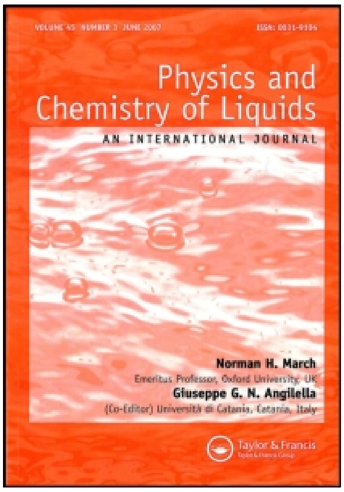

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Volumetric and ultrasonic behaviour of acetophenone with dichloro and trichlorobenzenes at 303.15 K

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Volumetric and ultrasonic behaviour of acetophenone with dichloro and trichlorobenzenes at 303.15 K

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Excess molar values (V^E) and speeds of sound (u) for the binary mixtures of acetophenone with 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene have been measured at 303.15 K. Excess volumes are positive over the entire composition range in all the three binary mixtures. Isentropic compressibilities (K_s) have been computed for the same systems from precise sound velocity and density data. Further, deviation in isentropic compressibility (ΔK_s) from ideal behaviour was also calculated. ΔK_s, values exhibit negative sign in all the mixtures. The experimental sound velocity data are analyzed in terms of free length theory (FLT) and collison factor theory (CFT). The measured data is explained on the basis of intermolecular interactions between unlike molecules.

Keywords: Excess volume; Isentropic compressibilities; Sound velocity; Molecular interactions

1. Introduction

Thermodynamic properties of binary mixtures, containing components capable of undergoing specific interactions, exhibit significant deviation from ideality arising not only from difference in molecular size and shape but also due to structural changes. A survey of the literature has shown that V^E data for the binary mixtures of acetophenone with 1-alkanols [1], benzene and substituted benzenes [2], chloroethanes and ethenes [3] have been reported. Further, isentropic compressibility data for the binary mixtures of acetophenone with 1-alkanols [1], aromatic hydrocarbons [4], chloroethanes and ethenes [5] were also reported earlier. In the present study, we report the excess volumes and isentropic compressibility data for the binary mixtures of acetophenone with 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene. The experimental sound velocity data have been analyzed in terms of

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free length theory (FLT) [6] and collision factor theory (CFT) [7]. The theoretical aspects of FLT and CFT have been described earlier [8].

The present study was undertaken to know the effect of addition of second and third chloro functions in the benzene nucleus that may influence both the sign and magnitude of excess volume and deviation in isentropic compressibility.

2. Experimental

2.1. *Materials and methods*

All the chemicals used were of analytical grade, 1,2-dichlorobenzene (S.D. Fine Chemicals), 1,3-dicholorobenzene (Fluka), 1,2,4-trichlorobenzene (Merck) and acetophenone (S.D. Fine Chemicals) were purified by the methods described earlier [9,10]. The purity of the samples was checked by comparing the densities of the components with those reported in the literature [9,11].

Densities were determined using a bicapillary type pycnometer which offered an accuracy of 2 parts in 10^5. The excess volumes were measured using a dilatometer of the type described earlier [12]. The dilatometers were kept in a thermostat maintained at 303.15 ± 0.01 K. The values of V^E are accurate to $\pm 0.003\,\mathrm{cm^3\,mol^{-1}}$.

Ultrasonic sound velocities were measured with a single–crystal ultrasonic interferometer at a frequency of 4 MHz at 303.15 K and the data were accurate to ±0.15%. All the measurements were made at constant temperature employing a thermostat, that could maintain temperature within ±0.01 K.

Isentropic compressibilities (K_s) were computed from the measured sound velocity and density, evaluated from measured excess volumes [13]. Isentropic compressibilities were accurate to $\pm 2\,\mathrm{TPa^{-1}}$.

3. Results and discussion

The experimental excess volumes of three binary mixtures of acetophenone with chloro substituted benzenes are given in table 1. Further, these data are graphically presented in figure 1 along with acetophenone with chlorobenzene [2] which was reported earlier. The measured V^E values were fitted to an empirical relation [14].

$$V^E(\mathrm{cm^3\,mol^{-1}}) = X_1(1 - X_1)\left[a_0 + a_1(X_1 - X_2) + a_2(X_1 - X_2)^2\right] \tag{1}$$

where a_0, a_1 and a_2 are adjustable parameters and X_1 is the mole fraction of acetophenone. The values of the parameters were obtained by the least-square method. Further, V^E results were also fitted to the semi-empirical equation proposed earlier [15].

$$V^E(\mathrm{cm^3\,mol^{-1}}) = X_1(1 - X_1)\left[b_0 + b_1X_1^3 + b_2X_2^3\right] \tag{2}$$

where X_1 and X_2 represent mole fractions of acetophenone and dichloro (or) trichlorobenzenes, respectively, b_0, b_1 and b_2 are constants. The computation of '*b*' coefficients in the above equation was described earlier [16,17]. The values of the two sets of constants are given in table 2 along with standard deviations. The standard deviation values given in table 2 point out that the equation of [15] also represents the V^E data precisely.

Table 1. Mole fraction of acetophenone (X_1), experimental and predicted excess volumes (V^E) for the binary mixtures of acetophenone (1) with dichloro and trichloro benzenes (2) at 303.15 K.

Mole fraction of acetophenone (X_1)	V^E Experimental ($cm^3\,mol^{-1}$)	V^E Redlich–Kister [14]	V^E Hwang ($cm^3\,mol^{-1}$) [15]
Acetophenone (1) + 1,2-dichlorobenzene (2)			
0.1014	0.024	0.023	0.024
0.1570	0.035	0.035	0.035
0.2217	0.046	0.048	0.047
0.3108	0.063	0.063	0.062
0.4360	0.079	0.079	0.078
0.5010	0.087	0.084	0.086
0.6221	0.086	0.086	0.086
0.7040	0.080	0.081	0.079
0.8219	0.062	0.062	0.061
0.8704	0.050	0.050	0.049
Acetophenone (1) + 1,3-dichlorobenzene (2)			
0.0924	0.040	0.039	0.039
0.1611	0.051	0.053	0.050
0.2076	0.056	0.059	0.059
0.3144	0.065	0.065	0.064
0.4018	0.070	0.067	0.065
0.5206	0.075	0.074	0.075
0.6210	0.072	0.069	0.069
0.7202	0.067	0.071	0.070
0.8130	0.062	0.065	0.064
0.9205	0.041	0.040	0.040
Acetophenone (1) + 1,2,4-trichlorobenzene (2)			
0.1076	0.010	0.010	0.009
0.2219	0.024	0.023	0.024
0.3014	0.033	0.033	0.033
0.3640	0.040	0.040	0.039
0.4224	0.048	0.046	0.047
0.5107	0.055	0.054	0.054
0.6277	0.058	0.059	0.060
0.7010	0.057	0.058	0.057
0.8220	0.046	0.047	0.048
0.8746	0.039	0.038	0.037

Data for density (ρ), computed from measured excess volumes and experimental sound velocity data (u), are included in columns 2 and 3 of table 3. Isentropic compressibility, K_s and the deviation in isentropic compressibility, ΔK_s, are also included in columns 4 and 5 of table 3. The deviation in isentropic compressibility, ΔK_s, values are graphically represented in figure 2 for against volume fraction along with those of acetophenone and chlorobenzene which was reported earlier [4]. The isentropic compressibility (K_s) and the deviation in isentropic compressibility (ΔK_s) were calculated using the following relations

$$K_s = u^{-2}\rho^{-1} \tag{3}$$

$$\rho = \frac{X_1M_1 + X_2M_2}{V^0 + V^E} \tag{4}$$

$$\Delta K_s = K_s - (\phi_1 K_{s1} + \phi_2 K_{s2}) \tag{5}$$

$$\phi_1 = \frac{X_1V_1^0}{X_1V_1^0 + X_2V_2^0} \tag{6}$$

$$V_1^0 = X_1V_1^0 + X_2V_2^0 \quad \text{and} \quad \phi_1 = 1 - \phi_2 \tag{7}$$

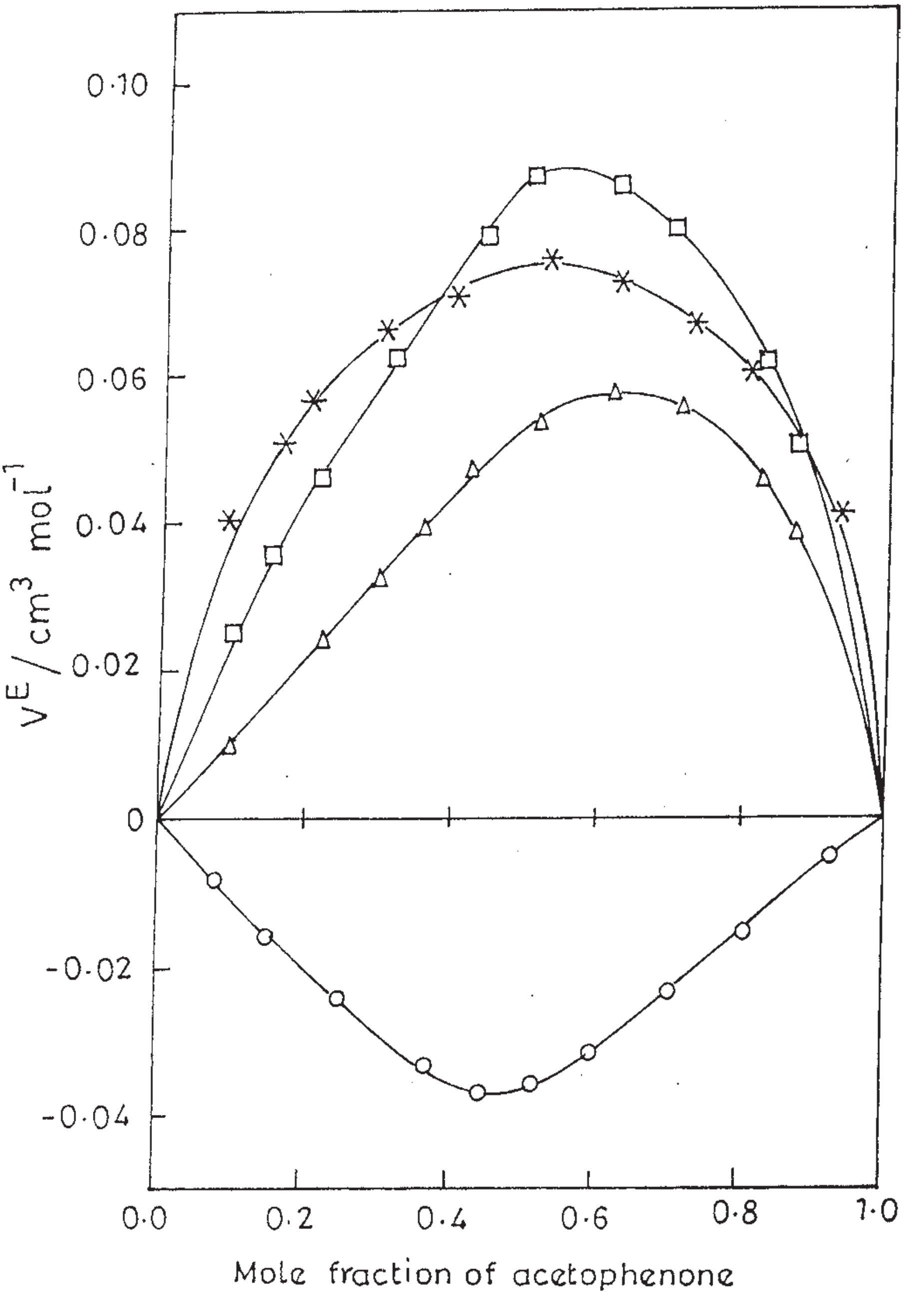

Figure 1. The values of V^E plotted against mole fraction X_1 of acetophenone; (○) *o*-chlorobenzene; (□) 1,2-dichlorobenenze; (⋆) 1,3-dichlorobenzene; (Δ) 1,2,4-trichlorobenzene at 303.15 K.

where X, M and V^0 denote the molefraction, molecular weight and molar volume of the mixture, and K_s, K_{s1} and K_{s2} denote compressibilities of the mixtures and the components 1 and 2, respectively. ΔK_s values indicate the deviation in isentropic compressibility from ideal value, which is assumed to be additive in terms of

Table 2. Standard deviation and values of constants from the Redlich–Kister equation, equation (1) and Hwang *et al*. equation (2).

	Equation (1)				Equation (2)			
System	a_0 (cm^3 mol^{-1})	a_1 (cm^3 mol^{-1})	a_2 (cm^3 mol^{-1})	$\sigma(V^E)$ (cm^3 mol^{-1})	b_0 cm^3 mol^{-1}	b_1 cm^3 mol^{-1}	b_2 cm^3 mol^{-1}	$\sigma(V^E)$ cm^3 mol^{-1}
Acetophenone (1) + 1,2,-dichlorobenzene (2)	0.3361	0.1192	0.0296	0.002	0.3262	0.1814	–0.1024	0.001
Acetophenone (1) + 1,3-dichlorobenzene (2)	0.2727	0.0440	0.3270	0.004	0.1637	0.4884	0.3836	0.003
Acetophenone (1) + 1,2,4-trichlorobenzene (2)	0.2130	0.1538	0.0270	0.001	0.2040	0.2191	–0.1471	0.002

Table 3. Volume fraction (ϕ_1) of acetophenone, density (ρ), sound velocity (u), isentropic compressibility (K_s) and deviation in isentropic compressibility (ΔK_s) of acetophenone (1) with dichloro and trichlorobenzenes (2) at 303.15 K.

ϕ_1	ρ (gm cc^{-1})	u (m s^{-1})	K_s (TPa^{-1})	ΔK_s (TPa^{-1})
Acetophenone (1) + 1,2-dichlorobenzene (2)				
0.0000	1.29920	1261	484	–
0.1052	1.26951	1286	476	−5
0.1617	1.25360	1299	473	−7
0.2288	1.23557	1311	471	−8
0.3196	1.20914	1331	467	−9
0.4460	1.17363	1356	463	−10
0.5111	1.15534	1370	461	−11
0.6316	1.12170	1392	460	−9
0.7124	1.09920	1408	459	−8
0.8277	1.06710	1430	458	−6
0.8749	1.05403	1438	459	−4
1.0000	1.01950	1460	460	–
Acetophenone (1) + 1,3-dichlorobenzene (2)				
0.0000	1.27715	1242	507	–
0.0700	1.25282	1266	498	−6
0.1643	1.23428	1285	491	−8
0.2115	1.22205	1296	487	−10
0.3195	1.19416	1319	481	−11
0.4074	1.17146	1339	476	−12
0.5264	1.14077	1367	469	−13
0.6265	1.11503	1387	466	−12
0.7249	1.08974	1408	463	−10
0.8165	1.06620	1426	461	−8
0.9222	1.03918	1448	459	−5
1.0000	1.01950	1460	460	–
Acetophenone (1) + 1,2,4-trichlorobenzene (2)				
0.0000	1.44214	1261	437	–
0.1009	1.39936	1289	430	−9
0.2098	1.35318	1314	428	−14
0.2866	1.32065	1333	426	−17
0.3476	1.29477	1345	427	−18
0.4051	1.27041	1358	427	−19
0.4929	1.23468	1374	429	−19
0.6109	1.18337	1395	434	−17
0.6858	1.15172	1410	437	−16
0.8113	1.09881	1433	443	−13
0.8665	1.07632	1443	446	−11
1.0000	1.01950	1460	460	–

volume fraction. ϕ_1 and ϕ_2 denote the volume fractions of the components 1 and 2, respectively and ρ is the density of the mixture.

The dependence of ΔK_s on volume fraction is expressed by an empirical equation

$$\Delta K_s = \phi_1\phi_2\left[C_0 + C_1(\phi_1 - \phi_2)C_2(\phi_1 - \phi_2)^2\right] \tag{8}$$

where C_0, C_1 and C_2 are the adjustable parameters. These values are calculated by the method of least squares and are given in table 4 along with standard deviation $\sigma(\Delta K_s)$.

The sound velocity data predicted in terms of FLT and CFT are given along with the experimental results in columns 3 and 4 of table 5. The methods and the details of calculations are discussed earlier [18]. The calculated values of molar volume (V_m) at absolute zero (V_0) available volume (V_a), free length (L_f), surface area (Y), collision factor (S), average radius of the molecules (r_m) per mole (B) of pure components are

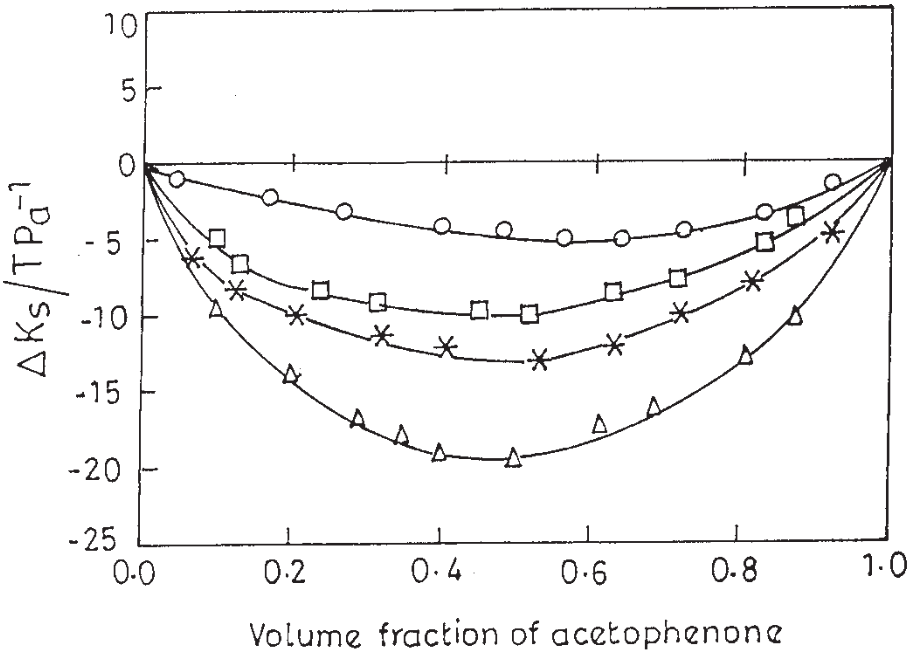

Figure 2. The values of ΔK_s plotted against mole fraction ϕ_1 of acetophenone; (○) *o*-chlorobenzene; (□) 1,2-dichlorobenenze; (⋆) 1,3-dichlorobenzene; (Δ) 1,2,4-trichlorobenzene at 303.15 K.

Table 4. Values of parameters c_0, c_1 and c_2 of equation (7) and the standard deviation of (ΔK_s) at 303.15 K.

System	c_0 (Tpa^{-1})	c_1 (Tpa^{-1})	c_2 (Tpa^{-1})	$\sigma(\Delta K_s)$ (Tpa^{-1})
Acetophenone (1) + 1,2-dichlorobenzene (2)	−40.55	7.80	−8.69	1
Acetophenone (1) + 1,3-dichlorobenzene (2)	−45.99	6.89	−40.53	1
Acetophenone (1) + 1,2,4-trichlorobenzene (2)	−73.77	2.35	−36.76	1

given in table 6. These data were taken from the literature [9,11,19]. The theoretical values of ultrasonic velocity in the systems under study have been evaluated using FLT and CFT equations. The calculated ultrasonic velocities along with the experimental velocities and the average percentage errors in the calculated values only that were compared with the experimental values are listed in table 5. These results clearly indicate that for the mixtures with 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene, CFT predicts the experimental data well while FLT gives maximum deviation.

The data included in table 1 shows that the V^E values are positive over the entire composition range in all the binary mixtures of acetophenone with dichloro and trichloro benzenes. According to Tiwari *et al.* [20], excess volumes are influenced by (i) loss of dipolar association and differences in size and shape and (ii) dipole–dipole, dipole–induced dipole interactions, and charge transfer complexation between unlike molecules. The former effect leads to expansion in volume and the latter contributes to contraction in volume. The actual value of V^E depends on the balance between these two opposing contributions. The experimental data in the present study suggest

Table 5. Experimental and predicted sound velocity data for the binary mixtures of acetophenone with dichloro and trichloro benzenes at 303.15 K.

Mole fraction of acetophenone (X_1)	U_{EXP} (m s^{-1})	U_{FLT} (m s^{-1})	U_{CFT} (m s^{-1})	% error	
				U_{FLT}	U_{CFT}
Acetophenone (1) + 1,2-dichlorobenzene (2)					
0.1014	1286	1278	1283	0.62	0.23
0.1570	1299	1286	1294	1.00	0.38
0.2217	1311	1295	1307	1.22	0.30
0.3108	1331	1309	1324	1.65	0.52
0.4360	1356	1329	1349	1.99	0.51
0.5010	1370	1339	1361	2.26	0.65
0.6221	1392	1359	1385	2.37	0.50
0.7040	1408	1372	1401	2.55	0.49
0.8219	1430	1393	1425	2.58	0.34
0.8704	1438	1401	1434	2.57	0.27
Acetophenone (1) + 1,3-dichlorobenzene (2)					
0.0924	1266	1259	1264	0.55	0.15
0.1611	1285	1270	1278	1.16	0.54
0.2076	1296	1278	1288	1.38	0.61
0.3144	1319	1295	1311	1.81	0.60
0.4018	1339	1311	1336	2.09	0.22
0.5206	1367	1332	1355	2.56	0.87
0.6210	1387	1350	1378	2.66	0.64
0.7202	1408	1369	1399	2.76	0.63
0.8130	1426	1387	1419	2.73	0.49
0.9205	1448	1408	1443	2.76	0.34
Acetophenone (1) + 1,2,4-trichlorobenzene (2)					
0.0920	1289	1268	1286	1.62	0.23
0.1076	1314	1267	1283	3.57	2.35
0.2219	1333	1281	1307	3.90	1.95
0.3040	1345	1288	1336	4.23	0.66
0.4224	1358	1305	1347	3.90	0.81
0.5107	1374	1311	1365	4.58	0.65
0.6277	1395	1333	1388	4.44	0.50
0.7010	1410	1372	1402	2.69	0.56
0.8220	1433	1364	1426	4.81	0.48
0.8746	1443	1373	1436	4.85	0.48

Table 6. Calculated values of molar volume (V_{m}), molar volume at absolute zero (V_0), molar available volume (V_{a}), free length (L_{f}), surface area (Y), collision factor (S), average molecular radius (r_{m}) and actual volume of molecules per mole (B) of pure liquid components at 303.15 K.

Component	V_{m} (cm^3 mol^{-1})	V_0 (cm^3 mol^{-1})	V_{a} (cm^3 mol^{-1})	L_{f} (A^0)	Y	S	r_{m} (A^0)	B
Acetophenone	117.8519	100.2987	17.5532	0.4280	80.0243	1.8243	2.8593	58.9496
1,2-Dichlorobenzene	113.1471	95.3471	17.8001	0.4380	81.2771	1.6054	2.8054	55.6643
1,3-Dichlorobenene	115.0970	96.5531	18.5441	0.4488	82.6380	1.5748	2.8246	56.8242
1,2,4-Trichlorobenzene	125.8211	107.2980	18.5232	0.4167	88.9021	1.5305	2.9509	64.7933

that the factors which are responsible for expansion in volume are dominant in all the binary mixtures.

The carbonyl group is highly polar and hence has a high percentage of ionic character [21]. There is a negative charge on the carbonyl oxygen atom of acetophenone. Hence, one could except strong interactions with isomeric chlorobenzenes as the number of chlorine atoms increases, since chlorine has a tendency to act as an electron acceptor. But the experimental results indicate prevailing of weaker interactions in all the binary mixtures. This may be attributed to the internal interaction between π-electrons of C=O bond and π-electrons of the benzene ring [22]. Similar behaviour of two adjacent groups, one being the phenyl group, has been observed in aromatic ethers and aromatic chlorides. Further more, it has been shown that the intramolecular interactions between phenyl and oxygen groups in aromatic ethers [23] and between phenyl and chlorine groups in aromatic chlorides [24] become weaker when the functional groups are separated by atleast two methylene groups.

Algebraic values of excess volume data for the systems of acetophenone with chlorobenzenes fall in the order:

1,2-dichlorobenzene > 1,3-dichlorobenzene > 1,2,4-trichlorobenzene

The above order suggests that the presence of hydrogen bonding may not be possible in these systems. The acetophenone being a highly polar molecule ($\mu = 2.96$) and it may enhance the polarity of 1,2-dichlorobenzene ($\mu = 2.26$) and 1,3-dichlorobenzene ($\mu = 1.38$). In general, negative excess volume data were reported in the literature for the binary mixtures that containing ketone and halogens [25–27]. Also negative V^E data were also reported earlier for the binary mixtures of ethyl methyl ketone with 1,2-dichlorobenzene and 1,2,4-trichlorobenzene [28,29]. Hence, one could except the negative excess volume in the mixture. But the observed positive V^E values suggest that the volume expansion factors dominating the volume contraction factors. This contension is supported by the positive excess volumes data for the binary mixtures of acetophenone with 1,2-dichloroethane and 1,2-dichloroethane with aliphatic ketones [3,30].

The π-electron density in derivatives of benzene ring depends upon the group that is attached to it. The heteromolecular interaction between component molecules necessarily depends upon the net electron density in the ring. Further, these interactions seem to depend upon relative orientation of the two groups in the ring. As the separation between the two groups increases, the intermolecular interaction is expected to decrease. The intermolecular interaction in ortho-isomer causes a large strain in the ring, causing an opposite pole at *ortho* side of the ring and thus giving a dipolar character, than *meta* and *para* derivatives. Hence, the interactions are thus expected to be stronger in the *ortho* derivatives than the other two isomers.

The molecular interactions operative between the two component molecules are due to the residual electric moments and dispersion forces and may not be significantly different from those forces that are present in pure liquids. Hence, the non-ideality being reflected in the present investigation may also be due to geometrical factors, difference in molecular shape and size of the components. Positive excess volumes in the present study suggest that there is disturbance in the packing arrangement of pure liquids leading to expansion in volume, on mixing of the components.

The difference in V^E values observed between dichloro and trichloro benzenes, is probably because of the difference in their shapes which lead to different alignments in the liquid mixture. Further, the chlorine atom at to 4th position in 1,2,4-trichloro benzene offers the least steric hindrance to acetophenone molecules and thus the electron donor–acceptor interactions in it are lower than those of 1,2-dichlorobenzene and 1,3-dichlorobenzene.

However, V^E values for mixtures of acetophenone with 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene are algebraically smaller than those for mixtures of acetophenone with chlorobenzene [2]. This shows that the addition of second (or) third chloro group in benzene ring has influenced the sign and magnitude of excess volume to a significant extent.

An examination of deviation in isentropic compressibility (ΔK_s) data in figure 2 shows that the quantity are negative over the entire volume fraction range in all the binary mixtures of acetophenone with chlorobenzenes. The values may be interpreted in terms of two opposing effects, namely (i) loss of mutual dipolar association and difference in size and shape of unlike molecules, and (ii) dipole–induced dipole and dipole–dipole interactions. The former effect contributes to an increase in free lengths of component mixtures which is described earlier [6]. This leads to negative deviation in sound velocity and positive deviation in isentropic compressibility. The latter effect, on the other hand contributes to positive deviation in sound velocity and negative deviation in isentropic compressibility. The sign and magnitude of the actual deviation depend on the relative strength of the two oppsing effects. Negative values of ΔK_s point out that the latter effect dominates in all the mixtures. The algebraic ΔK_s values for the systems fall in the order:

1,2-dichlorobenzene > 1,3-dichlorobenzene > 1,2,4-trichlorobenzene

Further, the negative values of ΔK_s in all the binary mixtures indicate the extence of strong interactions. A possible explanation may be that the oxygen atom of the carbonyl group of acetophenone being strongly electronegative, would act as a good electron acceptor towards the π-electrons of the aromatic ring, forming donor–acceptor complexes. It has been suggested [31] that ring, forming donor–acceptor complexes. It has been suggested [31] that deviations in isentropic compressibility become increasingly negative as the strength of interaction between molecules increases.

The large negative ΔK_s values for the binary mixture acetophenone + 1,2,4-trichlorobenzene are attributed to the presence of strong specific ($C{=}O \cdots Cl$) interaction of the type between acetophenone and 1,2,4-trichlorobenzene molecule, and also due to the fitting of smaller acetophenone molecules into the voids created by bigger molecules of 1,2,4-trichlorobenzene. The specific interaction could be of donor–acceptor type [32] in which the oxygen atom of carbonyl group of acetophenone with its unshared pair of electrons acts as electron–donor towards electron acceptor chlorine atoms of 1,2,4-trichlorobenzene. Further, presence of one more chlorine atom in 1,2,4-trichlorobenzene increases its electron-accepting capacity and therefore, it interacts more strongly towards acetophenone molecule as compared to 1,2-dichlorobenzene and 1,3-dichlorobenzene, causing deviation in isentropic compressibility (ΔK_s) more negative for acetophenone + 1,2,4-trichlorobenzene than for acetophenone + 1,2-dichlorobenzene and 1,3-dichlorobenzene. The observed trends in V^E support the above view. An examination, of deviation in isentropic compressibility data (ΔK_s) in figure 2 shows that algebraic values of ΔK_s are more negative when compared to acetophenone with chlorobenzene. This may be due to changes in free-spaces between pure components and liquid mixtures.

Furthermore, the sign of the deviation in isentropic compressibility plays a vital role in assessing the compactness due to molecular arrangement and the extent of molecular interactions in liquid mixtures and also provides an useful information about their structures [33]. A negative deviation in isentropic compressibility is an indication of strong interactions [31] and a positive sign [34] for weak interactions between component molecules.

A comparison between V^E and ΔK_s shows that the two quantities do not have the same sign over the whole range of composition. This supports the contention of Kaulgud [35] that V^E and K_s are determined by different factors. According to his theory, a mere knowledge of expansion and contraction in volume is not sufficient to predict the nature of sound velocity and compressibility deviations correctly, but the magnitude and sign of excess entropy has to be taken into account.

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