RK, Tripathi AD .1997).

The values of excess molar enthalpies H^E for all above-mentioned binary mixtures are exothermic in nature. The values of H^E for the system ATC+ $(CH_2)_5CO$ are highly -ve throughout the whole range with a minimum value of $\approx -2630 \text{ J.mol}^{-1}$. The extremely exothermic mixing of this system indicates strong specific interactions, the hydrogen bonding between the H of ATC and the O of $(CH_2)_5CO$. In the present mixtures which are of hydrogen bond forming systems, the chief providers to the H^E values are the number of Hydrogen bonds formed, the enthalpy of Hydrogen-bond formation and other specific interactions. The H^E values for the system ATC+ (C_4H_7NO) are also highly -ve all over the whole range with a lowest value of $\approx -2462 \text{ J.mol}^{-1}$ but less than the system ATC+ $(CH_2)_5CO$. Pyrrolidin-2-one consists of pyrrolidine in which the hydrogens at position 2 are replaced by an oxo group. It is an organic compound which consists of a five-membered lactam, thus it is the simplest γ -lactam. There is a resonance between electrons of oxygen and 5 membered ring, causing less exothermicity for the system ATC+ C_4H_7NO .

The H^E values for the system ATC+methyl ethyl ketone are more negative (-767 J.mol^{-1} at mole fraction 0.5) than the values for the system ATC+ acetophenone (-373 J.mol^{-1} at mole fraction 0.5), because in acetophenone, ethyl group of methyl ethyl ketone is replaced by phenyl group which causes resonance thus decreasing the exothermicity during the hydrogen bond formation.

Taking into consideration the reality that the little difference in electronegative character (0.5) between Oxygen and Chlorine leads to specific interactions, there is a chance of hydrogen bond-type interaction between the Chlorine of $CHCl_2.CHCl_2$ and hydrogen of all other mentioned compounds. When ATC combines with cyclohexanone or pyrrolidin-2-one, not only the O... H and O--Cl interactions (Pathak G, 1992) but interactions between CH_2 groups and chlorine atoms add to the H^E values. Several i.r. spectroscopic studies (Walmsley JA, 1976, 1978) of dilute solutions of pyrrolidin-2-one in non-ionic solvents have revealed that the self-association of pyrrolidin-2-one is somewhat strong. The molecule has a relatively high dipole moment $11.84 \times 10^{-30} \text{ C m}$ at $T=25^\circ\text{C}$. Besides its high dipole moment, C_4H_7NO has the carbonyl group (basic) and acidic -NH groups of the naturally occurring -CO- NH- peptide bond.

Table 2. Excess Molar Enthalpies of Acetylene tetrachloride ($\text{CHCl}_2\text{CHCl}_2$) (1) with Cyclohexanone (2), Pyrrolidin-2-one (2), Methyl ethyl ketone (2), and Acetophenone (2) at 303.15 K

$\text{CHCl}_2\text{CHCl}_2 +$ cyclohexanone		$\text{CHCl}_2\text{CHCl}_2 +$ pyrrolidin- 2-one	
x1	H^E	x1	H^E
	($\text{J}\cdot\text{mol}^{-1}$)		($\text{J}\cdot\text{mol}^{-1}$)
0.1123	-893	0.0879	-650
0.2345	-1697	0.1345	-966
0.2875	-1980	0.1665	-1171
0.3211	-2136	0.2165	-1467
0.4122	-2464	0.3087	-1929
0.5098	-2639	0.3777	-2193
0.6445	-2544	0.4567	-2398
0.7086	-2346	0.5567	-2490
0.7558	-2132	0.6578	-2367
0.7889	-1946	0.7089	-2215
0.8221	-1729	0.8034	-1758
0.8678	-1377	0.8511	-1437
0.9034	-1060	0.9087	-961
0.9567	-512	0.9699	-346
$\text{CHCl}_2\text{CHCl}_2 +$ METHYL ETHYL KETONE		$\text{CHCl}_2\text{CHCl}_2 +$ ACETOPHENONE	
x1	H^E	x1	H^E
	($\text{J}\cdot\text{mol}^{-1}$)		($\text{J}\cdot\text{mol}^{-1}$)
0.1567	-625	0.0876	-149
0.2234	-758	0.1543	-233
0.2987	-832	0.2021	-273
0.3456	-849	0.2532	-309
0.4088	-839	0.3145	-342
0.4678	-800	0.4098	-371
0.5071	-762	0.4567	-374
0.5633	-692	0.5123	-374
0.6345	-586	0.5678	-364
0.6678	-531	0.6198	-348
0.7568	-381	0.6744	-324
0.8022	-306	0.7223	-298
0.8694	-197	0.8085	-238
0.9089	-135	0.8567	-192
		0.9045	-143
		0.9324	-104

Table 3. Least Squares Coefficients of Eq 1 for the Excess Molar Enthalpies, and the standard deviations, σ , of Acetylene tetrachloride (CHCl₂.CHCl₂)(1) + Cyclohexanone (C₆H₁₀O)(2) or + pyrrolidin-2-one (2), or + Methyl ethyl ketone (2), or + Acetophenone (2) at 303.15 K

System	A0	A1	A2	A3	σ / (J mol ⁻¹)
CHCl ₂ CHCl ₂ (1) + C ₆ H ₁₀ O (2)	-10520	-2013	-0.2732	-2.676	0.2635
CHCl ₂ CHCl ₂ (1) + 2-Pyrrolidinone (2)	-9848	-2115	-2.891	-5.549	0.3209
CHCl ₂ CHCl ₂ (1) + MEK (2)	-3067	2113	-424	46.77	2.53
CHCl ₂ CHCl ₂ (1) + Acetophenone(2)	-1491	148.4	-359.8	-16.14	2.059

The interaction between cyclic ketones (>C=O) and Br- or Cl- compounds are managed by the complete saturation of their rings. C₄H₇NO or (CH₂)₅CO has saturated ring, which makes the interaction stronger. Thus showing higher -ve values of enthalpy of mixing.

The values of H^E_{m,1}, and H^E_{m,2} Vs mole fraction of each binary liquid mixtures have been plotted in Figures 2 and 3 which clearly supports the above-mentioned explanations.

Information about the difference between the enthalpy of complex formation in solution and the enthalpy in the pure form is given by the values of H^E_{m,1}, and H^E_{m,2}. The -ve values of H^E_{m,1}, and H^E_{m,2} are due to the presence of strong hydrogen bonds formed between Hydrogen atom of CHCl₂.CHCl₂ and non bonding pair of electrons present on the oxygen atom of (CH₂)₅CO or C₄H₇NO or CH₃C(O)CH₂CH₃ or C₆H₅C(O)CH₃ as reported elsewhere between CHCl₂.CHCl₂ and (CH₃)₂CO (Nath J, Tripathi AD, 1984).

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