Excess Molar Volume of Binary Mixtures of Tetrachloroethylene + Acetylacetone, + Acrylonitrile, + Anisole and + Tetrahydrofuran at 303.15 K

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Abstract: Excess molar volumes have been measured by means of a dilatometer for tetrachloroethylene (TCE) +acetyl acetone, + acrylonitrile, +anisole and+ tetrahydrofuran at 303.15 K. V^E_m values are positive over the entire range of composition for TCE- anisole and TCE – acetyl acetone and negative for TCE- Tetrahydrofuran. For TCE – acrylontrile, V^E_m has been found to be negative up to x = 0.8379 and positive onward. Values of V_m^E for the various systems have been fitted by the method of least squares with smoothing equation, and have been discussed from the viewpoint of the existence of specific interactions between the components.

Keywords: Tetrachloroethylene, dilatometer, excess volume, specific interaction.

INTRODUCTION

Acetyl acetone ($C_5H_8O_2$) is an organic compound that famously exists in two tautomeric forms that rapidly interconvert. The more stable tautomer is a diketone formally named pentane-2, 4-Dione. The less common tautomer is the enol form. The pair of tautomers rapidly interconvert and is treated as a single compound in most applications. It is a colourless liquid that is a precursor to acetyl acetonate, a common bidentate ligand. It is also a building block for the synthesis of heterocyclic compounds. Acrylonitrile is a chemical compound with the formula C_3H_3N. This colorless liquid often appears yellow due to impurities. It is an important monomer for the manufacture of useful plastics such as polyacrylonitrile. In terms of its molecular structure, it consists of a vinyl group linked to a nitrile.

Anisole, or methoxybenzene, is an organic compound with the formula $CH_3OC_6H_5$. It is a colorless liquid with a smell reminiscent of anise seed, and in fact many of its derivatives are found in natural and artificial fragrances. The compound is mainly made synthetically and is a precursor to other synthetic compounds. Tetrahydrofuran (THF) is an organic compound with the formula $(CH_2)_4O$. The compound is classified as heterocyclic compound, specifically a cyclic ether. It is a colorless, water-miscible organic liquid with low viscosity. THF has an odor similar to acetone. It is mainly used as a precursor to polymers. Being polar and having a wide liquid range, THF is a versatile solvent. Tetrachloroethylene, also known under the systematic name tetrachloroethene, or perchloroethylene ("perc" or "PERC"), and many other names, is a chlorocarbon with the formula $Cl_2C=CCl_2$. It is a colorless liquid widely used for dry cleaning of fabrics, hence it is sometimes called "dry-cleaning fluid." It has a sweet odor detectable by most people at a concentration of 1 part per million (1 ppm).

As a part of our continuing efforts to obtaining thermodynamic and physicochemical quantities on organic liquid mixtures [1-6], we have made measurements on excess volumes for organic liquid mixtures. Binary systems of tetrachloroethylene (CCl_2CCl_2) (and hereafter referred to simply as TCE) with acetyl acetone, acrylonitrile, anisole and tetrahydrofuran are of considerable interest from the viewpoint of the existence of specific interaction between the components in the liquid state. A binary mixture is formed by the replacements of like contacts by unlike contacts in the mixture. The specific interaction of TCE with these compounds is due to the fact that TCE can be visualized to be due to the presence of 4 Cl atoms and an olefinic π-electron system in C_2Cl_4 , on account of which it can act both as a σ & π–type sacrificial electron acceptor toward acetyl acetone, acrylonitrile, anisole and tetrahydrofuran. Latter will act as n- donors. Extensive studies concerning the properties of these systems have not been made in the literature. To the best of our knowledge, there are no literature values for excess volumes available for these systems for comparison. The measurements of excess volumes for the mixtures of TCE with benzene, toluene, p-xylene, cyclohexane and carbon tetrachloride at 303.15 have been reported in the literature [7]. These authors have interpreted

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Table 1: Densities of the Pure Components at 303.15 K

Compound	Density g. cm^{-3} Experimental	Literature
Tetrachloroethylene	1.60632	1.6064[a]
Acetylacetone	0.96345	0.9721[b]
Acrylonitrile	0.79474	0.7948[a]
Anisole and	0.98445	0.98462[a]
Tetrahydrofuran	0.87902	0.8791[a]

[a]Ref. [11], Riddick and Bunger (1970) [b]Ref. [12], Hand book of Physics and Chemistry.

their results through possible existence of specific interaction of TCE with other components. In the present programme, measurements of excess molar volumes (V^E_m) at 303.15 K have been reported for binary liquid mixtures of TCE with acetyl acetone, acrylonitrile, anisole and tetrahydrofuran and the results obtained have been interpreted in this paper.

EXPERIMENTAL SECTION

Materials

Tetrachloroethylene (Reedel, 99%) was dried and fractionally distilled over fused $CaCl_2$. Acetyl acetone (B.D.H, 99.5%) was dried over fused $CaCl_2$ and then distilled twice over P_2O_5. Acrylonitrile (B.D.H., 99%) was dried over fused $CaCl_2$ and distilled. Anisole (Bush Company Ltd., 99%) was distilled twice over sodium metal . Tetrahydrofuran (Thomas Baker & CO.,99.6%) was kept over KOH for a few days, refluxed over lithium aluminum hydride for about 6 hrs and then fractionally distilled. An Anton- Paar vibrating – tube densimeter (Model DMA 60/ 602) was used for the measurement of densities [1]. It was equipped with calibrated thermometers with a precision of 0.01 K, connected with a Heterofrig constant-temperature bath circulator, with a precision of 0.01 K. For the densimeter calibration, nitrogen and double-distilled water were used. The estimated precision in density measurement is higher than $3x10^{-5}$ $g.cm^{-3}$.

The purity of chemicals was checked by measuring their densities and comparing experimental values with the best available literature values (Table **1**).

Determination of Excess Molar Volume

The excess molar (V^E_m), which are accurate to ± 0.002 cm^3mol^{-1}, were measured by using a two – limbed Pyrex glass dilatometer [8, 9]. The mixtures were prepared by direct weighing of components. Known amounts of the two liquid components were introduced over mercury in the absence of air bubbles in the two limbs of the dilatometer. The dilatometer mounted on the stand and was immersed in the thermostat bath which was controlled to ± 0.01K. All the measurements were made on a thermostatically controlled, well stirred water bath. The mixing of the components was achieved by rocking the cell back and forth through a defined angle and the mercury levels in the capillary of the dilatometer was noted with a cathetometer which could read correct to ± 0.001cm. The working of the dilatometer was tested by measuring V^E_m for the system of Benzene+ Cyclohexane at 298.15 K as described elsewhere [7]. The measured value of excess molar volume for this system agrees well with the literature values.

RESULTS AND DISCUSSION

Excess molar volumes of binary mixtures of CCl_2CCl_2 + acetyl acetone, + acrylonitrile, + anisole and + tetrahydrofuran at 303.15 k are collected in Table **2**. The experimental results were fitted to the equation

$$V^E / (cm^3.mol^{-1}) = x_1 x_2 \sum_{i=0}^{m} A_i (x_1 - x_2)^i \quad (1)$$

Where x_1 is the mole fraction of TCE. The parameters A_n and standard deviations ,σ , are listed in Table **3**.

The standard deviations, σ, are calculated using equation

$$\sigma = [\sum (V^E - V^E_{calc})^2/(m-n)]^{1/2} \quad (2)$$

Where V^E is the experimental excess molar volume and V^E_{calc} calculated excess molar volume using equation (1), m is number of experimental data & n is number of constants characteristic of a system.

Graphical presentation of experimental values of data is presented in Figure **1**.

Table 2: Experimental Values of Excess Molar Volumes (V^E_m) of Tetrachloroethylene (Cl_2CCl_2C) (TCE) (1) + acetyl acetone (2), + acrylonitrile (2), + anisole (2), and + tetrahydrofuran (2) at 303.15 K

TCE + acetyl acetone	
X_1	V^E_m ($cm^3.mol^{-1}$)
0.0330	0.031
0.0997	0.079
0.1532	0.108
0.2319	0.142
0.2806	0.158
0.3391	0.176
0.3766	0.186
0.4087	0.19
0.4347	0.196
0.4473	0.197
0.4572	0.200
0.4638	0.201
0.4995	0.203
0.5202	0.204
0.5372	0.203
0.5386	0.202
0.5699	0.203
0.5739	0.202
0.5945	0.198
0.6288	0.195
0.6747	0.184
0.7352	0.164
0.8027	0.135
0.866	0.102
0.932	0.053
0.9835	0.006
TCE + acrylonitrile	
0.0280	-0.026
0.1042	-0.075
0.1552	-0.099
0.2291	-0.120
0.3038	-0.127
0.3585	-0.128
0.4109	-0.123
0.4647	-0.114
0.4918	-0.109
0.5356	-0.097
0.5431	-0.089
0.5712	-0.084
0.5891	-0.075
0.5976	-0.077
0.6383	-0.059
0.698	-0.042
0.7626	-0.022
0.8379	-0.0003
0.9111	0.008
0.9959	0.001
TCE + tetrahydrofuran	
0.0528	-0.056
0.1097	-0.09
0.1497	-0.108
0.2055	-0.126
0.2582	-0.139
0.2998	-0.147
0.3358	-0.149
0.3663	-0.151
0.3871	-0.152
0.3964	-0.151
0.4236	-0.151
0.4244	-0.151
0.4492	-0.149
0.4544	-0.149
0.4765	-0.147
0.4894	-0.144
0.5202	-0.14
0.5517	-0.134
0.5972	-0.126
0.6504	-0.115
0.7059	-0.102
0.7737	-0.083
0.8424	-0.062
0.8882	-0.046
0.9416	-0.026
0.9988	-0.007
TCE + anisol	
0.0706	0.022
0.0988	0.04
0.1459	0.059
0.2091	0.09
0.2618	0.114
0.3273	0.136
0.3674	0.15
0.4144	0.162
0.4733	0.181
0.4967	0.186
0.5518	0.19
0.5821	0.189
0.6085	0.19
0.6453	0.185
0.6952	0.174
0.7488	0.16
0.8093	0.135
0.8801	0.093
0.9523	0.047

(Table 2). Continued.

Table 2: Least Squares Coefficients of Eq 1 for the Excess Molar Volumes, and the standard deviations, σ, of Tetrachloroethylene (Cl_2CCl_2C) (1) + acetyl acetone (2), + acrylonitrile (2), + anisole (2), and +tetrahydrofuran (2) at 303.15 K

System	A0, $cm^3.mol^{-1}$	A1, $cm^3.mol^{-1}$	A2, $cm^3.mol^{-1}$	A3, $cm^3.mol^{-1}$	σ/ ($cm^3.mol^{-1}$)
CCl_2CCl_2 (1) + acetylacetone (2)	0.8083	0.1031	0.0664	-0.1853	0.003
CCl_2CCl_2 (1) + acrylonitrile (2)	-0.4171	0.5137	0.08695	0.07083	0.002
CCl_2CCl_2 (1) + anisole (2)	0.7354	0.2751	-0.1028	0.04281	0.003
CCl_2CCl_2 (1) +Tetrahydrofuran (2)	- 0.5712	0.2437	-0.1792	0.07643	0.002

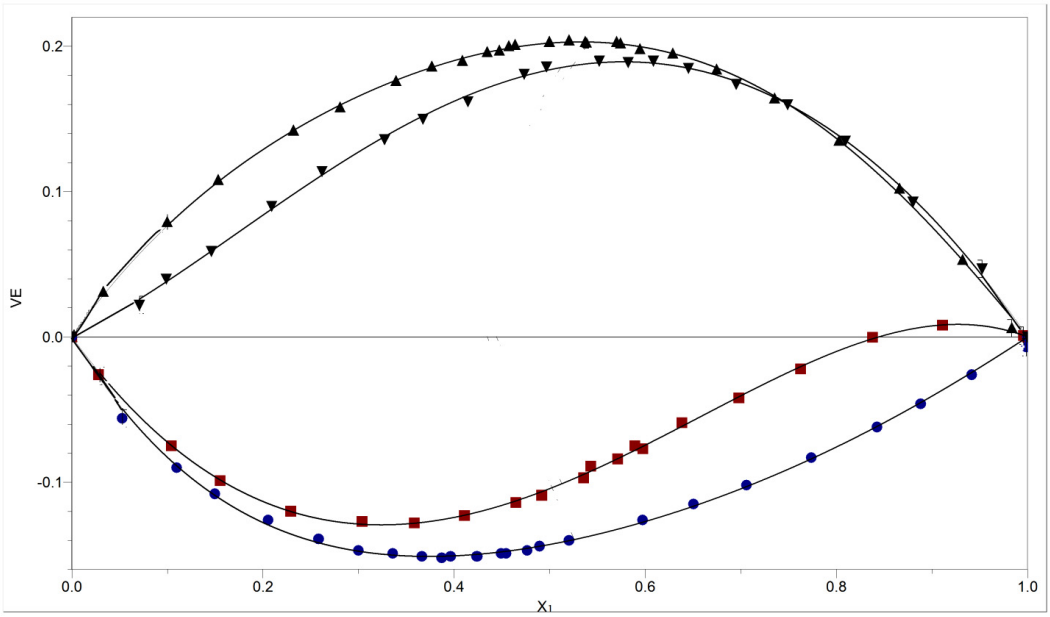

Figure 1: Excess molar Volumes of binary liquid mixtures of x_1 of Tetrachloroethylene (Cl_2CCl_2C) (1) + acetylacetone (2) ▲, + acrylonitrile(2) ■, + anisole (2) ●, and + tetrahydrofuran (2) ▼, at 303.15 K.

V^E_m (x_1 = 0.5) values lie in the increasing order: tetrahydrofuran <acrylonitrile< anisole< acetyl acetone. Table **3** shows that the values of V^E_m are negative for TCE-tetrahydrofuran whereas for TCE+ acrylonitrile, it is negative up to x=0.8379 and positive onward.

Negative V^E_m arise due to increased interactions between the unlike molecules or it would arise from specific interactions between the molecules of the two components [10]. Therefore increasing V^E_m for TCE +anisole, + acetyl acetone, which is positive, can be attributed to the decrease in specific interactions.

In spite of the presence of carbonyl groups in acetyl acetone, the system of TCE-acetyl acetone shows only moderately strong interactions between the unlike molecules. The negative excess molar volumes for TCE-tetrahydrofuran point to the existence of specific interactions between O(of THF) and Cl (of TCE) or between H atom of tetrahydrofuran or anisole and the π –electrons of the TCE , as it is also known that a complex is formed through hydrogen bonding between acetone and dibromomethane [3]. The specific interactions of TCE with all these compounds may be due to a charge transfer interaction of Cl atoms or π-electrons in CCl_2CCl_2 with lone pair electrons on oxygen atom of acetyl acetone, anisole and tetrahydrofuran and with lone pair electrons on nitrogen atom of acrylonitile. The negative values of V^E_m for the system TCE +tetrahydrofuran, and +acrylonitrile indicate the existence of specific interaction between these components, leading to the formation of molecular complexes in the liquid state. The values of V^E_m which are slightly negative for these two mixtures; indicate that the specific interaction is weak.

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