

Excess molar enthalpies of dichloromethane +cyclopentanone or + n-dibutyl ether or + Acetone or + dimethyl sulfoxide at the temperature 303.15 K

Abstract

Excess molar enthalpies H^E at $T= 303.15$ K have been determined for dichloromethane (CH_2Cl_2) (DCM)+ cyclopentanone ($((\text{CH}_2)_4\text{CO})$ or + di-n-butyl ether ($\text{C}_8\text{H}_{18}\text{O}$) or + acetone ($(\text{CH}_3)_2\text{CO}$) or + dimethyl sulfoxide (DMSO) ($(\text{CH}_3)_2\text{SO}$). The values of H^E for all the systems are exothermic in nature. The values of H^E of the different systems have been fitted with the Redlich-Kister equation with the help of the least squares method. Excess molar enthalpies data represent the occurrence of specific interactions between the components in the liquid state.

Keywords: CH_2Cl_2 , cyclopentanone, Microcalorimeter, acetone, Binary mixture

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Received on 25.10.2021

Accepted on 23.12.2021

Introduction

The cyclic ketone, cyclopentanone, Dibutyl ether, Acetone, or Propanone, Dimethyl sulfoxide and Dichloromethane are colorless liquids. Dibutyl ether is immiscible with water, but miscible with acetone and many organic solvents. Due to this property, dibutyl ether is used as solvent in various chemical reactions and processes.

Acetone is the smallest ketone. Dimethyl sulfoxide (DMSO) is a polar aprotic solvent which is capable of dissolving polar as well as nonpolar compounds and is soluble in many organic solvents and water, but not volatile as acetone. Dichloromethane is colorless, volatile liquid and also used as a solvent, although immiscible with water but miscible with lots of organic solvents.

The study of cyclic or acyclic ethers, acetone or DMSO or CH_2Cl_2 is of interest due to its industrial importance, and their interactions are more exceptional, thus making them better solvents. Dichloromethane is an organic compound with the formula CH_2Cl_2 , which is colorless, volatile liquid and also used as a solvent, although immiscible with water but miscible with lots of organic solvents.

Mixtures of CH_2Cl_2 with cyclopentanone ($((\text{CH}_2)_4\text{CO})$ or + di-n-butyl ether ($\text{C}_8\text{H}_{18}\text{O}$) or + acetone ($(\text{CH}_3)_2\text{CO}$) or + dimethyl sulfoxide (DMSO) ($(\text{CH}_3)_2\text{SO}$) are of meticulous significance from the opinion of the existence of an electron donor-acceptor interaction which leads to the creation of intermolecular complexes between the

components in the liquid form. The interaction of $(\text{CH}_2)_4\text{CO}$ or $+\text{C}_8\text{H}_{18}\text{O}$ or $+(\text{CH}_3)_2\text{CO}$ or $+(\text{CH}_3)_2\text{SO}$, can be thought of as being due to the occurrence of non-bonding pair of 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 engaged in the formation of hydrogen bonds with and act as a σ - acceptor toward 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, Tripathi, 1995, 2010).

A literature survey disclosed that broad studies on such systems have not been carried out. . The values of excess molar enthalpy data (H^E) 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 binary liquid mixtures of CH_2Cl_2 with cyclopentanone ($(\text{CH}_2)_4\text{CO}$) or $+$ di-n-butyl ether ($\text{C}_8\text{H}_{18}\text{O}$) or $+$ acetone $(\text{CH}_3)_2\text{CO}$ or $+$ dimethyl sulfoxide (DMSO) $(\text{CH}_3)_2\text{SO}$ at the temperature $T=303.15\text{K}$. The results obtained have been reported and deciphered in this paper.

Experimental Section

Dichloromethane (BDH, AR) was shaken with 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 CaCl_2 , and distilled over P_2O_5 . Purified dichloromethane was stored away from light in a ambered bottle having 4A^0 molecular sieves. Cyclopentanone ($(\text{CH}_2)_4\text{CO}$) or $+$ di-n-butyl ether ($\text{C}_8\text{H}_{18}\text{O}$) or $+$ acetone $(\text{CH}_3)_2\text{CO}$ or $+$ dimethyl sulfoxide (DMSO) $(\text{CH}_3)_2\text{SO}$, all chemicals were of AR quality and subjected to further purification by standard methods as given elsewhere (Pathak et.al.1992). These 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 found to be in good agreement with the literature values(Riddick and Bunger,1986).

Method

Excess molar enthalpies, H^E , were obtained by using a heat flux calorimeter (C-80 model from Setaram, France) (Tripathi et.al, 2018), whose temperature was controlled to within $\pm 0.001\text{K}$. 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 (Nath &Tripathi AD, 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.

Result and Discussion

The values of H^E , for different systems are collected in Table 1 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 the mole fraction of CH_2Cl_2 . The different parameters, and the standard deviations, σ , are collected in Table 2. The values of standard deviation of the fit, σ , are obtained by means of eq.2

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

where H^E is experimental values and H^E_{calc} refers to calculated excess enthalpy with the help of eq. (1), m^* represents no. of data measured experimentally & n^* is no. 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. 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. All four systems are showing negative values of H^E because of specific interactions between the components in the liquid state. The values of H^E decrease in the order at mole fraction, $x_1=0.5$:

Dimethyl sulfoxide >cyclopentanone>acetone >di-n-butyl ether

The etheral oxygen of dibutyl ether has a weak proton-accepting ability and creates a weak complex with DCM ($H^E = -476$) at $x_1=0.5$). Acetone is a, however, better proton acceptor than dibutyl ether, as our data suggest and forms a stronger complex with DCM ($H^E = -1076$ at $x_1=0.5$). The two methyl groups present on acetone increase the basicity of keto O atom.

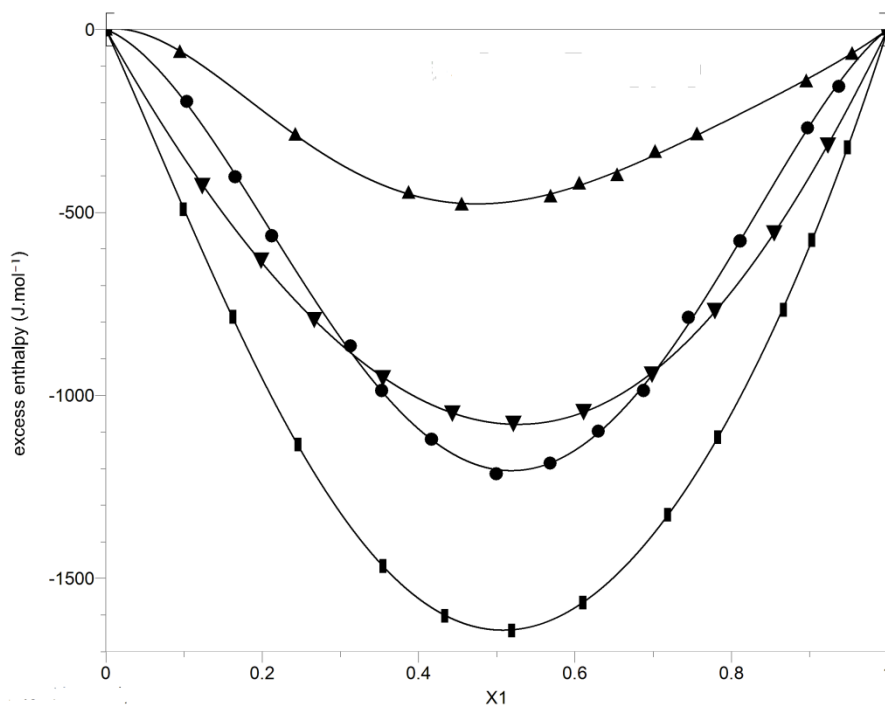


Fig. 1: Excess molar enthalpies of binary liquid mixtures of x_1 of dichloromethane (CH_2Cl_2 (1) + cyclopentanone (•) (2), + di-n-butyl ether (▲) (2), + acetone (▼) (2) and + dimethyl sulfoxide (■) (2) at the temperature 303.15 K.

The effect of saturation of the furan ring is marked and the DCM— $(\text{CH}_2)_4\text{CO}$ system is highly exothermic ($H^E = -1203$ at $x_1 = 0.5$). Due to the existence of hetero-molecules, this system has a high exothermic value, showing greater interactions. The hydrogen bonding in between hydrogen of DCM and the keto or ether oxygen causes interactions in such systems. Chloroform has been found to form hydrogen-bonded complexes with tetrahydrofuran and dioxane. The number of hydrogen bonds formed, the enthalpy of formation of hydrogen bonds, and other interactions are the key contributors to the value of H^E in hydrogen bond producing systems. Given that the little electronegativity difference (0.5) between O and Cl causes particular associations, a hydrogen bond-type specific interaction between the hydrogen of a keto or ether and the Cl of DCM is a significant possibility. The saturation or unsaturation of the ring determines the interactions between H atom of ketones and chloro compounds. The enthalpies of mixing in these systems are influenced not only by O - H and O - Cl interactions, but also by interactions between CH_2 Groups (as in $(\text{CH}_2)_4\text{CO}$) and Cl atoms.

The DMSO—DCM complex is vastly exothermic and -600 J/mol^{-1} (at $x_1 = 0.5$) greater than the acetone—DCM complex. The structures of DMSO and $(\text{CH}_3)_2\text{CO}$ are analogous, however the S atom of DMSO has unoccupied 3d orbitals, leading electron delocalization on the neighbouring carbon atom to be enhanced. As a result, the H atoms on the CH_3 groups of DMSO become more acidic than those on the CH_3 groups of $(\text{CH}_3)_2\text{CO}$ (Solomons, 1976). The associations between DMSO and DCM are projected to be higher than with those between DCM and $(\text{CH}_3)_2\text{CO}$, resulting to the DMSO—DCM system's stronger formation of complexes and significant increase of excess enthalpy.

Table1. Excess Molar Enthalpies of dichloromethane (CH₂Cl₂) (1) + cyclopentanone (2), or + di-n-butyl ether (2), or + acetone (2), or + dimethyl sulfoxide (2) at 303.15 K

Dichloromethane(1)+ cyclopentanone (2)		Dichloromethane(1)+ di-n-butyl ether (2)	
x1	H ^E (J.mol ⁻¹)	x1	H ^E (J.mol ⁻¹)
0.1034	-197	0.0945	-61
0.1654	-403	0.2423	-287
0.2123	-564	0.3871	-446
0.3128	-865	0.4551	-478
0.3528	-987	0.5686	-456
0.4166	-1120	0.6054	-421
0.4993	-1214	0.654	-398
0.5682	-1185	0.7023	-334
0.6298	-1098	0.7561	-286
0.6876	-987	0.8956	-141
0.7452	-787	0.9543	-66
0.8113	-578		
0.8976	-269		
0.9376	-156		
Dichloromethane +acetone		Dichloromethane +DMSO	
x1	H ^E (J.mol ⁻¹)	x1	H ^E (J.mol ⁻¹)
-427	-427	0.0987	-491
-631	-631	0.1623	-785
-793	-793	0.2456	-1134
-952	-952	0.3541	-1466
-1049	-1049	0.4333	-1602
-1077	-1077	0.5188	-1642
-1045	-1045	0.6099	-1566
-942	-942	0.7185	-1326
-768	-768	0.7822	-1114
-556	-556	0.8666	-766
-316	-316	0.9028	-575
		0.9484	-322

Table 2. Least Squares Coefficients of Eq 1 for the Excess Molar Enthalpies, and the standard deviations σ , of $\text{CH}_2\text{Cl}_2(1) + \text{cyclopentanone} (2)$, $+ \text{di-n-butyl ether} (2)$, $+ \text{acetone} (2)$ and $+ \text{dimethyl sulfoxide} (2)$ at the temperature 303.15 K.

System	A0	A1	A2	A3	$\sigma / (\text{J mol}^{-1})$
$\text{CH}_2\text{Cl}_2 (1) + \text{cyclopentanone} (2)$	-4812	-616.3	3554	207.9	9.7
$\text{CH}_2\text{Cl}_2 (1) + \text{di-n-butyl ether} (2)$	-1899	333	1249	-1238	5.9
$\text{CH}_2\text{Cl}_2 (1) + \text{acetone} (2)$	-4305	-485.9	191.4	210.3	2.8
$\text{CH}_2\text{Cl}_2 (1) + \text{dimethyl sulfoxide} (2)$	-6565	-232.5	846.5	-720.3	3.5

The interaction between cyclic ketones ($>\text{C}=\text{O}$) and Br- or Cl- compounds are managed by the complete saturation of their rings. $(\text{CH}_2)_5\text{CO}$ has saturated ring, which makes the interaction stronger. Thus showing higher -ve values of enthalpy of mixing as compared to dibutyl ether.

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