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Thermodynamic Study of Binary Liquid Mixtures of Benzene and 1,2-dichloroethane at T = 303.15 K

Harish Kumar*, [1] and Dheeraj Kumar*

*Dept. of Chemistry, Ch. Devi Lal University, Sirsa (Haryana) India – 125 055
E-mail: [1]harimoudgil1@rediffmail.com

Abstract

Thermodynamic studies like density (ρ), specific gravity, ultrasonic speed (u) and excess molar volume (V_m^E) and excess enthalpy (H_m^E) of binary liquid mixtures of benzene + 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) and relative association (R_A) have been calculated from density and ultrasonic speed measurement. 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 interaction present between binary liquid mixtures were 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.

Keywords: *Ultrasonic speed; Excess Molar Volume; Benzene; 1,2-dichlororethane.*

1. 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. Benzene is a colorless and highly flammable liquid with a sweet smell. It is mainly used as a precursor to heavy chemicals, such as ethylbenzene and cumene, which are produced on a billion kilogram scale. Because it has a high octane number, it is an important component of gasoline, comprising a few percent. The chemical compound 1,2-dichloroethane (DCE), 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 benzene has attracted considerable interest in the literature (Aminabhavi and Banerjee, 1998; Haijun et al., 1994; Sandhu and Singh, 1992). Thus, 1,2-dichloroethane in benzene 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 benzene has attracted considerable interest in our present study.

Research workers in the past have shown that NMR (Lin and Tsay, 1970; Schneider, 1959), IR (Grunwald and Coburn, 1958; Coggeshall and Saier, 1951) and Raman spectra (Pimental and Maclellan, 1960), have been used to study molecular interactions. The velocity measurement of the propagation of ultrasonic waves (Prasad and Prakash, 1976; Gopal and Rao, 1981; Franks et al., 1970; Kaulgud and Roa, 1979; Srivastva et al., 1983) and their absorption (Sette, 1955; Davanbakht et al., 1977) have already been found to be useful in the study of molecular interactions for inorganic, organic and organo-metallic binary systems. Likewise, researchers (Sharma and Gupta, 1986; Mehrotra and Upadhaya, 1987, Mehrotra et al., 1987; Srivastava, 1988; Mehrotra and Gehlaut, 1989; Kumar, 1989) have also employed ultrasonic measurements to look into the important consequences of ion-solvent interactions for the structure of electrolytic solutions. References (Schermuly et al., 1997; Wanger et al., 2000) related to the field of medicine, whereas references (Hickey, 2006; Becu, Manneville, Colin, 2006; Mehta and Kawaljet, 2002; Brasllev and Grfesex, 2002) based on studies on emulsions/microemulsions, polymer surfactants interactions (Alessandra et al., 1997) and ultrasonic destruction of surfactants (Weavers et al., 2005) are only a few cases to suggest versatility of the technique.

2. Experimental

1,2- dichloroethane (CAS No. 107-06-2) was procured from Fischer Scientific Ltd. and are further purified by the methods given in Furniss et al. (2004). Prior to the experimental measurements, all the organic liquids were

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*Corresponding Author

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 ±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 ± 0.3 %) at a constant temperature of 303.15 K by using a digital constant temperature water bath. The temperature stability is maintained within ± 0.001 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 (cm) moved by the reflector is given by $d = n\lambda/2$, where λ is the wavelength. The frequency, ν, of the crystal being accurately known (2.0 MHz), the speed of sound, u in $\mathrm{ms^{-1}}$ 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 (±0.01cm) in the centre. The density of solution was measured by a double arm pyknometer 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 1×10^{-6} $\mathrm{ohm^{-1}\ cm^{-1}}$) with 0.9970 and 0.9940 g $\mathrm{cm^{-3}}$ as its density at 298.15 K and 303.15 K, respectively with buoyancy corrected. The accuracy of the density results was ± 0.0001 (g $\mathrm{cm^{-3}}$). Before each series of measurements, the instrument was calibrated with triple distilled freshly degassed water. The density and ultrasonic speed of binary mixtures were also measured by an Anton Paar Densitiometer (DSA 5000). The accuracy of the density results was ± 0.00001 (g/$\mathrm{cm^3}$). 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.

3. 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 (Bhatia and Bhatia, 2009)

$$V_m^E = \frac{\left(X_1M_1 + X_2M_2\right)}{\rho_{mix}} - \left(\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right) \tag{1}$$

where ρ_{mix} is the density of the mixture and X_1, M_1, ρ_1 and X_2, M_2, ρ_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 (Nomoto, 1958)

$$u = \left(\frac{R_m}{V_{mix}}\right)^3 = \left(\frac{x_1R_1 + x_2R_2}{x_1V_1 + x_2V_2}\right)^3 \tag{2}$$

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 (Van Deal, 1975)

$$\frac{1}{x_1M_1 + x_2M_2}\cdot\frac{1}{u_{id.mix}^2} = \frac{x_1}{M_1u_1^2} + \frac{x_2}{M_2u_2^2} \tag{3}$$

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

Jacobson's Free Length Theory (FLT) (Jacobson, 1952)

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

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 $L_f = 2V_a/Y$. Here V_a represents the available volume per mole and Y is the surface area per mole and these may be expressed as:

$$V_a = \left(V_T - V_0\right) \tag{5}$$

$$Y = \left(36\pi \mathrm{N_A} V_0^2\right)^{1/3} \tag{6}$$

where 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:

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

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

$$T_C = x_1T_{C(1)} + x_2T_{C(2)} \tag{8}$$

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

$$L_f = 2\frac{\left[V_T - \left\{x_1V_{0(1)} + x_2V_{0(2)}\right\}\right]}{\left(x_1V_1 + x_2V_2\right)} \tag{9}$$

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

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

where u is the ultrasonic velocity at temperature T and u_∞ is 1600 m s^{-1}.

Schaaff's Collision Factor Theory (CFT) (Schaaffs, 1975; Schaaffs, 1963)

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

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 relations

$$b = \frac{4}{3}\pi r^3 N \tag{12}$$

where, r is the molecular radius which has been computed using the Schaaff's relation (Schaaffs, 1963)

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

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

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

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 (Nutsch-Kuhnkies, 1965; Pandey et al. (2003); Pandey et al., 1991) has also been employed to obtain the available volume (V_a) using the relation

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

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

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

$$K'' = 1+\frac{X}{2\alpha T} \tag{18}$$

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

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

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

$$X = 2\frac{(1+2\alpha T)}{\tilde{V}^{C_1}} \tag{21}$$

where, $\tilde{V}$ represents the reduced molar volume and c_1 is the Moelwyn-Hughes parameter and can be expressed as

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

$$C_1 = \frac{13}{3}+\frac{1}{\alpha T}\frac{4\alpha T}{3} \tag{23}$$

The thermal expansion coefficient (α) has been calculated using the equation:

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

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

$$k_s = \frac{1}{\rho u^2} \tag{25}$$

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

$$k_s^E = k_s - k_s^{id} \tag{26}$$

where, k_s^{id} the isentropic compressibility for the ideal mixture, was obtained according to Benson & Kiyohara (1979) and Acree (1983):

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

where ϕ_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, α_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 (Redlich and Kister, 1948)

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

where, A_j are the adjustable parameters.

Oswal and Phalak (1993) 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 ($C_{p,i}$) of a liquid mixture if the interaction parameter (χ_{12}) is known.

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

$$L_f = K\left(K_s\right)^{1/2} \tag{29}$$

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

where, ρ_0 and u_0 are the densities and ultrasonic speed of pure solvent, ρ and u are the density and ultrasonic speed of mixture respectively and K is the temperature dependent Jacobson constant (6.0816×10^4 at 35 ^{0}C).

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

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

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. ΔY, 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 (Bondi, 1968). Molecular interaction parameter for each binary mixture was obtained by fitting the PFP theory to the corresponding experimental equimolar H^E values (Morcom, 1973; Inglese and Kehiaian, 1982). 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 benzene 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 benzene 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) + benzene (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 benzene 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) + benzene (2) binary liquid mixture at 308.15 K.

Table 1. Comparison of experimental density, ρ and ultrasonic speed, u of pure liquids with literature values and molar volume, V^0 of pure liquids at 303.15 K.

Components	ρ (g·cm^{-3}) Expt.	ρ (g·cm^{-3}) Lit.	u (m·s^{-1}) Expt.	u (m·s^{-1}) Lit.	V^0 (cm^3 mol^{-1})
Benzene	0.8791	0.8762	1292	1290[1]	120.9
1,2-dichloroethane	1.2537	1.2542	1272	1270[2] #	66.5

value at 298.15 K

1. Kumar. (1989).

2. Bhatia et al. (2009).

Table 2. Density, ultrasonic speed and specific gravity of the binary liquid mixture of 1,2-dichloroethane (1) + Benzene (2).

Mole fraction x_1	Density ρ (g/cc)	Ultrasonic Speed u (m/s)	Specific Gravity (-)
0.05378	0.88579	1265.74	0.88754
0.10799	0.90323	1257.01	0.90718
0.22925	0.94391	1238.94	0.94804
0.31589	0.98547	1225.12	0.95874
0.41590	1.00862	1215.31	1.01304
0.51452	1.01085	1204.56	1.04578
0.61991	1.01452	1192.56	1.12457
0.71923	1.12485	1185.54	1.17586
0.83677	1.14457	1180.23	1.20052
0.90930	1.19884	1177.12	1.20409

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 + benzene.

Mole Fraction x_1	Molar Excess Volume V_m^E	Isentropic compressibility V_m^E ×10^7 (m^2 N^{-1})	Intermolecular free length $L_f \times 10^{11}$ (m)	Relative association R_A
0.05378	-0.95982	7.05	51.0514	0.00227
0.10799	-1.60647	7.01	50.9072	0.00954
0.22925	-2.88374	6.91	50.5245	0.02922
0.31589	-4.30926	6.76	50.0054	0.04473
0.41590	-6.92909	6.71	49.8272	0.05599
0.51452	-7.05387	6.82	50.2164	0.27290
0.61991	-5.74727	6.93	50.6299	0.71598
0.71923	-3.97742	6.33	48.3675	0.84377
0.83677	-2.66543	6.27	48.1648	0.99974
0.90930	-1.30041	6.02	47.1863	1.00326

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) + benzene (2) at 303.15 K.

		u (m·s^{-1})				% error			
x_1	Experimental	FLT	CFT	NOM	VD	FLT	CFT	NOM	VD
0.05378	1265.74	1265.32	1264.45	1263.32	1266.34	0.0331	0.1019	0.1911	0.0474
0.10799	1257.01	1255.23	1256.34	1255.60	1258.34	0.1416	0.0533	0.1121	0.1058
0.22925	1238.94	1237.45	1239.34	1236.79	1240.5	0.1202	0.0323	0.1735	0.1259
0.31589	1225.12	1224.26	1226.47	1222.35	1223.4	0.0702	0.1102	0.2261	0.1403
0.41590	1215.31	1216.34	1216.67	1211.25	1214.35	0.0847	0.1119	0.3340	0.0789
0.51452	1204.56	1201.98	1205.34	1201.37	1201.23	0.2141	0.0648	0.2648	0.2764
0.61991	1192.56	1191.23	1193.34	1191.34	1190.35	0.1115	0.0654	0.1023	0.1853
0.71923	1185.54	1184.34	1186.45	1183.34	1184.37	0.1012	0.0768	0.1855	0.0986
0.83677	1180.23	1179.34	1181.35	1178.34	1178.35	0.0754	0.0949	0.1601	0.1592

Table 5. Values of Parameters A_j of the Redlich-Kister equation and corresponding standard deviations, $\sigma(k_S^E)$ for the binary system 1,2- dichloroethane (1) + Benzene (2) *at 308.15 K.*

A_0	A_1	A_2	A_3	$\sigma(k_S^E)$ (T·Pa^{-1})
77.5	-38.20	9.20	-13.90	0.10

Table 6. Intermolecular Free Length (L_f), calculated from FLT, CFT and TAP theories for DCE (1) + Benzene (2) *binary mixture at 308.15 K.*

x_1	L_f(FLT)/nm	L_f(CFT)/nm	L_f(TAP)
0.0687	51.103	47.013	51.302
0.1099	50.863	48.006	50.825
0.1753	50.505	48.324	50.379
0.2648	50.015	48.687	50.116
0.3774	49.784	49.146	49.842
0.5213	49.115	49.214	49.347
0.6146	49.002	49.653	49.205
0.6879	48.754	50.103	46.702
0.7778	48.362	50.473	48.016
0.8989	48.148	50.764	48.047
0.9236	47.257	51.216	47.337

Table 7. Available Volume, V_a, calculated from FLT, CFT and TAP for binary mixture at 308.15 K.

x_1	$V_a \cdot 10^6$ (FLT) (m^3·mol^{-1})	$V_a \cdot 10^6$ (CFT) (m^3·mol^{-1})	$V_a \cdot 10^6$ (TAP) (m^3·mol^{-1})
	1,2-dichlororethane (1) + Benzene (2)		
0.0762	26.5634	27.7804	25.4689
0.1176	26.4765	28.4417	25.4520
0.2356	25.9854	29.4731	24.3814
0.2856	25.6721	31.2708	24.6844
0.3657	25.1376	33.6544	25.1804
0.4021	24.5455	33.5621	24.3585
0.5434	24.2341	34.6540	24.2134
0.6655	23.2231	35.3310	23.3710
0.7546	22.3423	35.5463	23.4126
0.8739	22.6745	35.3321	22.8734
0.9343	21.4316	35.7679	21.6714

Figure 1 shows the structures of 1,2-dichloroethane (DCE) and benzene. Figure 2 shows variation of molar excess volume with the mole fraction of 1,2-dichloroethane in benzene binary liquid mixture. Figure 3 shows variation of molar excess enthalpy with the mole fraction of 1,2-dichloroethane in benzene binary liquid mixture.

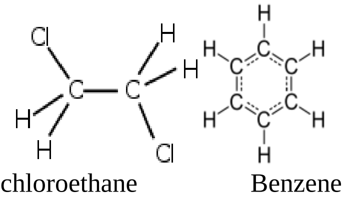

Figure 1. Structure of 1,2-dichloroethane and benzene.

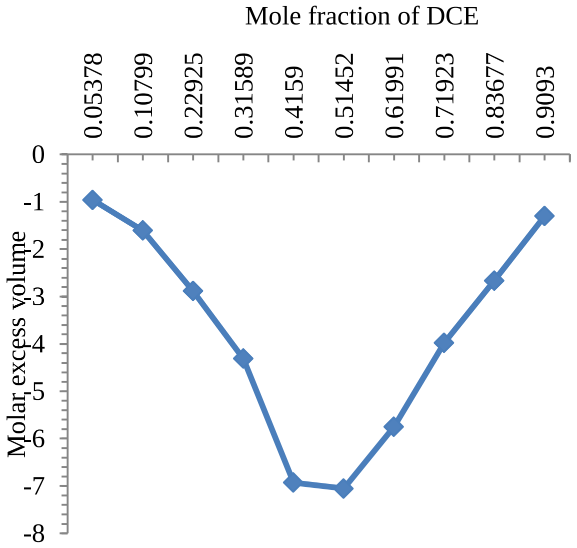

Figure 2. Variation of molar excess volume, V_m^E for the binary liquid mixture of benzene and 1,2-dichloroethane.

4. Discussion

Density and specific gravity of binary liquid mixtures of 1,2-dichloroethane in benzene 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 benzene shows decrease in isentropic compressibility over entire range of mole fraction. 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 (Flory et al, 1964; Abe and Flory, 1965; Aminabhavi and Gopalakrishna, 1995; Aminabhavi and Banerjee, 1998; Oswal and Prajapati, 1998; Ohomuru and Murakami, 1987).

In pure 1,2-dichloroethane there is the usual dispersive interaction. The effect of adding a non polar second

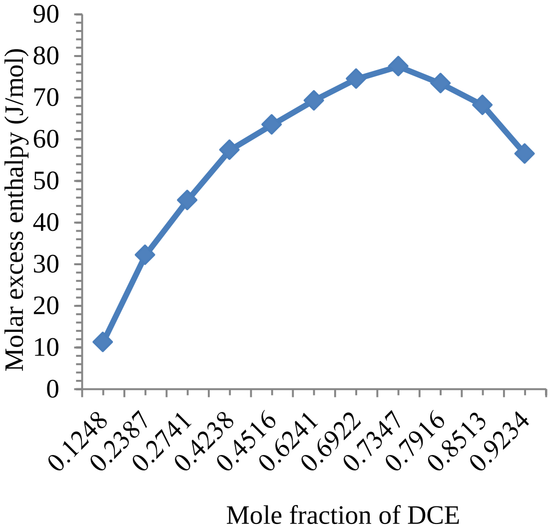

Figure 3. Variation of molar excess enthalpy (H_m^E) with the mole fraction (x_1) of 1,2-dichloroethane in benzene binary liquid mixture .

component is primarily to disrupt the dispersive interaction of the first component.

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 V_m^E data of the 1,2-dichloroethane in benzene binary liquid mixtures are negative throughout the composition range of benzene, 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 interaction between the two unlike organic molecules. Their respective contribution to the measured data is a function of the mole fraction of 1,2-dichloroethane.

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 (Internet, 2012).

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 ($\sigma(k_s^E)$) presented in Table 5, reveals that the results of ultrasonic velocity for 1,2-dichloroethane with benzene systems can be satisfactorily explained by Van Deal 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-dichlororethane in benzene (Table 2 & 3). The value of ultrasonic speed decreases with increase in mole fraction of 1,2-dichloroethane in benzene (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 benzene (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 of attractive intermolecular interaction with the mole fraction of 1,2-dichlororethane 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-dichlororethane in benzene (Table 3). It further confirms presence of specific chemical intermolecular interaction dominates over the weak dispersive interactions between the two binary liquid mixtures in comparison to pure liquids.

The behavior of binary liquid mixtures can be explained in term of 1) physical forces -dispersion 2) chemical forces – dipole-dipole interaction. The former factor increases the intermolecular free length as described by Jacobson free length theory. This is 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.

From Table 3, the decrease in the value of intermolecular 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 2). The observed negative values of molar excess volume (Table 3) indicates presence of specific chemical interaction between the binary liquid mixtures of 1,2-dichlororethane and benzene.

The H_m^E values of 1,2-dichloroethane + benzene are positive over the whole range of composition (Figure 3). The value of H_m^E is a maximum at a mole fraction of 1,2-dichloroethane of 0.7364. The excess heat is thus markedly asymmetrical in this system. Such asymmetry is common in mixtures in which specific interactions occur (Rowlinson, 1969). It is, however, difficult to comment specifically about the nature of these interactions from thermodynamic evidence alone. A weak complex formation (Staveley, Tupman and Hart, 1955) between the n-electrons of the various aromatic hydrocarbons 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) + benzene (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.

The intermolecular free length, , 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-dichlororethane + benzene) decreases with the increase in mole fraction of 1,2-dichlororethane (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-dichlororethane. 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-dichlororethane. 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.

The available volume (V_a) obtained using Free Length Theory (FLT) for the (1,2-dichlororethane + benzene) decreases with the increase in mole fraction of 1,2-dichlororethane (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-dichlororethane. 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 benzene in 1,2-dichlororethane. 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-dichlororethane.

5. Conclusions

Density (ρ), ultrasonic velocity (u), molar excess enthalpy (H_m^E), and excess molar volume (V_m^E) of binary liquid mixtures of 1,2-dichloroethane in benzene have been measured over the entire range of composition and at 308.15 K. From these experimental results, parameters such as isentropic compressibility (k_S^E), coefficients A_i, standard deviations ($\sigma(Y^E)$), intermolecular free length (L_f) 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 values of k_S^E and negative value of excess molar volume (V_m^E) and positive values of H_m^E for these mixtures imply that there are specific chemical attractive interaction between the two unlike molecules.

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