



## Thermodynamic study of binary liquid mixtures of toluene and 1,2-dichloroethane at T = 303.15 K

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### ABSTRACT

Thermodynamic studies like density ( $\rho$ ), specific gravity, ultrasonic speed ( $u$ ) and excess molar volume ( $V_m^E$ ) and molar excess enthalpy of binary liquid mixtures of toluene + 1,2-dichloroethane have been carried out over the different range of composition at 303.15 K. Thermodynamic parameters like isentropic compressibility  $K_s$ , intermolecular free length,  $L_f$ , Relative association,  $R_a$ , have been computed from experimental findings. The excess thermodynamic functions have been fitted to the Redlich-Kister polynomial equation. The experimental ultrasonic speeds have been analyzed in terms of Jacobson Free Length Theory (FLT), Schaaff's Collision Factor Theory (CFT), Nomoto's relation, and Van Dael's ideal mixture relation. Intermolecular Free Length,  $L_f$ , and available volume,  $V_a$ , have been calculated from FLT, CFT and thermoacoustic approach. It is observed that density and specific gravity increases and ultrasonic speed, isentropic compressibility and intermolecular free length decreases with the mole fraction of 1,2-dichloroethane. It is found that intermolecular interactions present between binary liquid mixtures are stronger than pure solvent-solvent interactions. Observed negative values of excess molar volume and positive value of molar excess enthalpy confirm the presence of specific chemical attractive force of interactions between the two binary liquid mixtures. © 2013 Trade Science Inc. - INDIA

### KEYWORDS

Ultrasonic speed;  
Excess molar volume;  
Molar excess enthalpy;  
Toluene and 1,2-dichloroethane.

### INTRODUCTION

The measurement of thermodynamic and acoustic properties contributes to the understanding of the physicochemical behavior of the binary and multi-component liquid mixtures. Excess properties of liquid systems, such as molar volumes, are required for testing

the theories of solutions, development of separation techniques and equipment, and for other industrial applications. Toluene is a common solvent, able to dissolve paints, paint thinners, silicone sealants, many chemical reactants, rubber, printing ink, adhesives (glues), lacquers, leather tanners, and disinfectants. It can also be used as a fullerene indicator, and is a raw material

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for toluene diisocyanate (used in the manufacture of polyurethane foam) and TNT. In addition, it is used as a solvent to create a solution of carbon nanotubes. The chemical compound 1,2-dichloroethane, commonly known by its old name of ethylene dichloride (EDC), is a chlorinated hydrocarbon, mainly used to produce vinyl chloride monomer (chloroethene), the major precursor for PVC production. It is a colourless liquid with a chloroform-like odour. 1,2-Dichloroethane is also used generally as an intermediate for other organic chemical compounds and as a solvent. Thus, a study of physical properties data on the binary mixture containing 1,2-dichloroethane and toluene has attracted considerable interest in the literature<sup>[1-3]</sup>. Thus, 1,2-dichloroethane in toluene mixed solvent would enable us to have a large number of solvents with appropriate physico-chemical properties, which can be used for a particular chemical process. Moreover, literature survey indicates that no ultrasonic study on this binary system has been reported at 303.15 K. Therefore, present study was undertaken in order to have deeper understanding of the intermolecular interaction between the components of the above binary liquid mixture. Thus, a study of thermodynamic properties data on the binary mixture of 1,2-dichloroethane in toluene has attracted considerable interest in our present study.

Research workers in the past have shown that NMR<sup>[4,5]</sup>, IR<sup>[6-7]</sup> and Raman spectra<sup>[8]</sup>, have been used to study molecular interactions. The velocity measurement of the propagation of ultrasonic waves<sup>[9-13]</sup> and their absorption<sup>[14,15]</sup> have already been found to be useful in the study of molecular interactions for inorganic, organic and organo-metallic binary systems. Likewise, researchers<sup>[16-21]</sup> have also employed ultrasonic measurements to look into the important consequences of ion-solvent interactions for the structure of electrolytic solutions. References<sup>[22,23]</sup> related to the field of medicine, whereas references<sup>[24-27]</sup> based on studies on emulsions/microemulsions, polymer surfactants interactions<sup>[28]</sup> and ultrasonic destruction of surfactants<sup>[29]</sup> are only a few cases to suggest versatility of the technique.

## EXPERIMENTAL

1,2-dichloroethane (CAS No. 107-06-2) was procured from Fischer Scientific Ltd. and are further puri-

fied by the methods given in Vogel text book of practical organic chemistry<sup>[30]</sup>. Prior to the experimental measurements, all the organic liquids were stored in dark bottles over 0.4 nm molecular sieves to reduce water content and were partially degassed with a vacuum pump under nitrogen atmosphere. The purities of all the samples determined by chromatographic analysis were better than 0.996 on a molar basis. Binary mixtures are prepared by mixing appropriate volumes of the liquid component in the specially designed glass bottles with air tight Teflon coated caps. The required properties are measured on the same day immediately after preparing each composition. The uncertainty in mole fraction is  $\pm 0.0001$ . A multi frequency digital micrometer reading ultrasonic interferometer (M-81, Mittal Enterprises, New Delhi) operating at 1, 2, 3 and 4 MHz was used to measure the ultrasonic velocity of the binary liquid mixtures (with an uncertainty of  $\pm 0.3\%$ ) at a constant temperature of 303.15 K by using a digital constant temperature water bath. The temperature stability is maintained within  $\pm 0.001\text{ K}$  by circulating thermostated water around the cell with a circulating pump connected to water bath. In order to minimize the uncertainty of the measurement, several maxima are allowed to pass and their number (fifty) is counted. All maxima are recorded with the highest swing of the needle on the micrometer scale. The total distance,  $d(\text{cm})$

moved by the reflector is given by  $d = \frac{n\lambda}{2}$ , where  $\lambda$  is the wavelength. The frequency  $\nu$ , of the crystal being accurately known (2.0 MHz), the speed of sound,  $u$  in  $\text{ms}^{-1}$  is calculated by using the relation  $u = \lambda\nu$ . Molar excess volume,  $V_m^E$  was calculated by specially designed double limbed glass dilatometer fitted with a microcapillary ( $\pm 0.01\text{ cm}$ ) in the centre. The density of solution was measured by a double arm pycnometer of bulb capacity 10 ml and a capillary of an internal diameter of about 1.0 mm. The mark of the stem was calibrated by double distilled water (conductivity less than  $1 \times 10^{-6}\text{ ohm}^{-1}\text{ cm}^{-1}$ ) with 0.9970 and 0.9940  $\text{g cm}^{-3}$  as its density at 298.15 K and 303.15 K, respectively with buoyancy corrected. The accuracy of the density results was  $\pm 0.0001\text{ (g cm}^{-3}\text{)}$ . Before each series of measurements, the instrument was calibrated with triple distilled freshly degassed water. The density and ultra-

sonic speed of binary mixtures were also measured by an Anton Paar Densitometer (DSA 5000). The accuracy of the density results was  $\pm 0.00001$  (g/cm<sup>3</sup>). Molar excess enthalpy was measured using two drop calorimeter Model 4000, Calorimetric Scientific Corporation, CSC. Weight measurement were performed on a Mettler Toledo AB 135-S/FACT, single pan analytical balance, with a precision of 0.01 mg. The densities, and ultrasonic speed,  $u$  of the pure liquids were in good agreement with the values found in the literature and are presented in TABLE 1.

## RESULTS

The molar excess volumes,  $V_m^E$ , of the solution were calculated from the densities of the pure liquids and their mixtures using the following equation<sup>[31]</sup>

$$V_m^E = \frac{(x_1 M_1 + x_2 M_2)}{\rho_{mix}} - \left( \frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (1)$$

Where  $\rho_{mix}$  is the density of the mixture and  $x_1, M_1, \rho_1$  and  $x_2, M_2, \rho_2$  are the mole fraction, molar mass, and the density of pure component 1 and 2, respectively.

The following relations have been used to correlate the sound velocity,  $u$ , of the binary liquid mixtures:

### Nomoto relation<sup>[32]</sup>

$$u = \left( \frac{R_m}{V_{mix}} \right)^3 = \left( \frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \right)^3 \quad (2)$$

Where  $x_1, x_2, V_1, V_2$  and  $R_1, R_2$  are mole fractions, molar volumes, and molar sound velocity of first and second components, respectively.

### Van dael relation<sup>[33]</sup>

$$\frac{1}{x_1 M_1 + x_2 M_2} \cdot \frac{1}{u_{id,mix}^2} = \frac{x_1}{M_1 u_1^2} + \frac{x_2}{M_2 u_2^2} \quad (3)$$

Where,  $M_1, M_2$  and  $u_1, u_2$  are the molar masses and sound velocities of first and second components, respectively, and  $u_{id,mix}$  is the ultrasonic velocity of the ideal mixture.

### Jacobson's free length theory (FLT)<sup>[34]</sup>

$$u_{mix} = \frac{K}{L_{f(mix)} \rho_{mix}^{1/2}} \quad (4)$$

Where  $K$  is the Jacobson constant which is temperature dependent only and its value is 642.15 at 313.15 K. The  $L_{f(mix)}$  is the intermolecular free length of the

binary mixtures, which is given by  $L_f = \frac{2V_a}{Y}$ . Here  $V_a$  represents the available volume per mole and  $Y$  is the surface area per mole and these may be expressed as

$$V_a = (V_T - V_0) \quad (5)$$

$$Y = (36\pi N_A V_0^2)^{1/3} \quad (6)$$

Here  $N_A$  is the Avogadro's number and  $V_0$  and  $V_T$  are the molar volumes at zero Kelvin and at temperature  $T$ , respectively. The  $V_0$  can be obtained from the following relation using critical temperature  $T_c$ :

$$V_0 = V_T \left( 1 - \frac{T}{T_c} \right)^{0.3} \quad (7)$$

The critical temperature,  $T_c$  is the mole fraction additive of the values of its pure components and is given by the relation:

$$T_c = x_1 T_{c(1)} + x_2 T_{c(2)} \quad (8)$$

The thermodynamic intermolecular free lengths,  $L_f$ , in the binary liquid mixtures have been calculated using the relation:

$$L_f = 2 \frac{[V_T - \{x_1 V_{0(1)} + x_2 V_{0(2)}\}]}{(x_1 V_1 + x_2 V_2)} \quad (9)$$

The ultrasonic intermolecular free lengths  $L_f$  have also been computed using the Schaaff's relation for available volume ( $V_a$ ):

$$V_a = V_T \left[ 1 - \frac{u}{u_\infty} \right] \quad (10)$$

Where,  $u$  is the ultrasonic velocity at temperature  $T$  and  $u_\infty$  is 1600 m.s<sup>-1</sup>.

### Schaaff's collision factor theory (CFT)<sup>[35-36]</sup>

$$u_{mix} = u_\infty (x_1 s_1 + x_2 s_2) \frac{[x_1 b_1 + x_2 b_2]}{V_{mix}} \quad (11)$$

Where,  $b$  and  $s$  are the geometric volume and collision factor, respectively. The actual volume of the molecule per mole of the liquid has been computed using the re-

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lations

$$b = \frac{4}{3} \pi r^3 N \quad (12)$$

Where,  $r$  is the molecular radius which has been computed using the Schaaff's relation<sup>[36]</sup>

$$r = \left( \frac{M}{\rho N} \right)^{1/3} \left[ \frac{3}{16\pi} \left[ 1 - \frac{\gamma RT}{Mu^2} \left( \sqrt{1 + \frac{Mu^2}{3\gamma RT}} - 1 \right) \right] \right]^{1/3} \quad (13)$$

$$b' = \left[ \frac{M}{\rho} - \frac{\gamma RT}{\rho u^2} \left( \left( 1 + \frac{Mu^2}{3\gamma RT} \right)^{1/2} - 1 \right) \right] \quad (14)$$

$$r = \left( \frac{3b'}{16\pi N} \right)^{1/3} \quad (15)$$

Where,  $b$  is the van der Waal's constant and is equal to four times the actual volume of the molecules per mole of the liquid, i.e.  $b=4b$ .

The thermoacoustical method<sup>[37-39]</sup> has also been employed to obtain the available volume,  $V_a$  using the relation

$$V_a = V_T \left( \frac{1}{K' + 1} \right) = V_T \left( \frac{1}{K'' + K' + 1} \right) \quad (16)$$

The  $K'$ ,  $K$ , and  $K''$  are known as isothermal, isobaric and isochoric acoustical parameters, respectively, and can be expressed by the relation

$$K' = K + K'' = \frac{1}{2} \left[ 3 + \frac{S^* (1 + \alpha T) + X}{\alpha T} \right] \quad (17)$$

$$K'' = 1 + \frac{X}{2\alpha T} \quad (18)$$

$$K = \frac{1}{2} \left[ 1 + \frac{S^* (1 + \alpha T)}{\alpha T} \right] \quad (19)$$

$$S^* = 1 + \frac{4\alpha T}{3} \quad (20)$$

The  $X$  is known as the isobaric temperature coefficient of internal pressure and can be expressed as

$$X = 2 \frac{(1 + 2\alpha T)}{V^{\tilde{C}_1}} \quad (21)$$

Where  $\tilde{V}$  represents the reduced molar volume and  $C_1$  is the Moelwyn-Hughes parameter and can be expressed as

$$\tilde{V} = \left[ \frac{\alpha T / 3}{1 + \alpha T} + 1 \right]^3 \quad (22)$$

$$C_1 = \frac{13}{3} + \frac{1}{\alpha T} \frac{4\alpha T}{3} \quad (23)$$

The thermal expansion coefficient,  $\alpha$ , has been calculated using the equation:

$$\alpha = \left( \frac{1}{\rho} \right) \left( \frac{\partial \rho}{\partial T} \right)_p \quad (24)$$

The isentropic compressibility has been calculated from Newton-Laplace's equation

$$k_s = \frac{1}{\rho u^2} \quad (25)$$

The excess isentropic compressibility was found out by using the relation,

$$k_s^E = k_s - k_s^{id} \quad (26)$$

Where,  $k_s^{id}$  the isentropic compressibility for the ideal mixture, was obtained according to Benson and Kiyohara<sup>[40]</sup> and Acree<sup>[41]</sup>:

$$k_s^{id} = \sum_i \phi_i \left[ k_{s,i} + \frac{TV_i \alpha_i^2}{C_{p,i}} \right] - T \left( \sum_i x_i V_i \right) \frac{\left( \sum_i \phi_i \alpha_i \right)^2}{\left( \sum_i x_i C_{p,i} \right)} \quad (27)$$

Where,  $\phi_i$  is the volume fraction of component  $i$  in the mixture,  $x_i$  is the corresponding mole fraction,  $T$  is the absolute temperature, and  $k_{s,i}$ ,  $V_i$ ,  $\alpha_i$  and  $C_{p,i}$  are the isentropic compressibility, the molar volume, the cubic expansion coefficient, and the molar heat capacity of pure components respectively. The cubic expansion coefficients were obtained from experimental density measurements performed in our laboratory at different temperatures.

The excess isentropic compressibility of the binary mixture were fitted with a Redlich-Kister polynomial equation<sup>[42]</sup>

$$k_s^E = x_1 x_2 \sum_{j=0}^n A_j (x_1 - x_2)^j \quad (28)$$

Where,  $A_j$  are the adjustable parameters.

Oswal<sup>[43]</sup> extended the Prigogine–Flory–Patterson (PFP) theory to estimate the isentropic compressibility's and speeds of sound of liquid mixtures. At a given temperature,  $T$ , the PFP theory can be used to calculate the molar volumes,  $V$  and the molar heat capacities,  $C_p$ , of a liquid mixture if the interaction parameter,  $x_{12}$ , is known.

Inter molecular free length and relative association has been calculated by the following formula:

$$L_f = K (K_s)^{1/2} \quad (29)$$

$$R_A = \frac{\rho}{\rho_0} \left( \frac{u_0}{u} \right)^{1/3} \quad (30)$$

Where  $\rho_0$  and  $u_0$  are the densities and ultrasonic speed of pure solvent,  $\rho$  and  $u$  are the density and ultrasonic speed of mixture respectively and  $K$  is the temperature dependent Jacobson constant ( $6.0816 \times 10^4$  at 35°C).

The deviation parameters of binary liquid mixtures have been evaluated using the general equation:

$$\Delta Y = Y_{\max} - (X_1 Y_1 + X_2 Y_2) \quad (31)$$

Where,  $Y$  indicates the parameter such as isentropic compressibility, inter molecular free length and ultrasonic speed.  $X_1$  and  $X_2$  are the mole fraction of component 1 and 2 respectively.  $\Delta Y$ ,  $Y_1$ ,  $Y_2$ , and  $Y_{\max}$  are the deviation parameter, parameters of the component 1 and 2 and observed parameters, respectively.

The number of contact sites per segment of a molecule, has been estimated using Bondi's method<sup>[44]</sup>. Molecular interaction parameter for each binary mixture was obtained by fitting the PFP theory to the corresponding experimental equimolar  $V^E$  values<sup>[45-46]</sup>. Once the interaction parameter is obtained, the isentropic compressibility and the speed of sound can be estimated.

Physical properties of pure substance like density, ultrasonic speed at 308.15 K are shown in TABLE 1. Density, speeds of sound,  $u$ , and specific gravity of binary liquid mixture of 1,2-dichloroethane in toluene over the different composition range at a temperature of 308.15 K are reported in TABLE 2. Values of molar excess volume,  $V_m^E$ , isentropic compressibility,  $K_s$ , intermolecular free length,  $L_f$ , and relative association,  $R_A$ , of the binary liquid mixture is shown in TABLE 3.

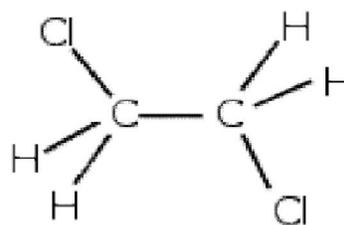
TABLE 4 shows molar excess volume of the binary liquid mixture of 1,2-dichloroethane in toluene at 308.15 K. Theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's (NOM) and Van Dael and Vangeel's (VD) ideal mixing relation were compared with experimental values and their percentage error for 1,2-dichloroethane (1) + toluene (2) at 303.15 K were shown in TABLE 4. The values of the coefficients of Redlich-Kister polynomial equation for all the binary mixtures along with values of the standard deviation are represented in TABLE 5 for 1,2-dichloroethane in toluene binary liquid mixture at 308.15 K.

TABLE 6 shows Intermolecular Free Length,  $L_f$ , calculated from Free Length Theory (FLT), Collision Factor Theory (CFT), and Thermoacoustic Approach (TAP). TABLE 7 shows available volume,  $V_a$ , calculated from FLT, CFT and TAP for 1,2-dichloroethane (1) + toluene (2) binary liquid mixture at 308.15 K.

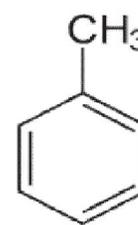
Figure 1 shows variation of molar excess volume with the mole fraction of 1,2-dichloroethane in toluene binary liquid mixture. Figure 2 shows variation of molar excess enthalpy with the mole fraction of 1,2-dichloroethane in toluene binary liquid mixture.

## DISCUSSION

Density and specific gravity of binary liquid mixtures of 1,2-dichloroethane in toluene increases with the mole fraction of 1,2-dichloroethane while ultrasonic speed decreases with the mole fraction of 1,2-dichloroethane (TABLE 2). Binary systems of 1,2-dichloroethane in toluene shows decrease in isentropic compressibility over entire range of mole fraction of 1,2-dichloroethane. From TABLE 3, it is observed that the values of excess molar volume are negative while values of isentropic compressibility are positive, such trends of negative value of speed of sound and positive value of isentropic compressibility is quite common<sup>[47-52]</sup>.



1,2-dichloroethane



Toluene

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In pure 1,2-dichloroethane there is the usual dispersive interaction. The effect of adding a polar second component is primarily to disrupt the dispersive interaction of the first component.

The behavior of binary liquid mixtures can be explained in term of 1) physical forces -dispersion 2) chemical forces – dipole-dipole interaction<sup>[53]</sup>. The former factor increases the intermolecular free length as described by Jacobson<sup>[54]</sup>. This in turn, causes negative deviation in sound speed and positive deviation in compressibility. On the other hand, the latter factor decreases the intermolecular path lengths leading to a positive deviation in sound speed and negative deviation in compressibility and excess molar volume,  $V_m^E$ . The actual values depend upon the relative strength of two opposing effects. The observed positive values of  $K_s^E$  and negative value of excess molar volume (TABLE 3) imply that there are attractive dipole-induced dipole chemical interaction between the two unlike molecules.

**TABLE 1: Comparison of experimental densities,  $\rho$  of pure liquids with literature**

values at 298.15K	ultrasonic speed	$u$ and molar volume	$V^0$ at 303.15K
Components	$\rho$ ( $\text{g cm}^{-3}$ )	$u$ ( $\text{m s}^{-1}$ )	$V^0$ ( $\text{cm}^3 \text{mol}^{-1}$ )
	Expt. Lit.	Expt. Lit.	at 308.15K
Toluene	0.8791 0.8762	1292 1290	120.9
1,2- dichloroethane	1.2537 1.2542	1272# 1270#	66.5

# value at 298.15K

**TABLE 2 : Density, ultrasonic speed and specific gravity of the binary liquid mixture of 1,2-dichloroethane (1) + Toluene (2)**

Mole fraction ( $X_1$ )	Density ( $\text{g/cc}$ )	Ultrasonic speed ( $u$ ) ( $\text{m/s}$ )	Specific Gravity
0.0679	0.88375	1267.24	0.88457
0.1581	0.90325	1258.18	0.90725
0.2225	0.94399	1250.26	0.93584
0.3170	0.96389	1238.25	0.95457
0.4164	0.98887	1224.59	0.98998
0.5196	1.02494	1209.32	1.02942
0.6207	1.05499	1201.58	1.08564
0.7202	1.16482	1192.56	1.10457
0.8228	1.18869	1181.56	1.15478
0.9299	1.19470	1176.89	1.19993

Since,  $V_m^E$  is a packing effect and  $H_m^E$  is an interactional effect between the A and B constituents of an

(A+B) mixture and as data of the 1,2-dichloroethane in toluene binary liquid mixtures are negative throughout the composition range of toluene, this suggests that as compared to the dispersion forces, negative value of  $V_m^E$  in general, always cause close packing of the molecules due to specific attractive chemical interaction between the two unlike molecules. Their respective contribution to the measured data is a function of the mole fraction of 1,2-dichloroethane.

**TABLE 3: Molar excess volume,  $V_m^E$ , isentropic compressibility,  $K_s^E$ , intermolecular free length,  $L_f$ , and relative association,  $R_a$ , between binary liquid mixtures of 1,2-dichloroethane + Toluene**

Mole Fraction ( $X_1$ )	Molar Excess Volume, $V_m^E$ (-ve)	Isentropic Compressibility $K_s$ , $\times 10^{-7}$ ( $\text{m}^2/\text{N}$ )	Intermolecular free length, $L_f$ ( $10^{-11} \text{ m}$ )	Relative association, $R_a$
0.0679	0.92123	7.05	51.04983	1.0029
0.1581	1.30733	6.99	50.85938	1.0125
0.2225	1.73685	6.78	50.06495	1.0211
0.3170	2.40359	6.77	50.02683	1.0343
0.4164	3.24597	6.74	49.94104	1.0497
0.5196	4.74267	6.67	49.67385	0.9678
0.6207	3.32389	6.57	49.27663	0.9761
0.7202	2.47953	6.04	47.25074	0.9859
0.8228	1.74284	6.03	47.20932	0.9982
0.9299	1.17547	6.04	47.27729	1.0035

The conclusion is further fortified by the increasing value of relative association,  $R_a$  included in TABLE 3. All the trends of the above parameters indicate that the mixtures are less compressible than their corresponding ideal mixtures. Generally, the deviation parameter is considered to be the reflecting agents of the magnitude of polarity at the site of interaction in the molecules<sup>[55]</sup>.

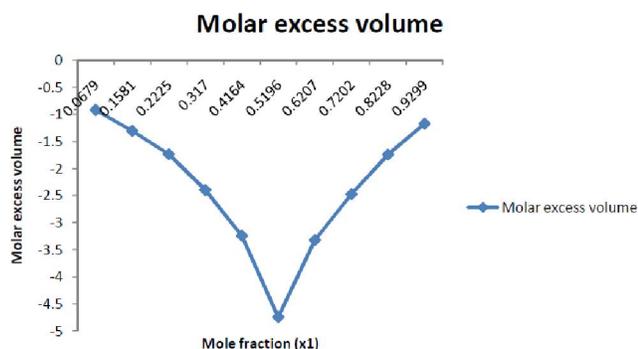
The intermolecular free length,  $L_f$ , can be related to the space filling ability assuming that the molecules are incompressible hard spheres having uniform radius. The study of standard deviations, presented in TABLE 5, reveals that the results of ultrasonic velocity for 1,2-dichloroethane with toluene systems can be satisfactorily explained by Van Deaal Ideal Mixture relation (minimum  $< 0.1$ ).

It is observed that value of density and relative association increases with increase in mole fraction of 1,2-dichloroethane in toluene (TABLE 2 & 3). The value

**TABLE 4 : Theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's (NOM) and Van Dael and Vangeel's (VD) ideal mixing relation and percentage error for 1,2-dichloroethane (1) + toluene (2) at 303.15 K**

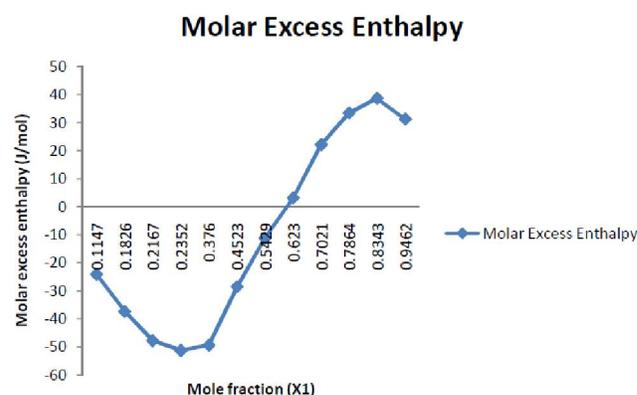
$x_1$	$u$ ( $ms^{-1}$ )					% error			
	Experimental	FLT	CFT	NOM	VD	FLT	CFT	NOM	VD
0.0679	1267.24	1266.12	1265.34	1268.45	1269.34	0.0883	0.1499	0.0954	0.1657
0.1581	1258.18	1257.56	1256.45	1259.34	1260.49	0.0492	0.1375	0.0921	0.1835
0.2225	1250.26	1249.47	1248.59	1251.89	1253.30	0.0631	0.1335	0.1303	0.2431
0.3170	1238.25	1237.57	1236.49	1239.59	1241.12	0.0549	0.1421	0.1082	0.2317
0.4164	1224.59	1223.69	1222.49	1226.21	1226.78	0.0734	0.1714	0.1322	0.1788
0.5196	1209.32	1207.56	1207.34	1210.34	1211.34	0.1455	0.1637	0.0843	0.1670
0.6207	1201.58	1199.79	1198.89	1203.21	1203.32	0.1489	0.2238	0.1356	0.1448
0.7202	1192.56	1191.38	1191.34	1193.48	1192.37	0.0989	0.1023	0.0771	0.0159
0.8228	1181.56	1180.42	1179.45	1182.90	1182.89	0.0964	0.1785	0.1134	0.1125

of ultrasonic speed decreases with increase in mole fraction of 1,2-dichloroethane in toluene (TABLE 2). This is the general trend showing presence of strong intermolecular interaction between the two binary liquid mixtures. The decrease in the value of intermolecular free length with increase in mole fraction of 1,2-dichloroethane in toluene (TABLE 3) further confirms presence of attractive intermolecular forces between the two binary liquid mixtures. The value of intermolecular free length decreases with increase in magnitude with the mole fraction of 1,2-dichloroethane in the binary liquid mixtures. Above results were further supported by the values of relative association. It is observed that value of relative association increases with increase in mole fraction of 1,2-dichloroethane in toluene (TABLE 3). It further confirms presence of specific chemical attractive dipole-induced dipole interaction between the two binary liquid mixtures in comparison to pure liquids.

**Figure 1 : Variation of molar excess volume, ( $V_s^E$ ) for the binary liquid mixture of toluene and 1,2-dichloroethane**

From TABLE 3, the decrease in the value of inter-

molecular free length substantive the above argument undoubtedly and undeniably unveils the fact the specific interaction are being operative between the molecules of solvent and co-solvents in the mixture. The negative value of molar excess volume increases up to middle i.e. up to mole fraction of 0.5145 and then decreases (Figure 1). The observed negative values of molar excess volume (TABLE 3) indicates presence of specific chemical interaction between the binary liquid mixtures of 1,2-dichloroethane and toluene.

**Figure 2 : Variation of molar excess enthalpy ( $H_s^E$ ) with the mole fraction ( $X_1$ ) of 1,2-dichloroethane in toluene binary liquid mixture**

The  $H^E$  values of 1,2-dichloroethane + toluene are negative up to a mole fraction of 0.5429 and then positive (Figure 2). The excess heat is thus markedly asymmetrical in this system. Such asymmetry is common in mixtures in which specific interactions occur<sup>[56]</sup>. It is, however, difficult to comment specifically about the nature of these interactions from thermodynamic evidence alone. A weak complex formation<sup>[57]</sup> between

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the n-electrons of toluene under the present investigation with 1,2-dichloroethane could be a probable explanation for the results obtained.

Theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's (NOM) and Van Dael and Vangeel's (VD) ideal mixing relation were compared with experimental values and their percentage error for 1,2-dichloroethane (1) + toluene (2) at 303.15 K were shown in TABLE 4. It is observed that value of theoretical ultrasonic speed calculated from free length theory was found to be in close agreement with the experimental values. The value of theoretical ultrasonic speed calculated from Nomotos relation shows large deviation from experimental values.

**TABLE 5 : Values of parameters  $A_j$  of the Redlich-Kister equation and corresponding standard deviations,  $\sigma(k_s^E)$  for the binary systems at 308.15K**

$A_0$	$A_1$	$A_2$	$A_3$	$\sigma(k_s^E) (T \text{ Pa}^{-1})$
<b>1,2-dichloroethane (1) + Toluene (2)</b>				
65.3	-34.50	7.40	-11.40	0.11

**TABLE 6 : Intermolecular free length ( $L_f$ ), calculated from FLT, CFT and TAP theories for binary mixtures at 308.15 K**

$x_1$	$L_f(\text{FLR})/\text{nm}$	$L_f(\text{TAP})$	$L_f(\text{CFT})/\text{nm}$
<b>1,2-dichloroethane (1) + Toluene (2)</b>			
0.0687	51.037	50.013	51.302
0.1099	50.860	50.206	50.825
0.1753	50.094	50.424	50.379
0.2648	50.015	50.687	50.116
0.3774	49.874	50.746	49.842
0.5213	49.515	50.814	49.347
0.6146	49.442	50.953	49.205
0.6879	49.154	51.103	46.702
0.7778	47.762	51.473	48.016
0.8989	47.448	51.564	48.047
0.9236	47.157	51.616	47.337

The intermolecular free length,  $L_f$ , can be related to the space filling ability assuming that the molecules are incompressible hard spheres having uniform radius. The intermolecular free length,  $L_f$ , obtained using free length theory (FLT) for the (1,2-dichloroethane + toluene) decreases with the increase in mole fraction of 1,2-dichloroethane (TABLE 6). However, the  $L_f$  value obtained from Schaaf's collision factor theory (CFT) increases with the increase in the mole fraction of 1,2-dichloroethane. The change in the slope of the isotherms

of  $L_f$  as a function of mole fraction in the higher mole fraction region predicted by FLT and CFT shows that the entropy effect related to the structural rearrangement of solvent molecules due to disruption of dispersive interactions between like molecules. However, the thermoacoustic approach (TAP) predicts that the  $L_f$  values in these binary mixtures decreases with increase in the mole fraction of 1,2-dichloroethane. The  $L_f$  values for these binary mixtures obtained from the ultrasonic methods are higher than those obtained from the free length theory and the thermoacoustical approach.

**TABLE 7 : Available volume,  $V_a$ , calculated from FLT, CFT and TAP for binary mixture at 308.15 K**

$x_1$	$V_a \cdot 10^6 (\text{FLR}) / (m^3 \cdot \text{mol}^{-1})$	$V_a \cdot 10^6 (\text{CFT}) / (m^3 \cdot \text{mol}^{-1})$	$V_a \cdot 10^6 (\text{TAP}) / (m^3 \cdot \text{mol}^{-1})$
<b>1,2-dichloroethane (1) + Toluene (2)</b>			
0.0762	31.4634	30.5804	29.7689
0.1176	31.0765	30.1417	29.2420
0.2356	30.8754	29.7731	28.8814
0.2856	30.4721	29.2708	28.2844
0.3657	29.8376	28.7544	27.7804
0.4021	29.1455	28.2621	27.3585
0.5434	28.8341	27.8040	26.9134
0.6655	28.3231	27.3310	26.2710
0.7546	27.7423	26.8463	25.8126
0.8739	27.2745	26.2321	25.3734
0.9343	26.7316	25.7679	24.7214

The available volume,  $V_a$ , obtained using Free Length Theory (FLT) for the (1,2-dichloroethane + toluene) decreases with the increase in mole fraction of 1,2-dichloroethane (TABLE 7). However, the  $V_a$  value obtained from Schaaf's Collision Factor Theory (CFT) increases with the increase in the mole fraction of 1,2-dichloroethane. The change in the slope of the isotherms of available volume as a function of mole fraction in the higher mole fraction region predicted by FLT and CFT shows that the entropy effect related to the structural rearrangement of solvent molecules due to stronger specific chemical interactions between unlike molecules of toluene in 1,2-dichloroethane. However, the thermoacoustic approach (TAP) predicts that the  $V_a$  values in these binary mixtures decrease with increase in the mole fraction of 1,2-dichloroethane.

## CONCLUSIONS

Density ( $\rho$ ), ultrasonic velocity ( $u$ ), molar excess

enthalpy,  $H_m^E$ , and excess molar volume,  $V_m^E$  of binary liquid mixtures of toluene and 1,2-dichloroethane have been measured over the entire range of composition and at 308.15 K. From these experimental results, parameters such as isentropic compressibility,  $K_m^E$ , coefficients  $A_j$ , standard deviations  $\sigma(Y^E)$ , intermolecular free length,  $L_j$  and relative association,  $R_a$  have been estimated. The excess functions have been fitted to the Redlich-Kister polynomial equations. Intermolecular Free Length,  $L_f$  and available volume,  $V_a$ , have been calculated from FLT, CFT and Thermoacoustic Approach. The observed positive values of  $K_s^E$  and negative value of excess molar volume  $V_m^E$  and first negative and then positive values of  $H_m^E$  for these mixtures imply that there are specific chemical attractive dipole-induced dipole interaction between the two unlike molecules.

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