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Excess Molar Volumes of Binary Mixtures of Acetylene Tetrachloride ($CHCl_2CHCl_2$)+Benzene(C_6H_6),+Toluene($C_6H_5CH_3$)+Acetone(CH_3COCH_3) and + Pyridine (C_5H_5N) at 303.15 K

Abstract
Excess molar volumes, V^E, at T = 303.15 K, have been measured for binary liquid mixtures of Acetylene tetrachloride ($CHCl_2$ $CHCl_2$) + Benzene (C_6H_6),+Toluene($C_6H_5CH_3$),+ Acetone (CH_3COCH_3), and + Pyridine (C_5H_5N) at 303.15 K. The values of V^E have been fitted in appropriate equations using a least-squares method. V^E has been found to be negative throughout the entire range of composition for all mixtures. The results obtained have been discussed from the viewpoint of existence of specific interactions between the components in the liquid state.

Keywords: Acetylene tetrachloride, acetone, toluene, specific interaction, excess volume.

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Introduction

Mixtures of Acetylene tetrachloride ($CHCl_2$ $CHCl_2$)+ Benzene(C_6H_6),+Toluene($C_6H_5CH_3$),+Acetone(CH_3COCH_3) ,and + Pyridine(C_5H_5N) are of meticulous attention from the perspective of electron transfer interaction which results to the creation of new complexes between the different species taken in the liquid state. The specific interaction of $CHCl_2$ $CHCl_2$ with the above compounds can be visualized as resulting from the presence of two H atoms and four number of Cl atoms of Acetylene tetrachloride, which can make this species perform as σ-acceptor in the direction of these compounds. In contrast, C_6H_6,$C_6H_5CH_3$, can participate in the creation of H-bond with, and perform as π-donors on the way to $CHCl_2CHCl_2$, whereas CH_3COCH_3 and C_6H_5N , together will operate as n-donors . Although Many workers (Nath J.et.al.1983,1984, Pathak G. et.al.1995, Tripathi AD 2010) have measured excess volumes, V^E , speeds of sound, u, dielectric constants, excess enthalpy and refractive indices, for acetone or cyclopentanone, furan or methylfuran with tetrachloroethane and dibromomethane, wide-ranging studies regarding interactions between the

components of different mixtures of chloroalkanes and donor components of additional complexity are not accessible in the literature. Consequently, in this work, we have measured excess volumes, V^E, of $CHCl_2$ $CHCl_2$+C_6H_6,+$C_6H_5CH_3$,+ CH_3COCH_3 ,and + C_5H_5N at the temperature 303.15K, and the achieved data are collected and interpreted in this paper.

EXPERIMENTAL SECTION

Materials

C_6H_6,and $C_6H_5CH_3$, both were of AR quality, were subjected for purification in the same way as given by by elsewhere (Nath et.al. 1983). Acetone (AR grade) was kept over anh. $CaCl_2$ for 8 hrs and then fractionally distilled from P_2O_5. $CHCl_2$ $CHCl_2$ (Reidel) was shudderd with K_2CO_3 solution and was further dried over anhydrous K_2CO_3, and then finally distilled . Pyridine is purified in the manner as given in our earlier communication (Tripathi AD 2010). An Anton- Paar vibrating – tube densimeter (Model DMA 60/ 602) was taken for the measurement of densities. A thermometer with a precision of 0.01 K was used. For the densimeter calibration, N_2 and distilled H_2O were used. The estimated precision in density measurement is higher than $3x10^{-5}$ $g.cm^{-3}$.

The purity of chemicals was checked by determining their densities and the results obtained were compared with the literature values(Riddick JA. 1970).For dosimeter calibration, nitrogen and distilled H_2O were used. The estimated precision in density measurement is higher than $3x10^{-5}$ $g.cm^{-3}$.

Method

Excess volumes, V^E, were obtained (in the order of reproducibility of $\pm$0.002 cm^3,mol^{-1}), with the help of a two-branched, glass made dilatometer that was a similar which is was utilized in our prior publication (Nath J.et.al.1983). Weighed quantities of the two liquids were locked up individually over Hg in the inadequacy of air gaps in both the extremities of the dilatometer, which (situated on a wooden stand) was submerged in water of a thermostat (reproducibility $\pm$0.01 K). Both the liquids were mixed by shaking the cell from side to side through a specific angle, and the Hg level in the capillary was noted by means of a a cathetometer (accuracy of 0.001 cm). The functioning of the dilatometer was tested by measuring V_m^E for the system of C_6H_6+ C_6H_{12} at 303.15 K as described elsewhere (Nath J et.al.1983). The measured value of excess molar volume for this system agrees well with the literature data.

Results and discussion

The data obtained for V^E of the binary mixtures of $CHCl_2$ $CHCl_2$ at the Temperature 303.15 K are reported in Table 1 and plotted against mole fraction $x1$ in Figure 1. V^E data for all binary mixtures have been fitted by using following equation

$$V^E /(J.mol^{-1}) = x1x2 \sum_{i=0}^{m} Ai(x1 - x2)^i \qquad (1)$$

where $x1$ refers to the mole fraction of $CHCl_2$ $CHCl_2$. The values of all constants A_i alongwith standard deviations, σ, are collected in Table 2.

Following equation have been used to calculate standard deviations, σ

$$\sigma = \left[\frac{\sum(V^E - V^E_{cal})^2}{(m-n)}\right]^{1/2} \qquad (2)$$

where V^E is the experimental value of excess molar volume and V^E_{calc} refers to calculated value by means of eq.1, m represents number of experimental data and n , the number of constants . In fig.1 , a plot of experimental values of V^E vs mole fraction is given.

It is observed that if V^E values are negative, interaction factor leads whereas the positive V^E values are indicative of steric factor in the binary mixtures.

When values of V^E are negative, it is due to increased interactions between the dissimilar molecules or it would arise from specific interactions between the molecules of the two components. These -ve values of V^E shows that between unlike molecules, there is high probability of the H-bonded type interaction which occurs at the time of mixing. The packing effect may be the reason behind this. When the values of V^E are +ve , the decrease in specific interactions may take place.

The sign of V^E shows the force of association acting between the molecules of the different parts. Negative values of V^E is due to a closer move toward dissimilar molecules , cause to decrease in absolute volume and compressibility. Various types of powers acting between the contrasting components are dispersion , hydrogen bonding, dipole–dipole, charge transfer and dipole induced dipole type interactions. Attraction between the molecules is expected due to dispersion forces , and the relative magnitudes of the A–A, B–B, A–B type contacts between the molecules of components A and B of a mixture are essential for determination of excess properties. In the case, if shape and size of components of a mixture do not differ very much, the

dispersion forces causes +ve contributions to V^E. However, other remaing interactions must lead to -ve contributions to V^E . All systems are operated by dispersion forces , and if there is more than one type of interaction occur in a system, the sign of V^E depends upon the total effect of the contributions made by all types of interactions.

From the Table 1, it is clear that V^E is negative all over the entire range of mole fraction for binary liquid mixtures of $CHCl_2CHCl_2$ + $Benzene(C_6H_6)$,+$Toluene(C_6H_5CH_3)$,+Acetone(CH_3COCH_3) ,and + $Pyridine(C_5H_5N)$. At $x1$ = 0.5, the values of V^E for the different systems of $CHCl_2CHCl_2$ has the order:

$$Benzene(C_6H_6), > Toluene(C6H_5CH_3) > Acetone(\ CH_3COCH_3) > Pyridine(C_5H_5N)$$

The -ve values of V^E for mixtures of $CHCl_2CHCl_2$ $Benzene(C_6H_6)$,+$Toluene(C6H_5CH_3)$,+Acetone(CH_3COCH_3) ,and + $Pyridine(C_5H_5N)$ can be expected due to a closer approach of the dissimilar molecules in solution, thus representing the presence of specific interaction between π electrons of benzene or toluene and H (of $CHCl_2CHCl_2$), or between O atom of acetone or N atom of pyridine , it is similar to that a complex is created by means of hydrogen bonding between CH_3COCH_3 and CH_2Br_2 in the liquid state as given elsewhere (Tripathi AD 2010). $CHCl_2CHCl_2$ in this case will perform as σ-acceptor . The specific interactions of $CHCl_2CHCl_2$ with all these compounds may also be due to a charge transfer interaction of Cl atoms of $CHCl_2CHCl_2$ with lone pair electrons on oxygen atom of acetone or N atom of pyridine. It is observed that the strength of these intermolecular forces is more for the those systems which have more Cl atoms connected to C−H pair atoms. It is thus revealed that the factor due to interaction is presiding over for the mixtures with -ve sign of V^E values while the factor due to steric hindrance succeeds for mixtures with +ve sign. For interaction between the alkanes having chloro group and cycloketones , different forms of interaction occur : formation of charge-transfer complexes, due to the interactions of Cl atoms from chloro-compounds with the non-bonding pair electrons of the oxygen atom in ketones, hydrogen bonding, due to the interaction of H atoms from chloroalkanes with the non-bonding -pair electrons of the O atom present on ketones. Also there is likelihood of dipole-dipole interactions between dissimilar molecules, which has been explained as being due to the charge-transfer interaction between Cl atoms of $CHCl_2CHCl_2$ and the nonbonding -pair electrons present on acetone or pyridine molecule.

Table 1. Experimental Values of the Excess Molar Volumes, V^E, for Acetylene tetrachloride ($CHCl_2$ $CHCl_2$)+ Benzene(C_6H_6),+Toluene($C_6H_5CH_3$),+Acetone(CH_3COCH_3) ,and + Pyridine(C_6H_5N), at 303.15 K.

$x1CHCl_2CHCl_2 + (1 - x1)C_6H_6$

$x1$	V^E ($Cm^3.mol^{-1}$)
0.0987	-0.004
0.1434	-0.008
0.2098	-0.018
0.2567	-0.025
0.3099	-0.032
0.3675	-0.043
0.4123	-0.045
0.4644	-0.046
0.5411	-0.049
0.6088	-0.041
0.7233	-0.031
0.8177	-0.017
0.9064	-0.008
0.9544	-0.003

$x1CHCl_2CHCl_2 + (1 - x1)C_6H_5CH_3$

$x1$	V^E ($Cm^3.mol^{-1}$)
0.0678	-0.038
0.1075	-0.059
0.1789	-0.096
0.2045	-0.118
0.2611	-0.134
0.3245	-0.150
0.3597	-0.157
0.4156	-0.163
0.4698	-0.163
0.5145	-0.159
0.6789	-0.113
0.7231	-0.095
0.8677	-0.034
0.9034	-0.025

0.9586	-0.006
0.0678	-0.038

$x1CHCl_2CHCl_2 + (1 - x1)CH_3COCH_3$

$x1$	V^E ($Cm^3.mol^{-1}$)
0.1124	-0.303
0.1785	-0.430
0.1902	-0.458
0.2608	-0.544
0.3266	-0.621
0.3678	-0.630
0.4311	-0.653
0.5288	-0.654
0.6444	-0.601
0.7089	-0.545
0.7654	-0.480
0.8043	-0.425
0.8567	-0.337
0.9099	-0.230
0.9533	-0.127

$x1CHCl_2CHCl_2 + (1 - x1)C_5H_5N$

$x1$	V^E ($Cm^3.mol^{-1}$)
0.0784	-0.023
0.1133	-0.026
0.1765	-0.040
0.2234	-0.049
0.2965	-0.061
0.3244	-0.065
0.3897	-0.073
0.4522	-0.078
0.5213	-0.085
0.6155	-0.077
0.7098	-0.069
0.7567	-0.062
0.8009	-0.053
0.8666	-0.039
0.9316	-0.022

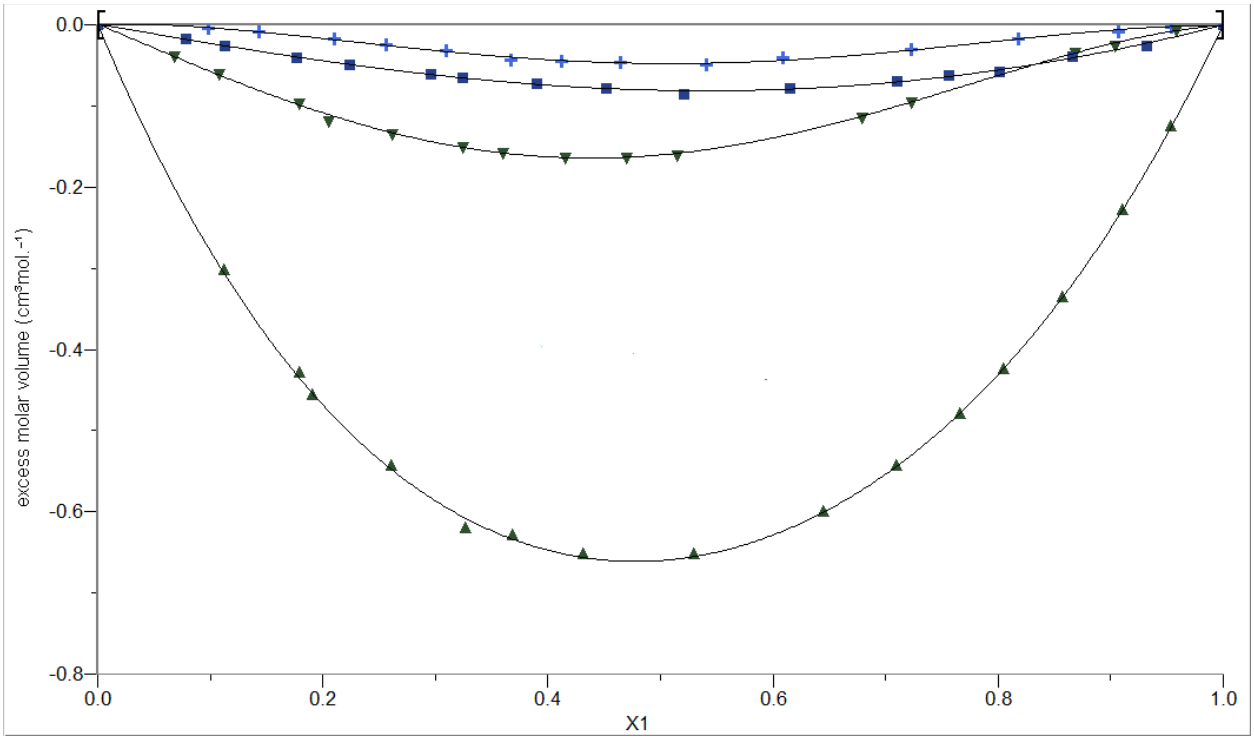

Fig.1 Excess molar volumes of binary liquid mixtures of X_1 of Acetylene tetrachloride(CHCl2.CHCl2(1) with Benzene (C_6H_6(2) ( ) , + toluene ( )(2) ,+acetone( ) , (2) and + pyridine ( ) (2) at 303.15 K. The smoothed curves are based on the parameters A0,A1, A2and A3 given in Table 2.

Table 2. Least Squares Coefficients of Eq 1 for the Excess Molar Volumes , and the standard deviations,σ,of Acetylene tetrachloride (CHCl2.CHCl2)(1) +Benzene(C_6H_6)(2)or + Toluene (2),or + Acetone (2),or +Pyridine(2) at 303.15 K

System	A0	A1	A2	A3	σ/ (J mol^{-1})
$CHCl_2$ $CHCl_2$(1)+ C_6H_6 (2)	-0.1907	-0.0148	0.2069	0.0008	0.002
$CHCl_2$ $CHCl_2$(1) + C_6H_5 CH_3 (2)	-0.6417	0.2416	0.2954	0.0007	0.003
$CHCl_2$ $CHCl_2$(1) + CH_3 $COCH_3$ (2)	-2.641	0.1962	-0.4711	-0.0008	0.004
$CHCl_2$ $CHCl_2$(1) + C_6H_5N (2)	-0.3217	- 0.04854	0.03298	0.0007	0.002

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