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Excess Molar Volumes for acetylene tetrachloride + 1, 4-dioxane or methyl ethyl ketone or pyridine at 308.15 K

Abstract
Excess molar volumes (V^E) of acetylene tetrachloride with 1,4-dioxane or methyl ethyl ketone or pyridine have been determined at 308.15 K and atmospheric pressure over the whole mole fraction variety with the aid of dilatometer. The effects have been conferred in terms of dipole–dipole interactions between acetylene tetrachloride and other donor atoms in the liquid state.

Keywords: Microcalorimeter, excess volume, dilatometer, least square fitting, lone pair

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Introduction

In our previous paper (Tripathi AD et al,2021) we have studied the excess molar volumes of Binary Liquid Mixtures of cyclohexanone, + methylene chloride, +chloroform, + CH_2ClCH_2Cl, +$CHClCCl_2$ and + CCl_3CH_3 at 303.15 K. In continuation of these studies on the thermodynamic and other properties of some mixtures of chloroalkanes and bromo alkanes with n-donor organic solvents (Tripathi AD,2010,2018,2020), the current paper shows the excess molar volumes (V^E) obtained experimentally by using dilatometer for the binary liquid mixtures of acetylene tetrachloride ($CHCl_2.CHCl_2$) with 1,4-dioxane($C_4H_8O_2$) or methyl ethyl ketone ($CH_3COC_2H_5$)or pyridine(C_5H_5N) at 308.15 K and atmospheric pressures and the results obtained have been discussed in terms of destruction and creation of bonds, influence of the lone pair electrons of O atom or N atom during creation of new bonds , and establishing of unlike-pair interactions, and its competition with acetylene tetrachloride self-association in the liquid state. These results can be used in providing an additional complete behavior of the present mixtures.

Experimental

Materials

The high pressure liquid chromatography quality chemicals (purchased from Qualigens Fine Chemicals, Mumbai)acetylene tetrachloride,pyridine and ethyl methyl ketone , and $C_4H_8O_2$ of said lowest mass fraction purities of 0.996, 0.99 and 0.995, respectively. Acetylene tetrachloride was purified as given in earlier paper(Pathak G.et.al.1992). Pyridine and methyl ethyl ketone was used as such. $C_4H_8O_2$ became stored over sodium cord earlier than use . All organic liquids were stored in Ambered bottles over molecular sieves(4 Å in size), in order to decrease the moisture percentage. Before taking measurements , all chemicals were degassed inside vacuum.

Method

V^E were obtained by using , two-limbed Pyrex glass dilatometer with an uncertainty of $\pm 2.10^{-3}$ cm^3 mol^{-1} , it was same as used by Nath and Tripathi,1983. Weighed amounts of the two organic liquids were kept above purified Hg in the lack of air holes in the both arms of the dilatometer, kept on a wooden rest and the complete assembly was submerged in a water thermostat (Accuracy±0.01 K). The combination of the two liquids have been acquired by way of swinging the cell backward and forward through a definite attitude, and the Hg ranges in the capillary were read by means of a a cathetometer ($\pm 1.10^{-3}$ cm accurate).

Result and discussion

Experimental data at 308.15 K for V^E, in terms of $CHCl_2.CHCl_2$ mole fractionx_1 , are collected in **Table 1** and represented in Fig. 1. Excess volume data for different mixtures were fitted to an appropriate equation of the under given form

$$V^E = x_1(1-x_1)[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2 + A_3(x_1 - x_2)^3$$

The values of the all coefficients arising from the fits and the corresponding standard deviations are summarized in **Tables 2**. Standard deviation is calculated as given in our earlier paper. (Tripathi, AD et.al.2021)

The plot permit us to envisage the trend of $\boldsymbol{V^E}$changes when increasing the mole fraction of $CHCl_2.CHCl_2$. The values of V^E , which are negative for all the systems , increase in the order

Methyl ethyl ketone>1,4,dioxane >Pyridine

High negative values of V^E for the system of $CHCl_2.CHCl_2$+methyl ethyl ketone system are an indication of creation of strong molecular complex between these components in the liquid state. The excess volume of a binary mixture can be visualized as the balance of two types of contributions arising from the breaking of cohesion (like molecule interaction)forces in pure liquids during the mixing process and one negative input arising from the newly established similar or unlike-pair interactions. The interaction between $CHCl_2.CHCl_2$+methyl ethyl ketone or + 1,4-dioxane can occur due to combination of H atom of $CHCl_2.CHCl_2$ and lone pair electrons present on the O atom of methyl ethyl ketone. Possibility of charge-transfer complex formation may arise when Cl atom combination with lone pair electrons on O atom takes place in the liquid state. Since 1,4-dioxane has two O atms in its structure but it has less negative values of V^E than methyl ethyl ketone. In the present case, H-bonding and other interactions takes place between the components. It clearly indicates that other interactions are chief contributors to excess volume other than hydrogen bonding.

The interaction for the system , $CHCl_2.CHCl_2$ +pyridine, the values of excess volume is less negative than other components, thus showing the weak interaction between H atom of $CHCl_2.CHCl_2$ and lone pair electrons on the N atom of Pyridine.

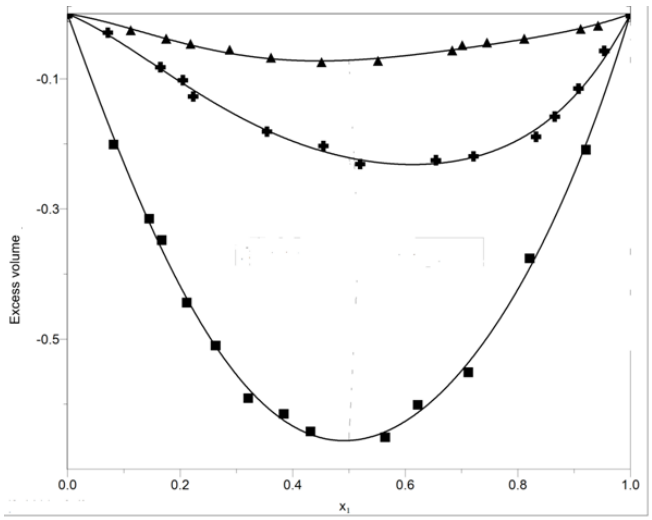

Fig. 1: Excess molar volumes of binary liquid mixtures of x1 of acetylene tetrachloride ($CHCl_2CHCl_2$)(1) + (1,4-$C_4H_8O_2$)(2) (✚),+methyl ethyl ketone($CH_3COC_2H_5$)(2) (■),+ and +C_5H_5N (2)(▲) at the temperature 308.15 K.

Table 1. Experimental Values of Excess Molar Volumes, for acetylene tetrachloride, + 1,4-dioxane or methyl ethyl ketone or pyridine at 308.15 K

x$CHCl_2CHCl_2$ + (1 - *x*)(1,4-$C_4H_8O_2$)		*x*$CHCl_2CHCl_2$ + (1 - *x*)$CH_3COC_2H_5$	
x1	**V^E ($Cm^3.mol^{-1}$)**	**x1**	**V^E ($Cm^3.mol^{-1}$)**
0.0718	-0.029	0.0822	-0.201
0.165	-0.082	0.1453	-0.315
0.2051	-0.196	0.1675	-0.348
0.2232	-0.127	0.2122	-0.444
0.3544	-0.181	0.2633	-0.510
0.4544	-0.203	0.3211	-0.591
0.5199	-0.231	0.3843	-0.615
0.6543	-0.225	0.4318	-0.642
0.7211	-0.219	0.5644	-0.681
0.8321	-0.189	0.6222	-0.601
0.8655	-0.158	0.7122	-0.561
0.9076	-0.115	0.8211	-0.376
0.9534	-0.057	0.9211	-0.209

x$CHCl_2CHCl_2$ + (1 - *x*)Pyridine	
x1	V^E ($Cm^3.mol^{-1}$)
0.1122	-0.026
0.1754	-0.036
0.2187	-0.047
0.2881	-0.056
0.3613	-0.068
0.4512	-0.075
0.5513	-0.073
0.6833	-0.057
0.7011	-0.041
0.7441	-0.042
0.8112	-0.039
0.9117	-0.024
0.9423	-0.019

Table 2. Table2.Redlich-Kister Coefficients and Standard Deviation σ for different systems at 308.15K

System	A0	A1	A2	A3	σ/ (Cm^3 mol^{-1})
$CHCl_2CHCl_2$ (1) + (1,4-$C_4H_8O_2$)(2)	-0.8845	-0.3617	-0.1315	-0.2994	0.007
$CHCl_2CHCl_2$ (1) + $CH_3COC_2H_5$ (2)	-2.623	0.0856	-0.017	-0.3211	0.012
$CHCl_2CHCl_2$ (1) + C_5H_5N (2)	-0.2853	0.0807	0.059	-0.179	0.003

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