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Excess Volume for Acetylene Tetrachloride with Pyridine, Methoxybenzene, 2-Butanone and 1,4-Dioxane at 298.15K

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ABSTRACT
A dilatometric measurement have been carried out for getting excess volumes, V^E, in the liquid state for mixtures of acetylene tetrachloride ($CHCl_2CHCl_2$), with pyridine (C_5H_5N), methoxybenzene ($C_6H_5O CH_3$), 2-butanone ($CH_3COC_2H_5$) and 1,4-dioxane (1,4-$C_4H_8O_2$) at 298.15K and under atmospheric pressure. The values of excess molar volume, V^E, are negative in sign for all the mixtures over whole composition range. Obtained data have been fitted by Redlich-Kister type polynomial smoothing equation. The results are discussed in the light of molecular interactions occurred between components in the liquid state.

Keywords: Excess Volume, Acetylene Tetrachloride, Pyridine, Methoxybenzene

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INTRODUCTION

Methodical studies of the excess properties grant significant conclusion regarding the deeper understanding of the structure of liquid and the inter or intra molecular interactions.

Pyridine have nitrogen atom in its structure which has nonbonding electrons and act as n-donor toward interaction with acetylene tetrachloride, methoxybenzene, 2-butanone and 1,4-dixane. Latter compounds have O atom in its structure which also possess nonbonding electrons and interact with acetylene tetrachloride. All these compounds perform as n-donors towards $CHCl_2CHCl_2$. Thus acetylene tetrachloride acts as σ-acceptor in the interaction with all other mentioned compounds. Nath and tripathi (1983, 1984) have measured excess volume, ultrasonic velocity and dielectric data (1984) for $CHCl_2CHCl_2$+acetone and discussed their results in context of donor-acceptor interaction between different components. Extensive work concerning the properties of above-said binary mixtures is not available in the literature. Hence in the present work, measurements of excess volume (V^E) were made for $CHCl_2CHCl_2$ with C_6H_5N, $C_6H_5 O CH_3$, $CH_3COC_2H_5$ and 1,4- $C_4H_8 O_2$ at 298.15K and under atmospheric pressure.

EXPERIMENTAL

Na wire was used for storing 1,4-dioxane(BDH). Acetylene tetrachloride or 1,1,2,2-Tetrachloroethane and 2-butanone were vibrated with aqueous K_2CO_3, detached, and then kept over anh. K_2CO_3 for drying purpose, and then distilled fractionally. Distillation of Anisole was done from Na (sodium). Pyridine (BDH) was used as such. Vibrating tube densimeter was used for obtaining densities of these chemicals and have been compared with best available literature data (Riddick and Bungar, 1970), which are found in good agreement.

Excess volumes, V^E, with a precision ±0.002 cm^3 mol^{-1}, were determined by means of a two-branched dilatometer which was analogous to that used in our previous measurements and the functioning of the dilatometer was checked as explained in previous publication (Nath and Tripathi, 1983; Singh et. al., 2021). The instrument (build up on a wooden stand) was submerged in water filled thermostat retained at the desired temperature (fluctuates within ±0.0l Kelvin). The improbability in the mole fractions in various mixtures is ±0.0002. The heights of Hg level in the capillary of the dilatometer were measured by means of a cathetometer (accuracy ±0.001 cm).

RESULTS AND DISCUSSION

The values of excess molar volume for the systems of acetylene tetrachloride with pyridine, methoxybenzene, 2-butanone and 1,4-dioxane at 298.15K are given in Table1. The values of excess molar volume, $V^E/cm^3.mol^{-1}$ for the different mixtures of acetylene tetrachloride have been plotted against the mole fraction, *x*, of acetylene tetrachloride, in Figure 1.

Table 1: Values of Experimental Excess volumes for Different mixtures at 298.15K

$xCHCl_2CHCl_2+(1-x)C_5H_5N$		$xCHCl_2CHCl_2+(1-x)C_6H_5OCH_3$	
x	V^E	x	V^E
0.0784	-0.025	0.0678	-0.029
0.1133	-0.033	0.1212	-0.044
0.1765	-0.047	0.1885	-0.060
0.2234	-0.056	0.2454	-0.069
0.2965	-0.068	0.3023	-0.076
0.3244	-0.072	0.3678	-0.082
0.3897	-0.081	0.4116	-0.084
0.4522	-0.085	0.4799	-0.085
0.5213	-0.087	0.5562	-0.083
0.6155	-0.085	0.6223	-0.079
0.7098	-0.076	0.7134	-0.069
0.7567	-0.069	0.7899	-0.058
0.8009	-0.061	0.8766	-0.041
0.8666	-0.046	0.9444	-0.022
0.9316	-0.028		
$xCHCl_2CHCl_2+(1-x)\ CH_3COC_2H_5$		$xCHCl_2CHCl_2+(1-x)1,4\text{-}\ C_4H_8O_2$	
x	V^E	x	V^E
0.0967	-0.218	0.0855	-0.039
0.1298	-0.294	0.1345	-0.061
0.1756	-0.407	0.1888	-0.101
0.2432	-0.5	0.2412	-0.119
0.3076	-0.59	0.3099	-0.155
0.3555	-0.642	0.3788	-0.173
0.4019	-0.678	0.4156	-0.196

0.4517	-0.702	0.5077	-0.22
0.5562	-0.701	0.5789	-0.229
0.6286	-0.657	0.6231	-0.229
0.7011	-0.543	0.6987	-0.208
0.7899	-0.456	0.7444	-0.187
0.8677	-0.378	0.8567	-0.154
0.8902	-0.254	0.9032	-0.104
0.9213	-0.142	0.9432	-0.064

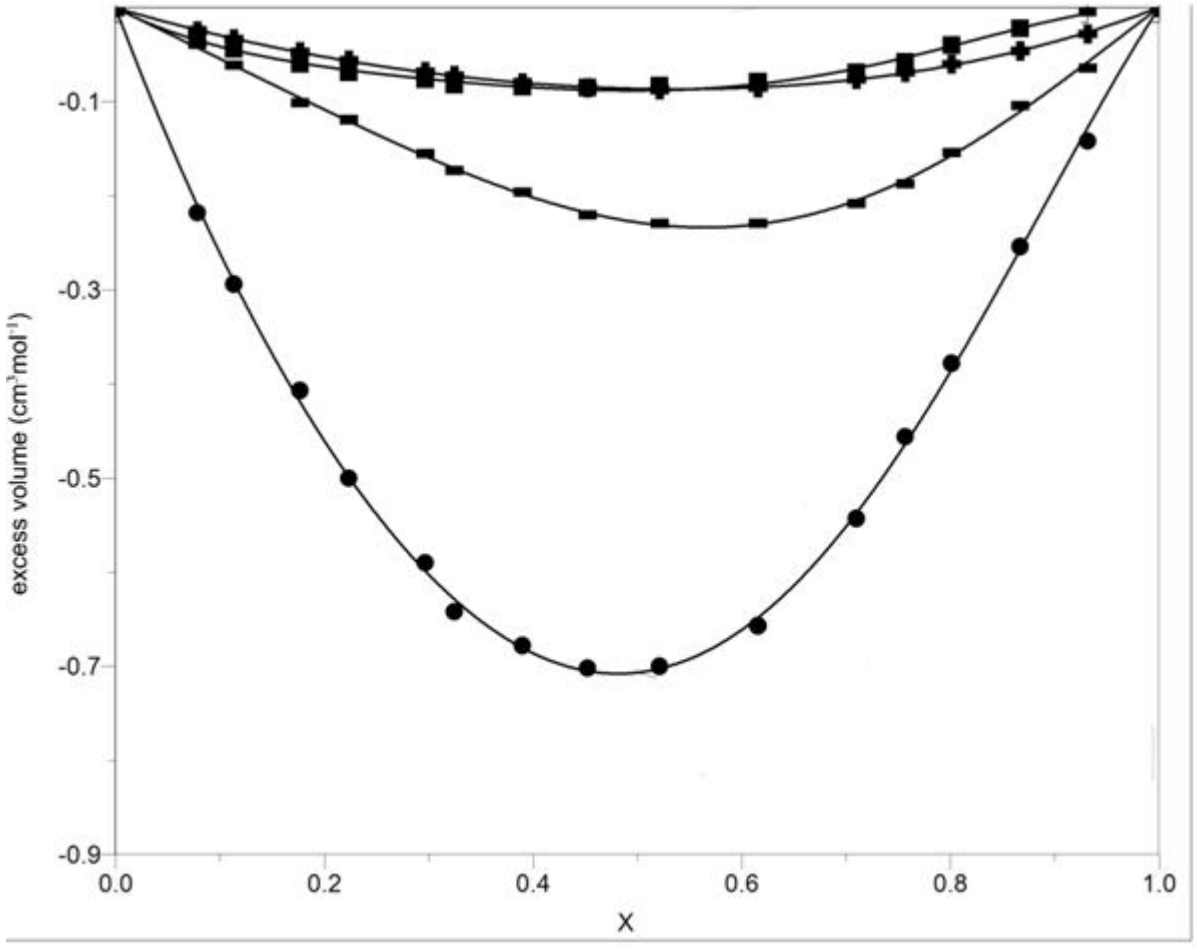

Figure 1: Excess volumes for various mixtures against mole fraction. $xCHCl_2CHCl_2+(1-x)$**C_5H_5N**(✚); **x**$CHCl_2CHCl_2+(1-x)C_6H_5OCH_3$ (■); $xCHCl_2CHCl_2 + (1 - x)\ CH_3COC_2H_5$ (●) $xCHCl_2CHCl_2 + (1 - x)$ ($1,4-C_4H_8O_2$) (▬) at 298.15K

Excess volume data for different mixtures were fitted to an appropriate equation as given below:

$$V^E = x\,(1-x)\sum_{i=1}^{N} A_i\,(2x-1)^{i-1} \quad - \quad \textbf{(1)}$$

In the above equation, x, represents the mole fraction of acetylene tetrachloride**.** The values of the all coefficients arising from the fits and the consequent standard deviations are summarized in Table 2. Standard deviation is calculated in the same way as given in our earlier paper. (Tripathi, AD et. al. 2021).

Table 2: Least Squares Coefficients of Eq 1 for the Excess Molar Volumes, and the standard deviations, σ, of $CHCl_2CHCl_2$(1)+ C_5H_5N (1-x); $CHCl_2CHCl_2$(1) +$C_6H_5OCH_3$ (1-x); $CHCl_2CHCl_2$(1) +$CH_3COC_2H_5$(1-x); and $CHCl_2CHCl_2$(1)+ (1,4-$C_4H_8O_2$)(1-x) at the temperature 298.15K

System	A0	A1	A2	A3	σ/ (cm^3 mol^{-1})
$CHCl_2CHCl_2$(x)+ C_5H_5N (1-x)	-0.3443	-0.0498	-0.0307	0.003	0.001
$CHCl_2CHCl_2$(x) +$C_6H_5OCH_3$(**1-x**)	-0.3523	0.0074	0.0773	0.292	0.004
$CHCl_2CHCl_2$(x) +$CH_3COC_2H_5$(**1-x**)	-2.827	0.2409	0.4976	0.388	0.008
$CHCl_2CHCl_2$(x)+ (1,4-$C_4H_8O_2$)(**1-x**)	-0.9123	0.3228	0.2261	0.179	0.004

The data show that the excess volume, V^E shows negative trend for the system of acetylene tetrachloride with pyridine, methoxybenzene, 2-butanone and 1,4-dioxane at the temperature 298.15K. At mole fraction, x=0.5, the excess volume decreases in the following order:

Pyridine > methoxybenzene > 1,4-dioxane> 2-butanone

The negative values of V^E for all above mentioned systems indicate presence of creation of complexes between two components. The molecular interaction of pyridine with $CHCl_2$-$CHCl_2$ can be explained owing to the existence of two electrons on the N atom of pyridine, due to which it can perform as an n-donor in the direction of acetylene tetrachloride. The presence of benzene ring in pyridine can also take part in forming charge transfer complexes via Cl-π type interaction. 2-Butanone and 1,4-dioxane may also perform as n-donor components due to existence of lone pairs of electrons on the O atom. Methoxybenzene having -OCH3 (methoxy) group along with a benzene ring may perform as an nπ-type donor in the direction of acetylene tetrachloride. Acetylene tetrachloride will perform as σ-acceptor and forms intermolecular complexes due to hydrogen bonding with pyridine, methoxybenzene, 2-butanone and 1,4-dioxane. There is also chance to create a charge-transfer complex formation between chlorine atom of acetylene tetrachloride and lone pair electrons present in proton acceptor compounds. Highly negative values of V^E for the system of $CHCl_2$-$CHCl_2$ with 2-butanone may be explained as being due to electron repelling methyl group along with the lone pair electrons present on the O atom of 2-butanone.

CONCLUSION

For getting non-ideal behavior of acetylene tetrachloride with pyridine,methoxybenzene,2-butanone and 1,4-dioxane at the temperature 298.15K, excess molar volume of these systems have been determined in the liquid state.

The values of excess volumes obtained for these systems represent donor-acceptor interaction, in which CHCl2-$CHCl_2$ acts as σ-acceptor toward other compounds. Methoxybenzene performs as an nπ-type donor. 2-Butanone, pyridine and 1,4-dioxane may perform as an n-donors due to occurrence of lone pair of electrons present on O and N atom of latter compounds. However presence of C_6H_6 ring in pyridine may form charge transfer complexes via Cl-π type interaction with $CHCl_2$-$CHCl_2$.

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