Thermo-acoustic studies on binary liquid mixtures of ethyl propionate and 1,2-dichlorobenzene/1,3-dichlorobenzene/1,2,4-trichlorobenzene at 303.15 to 318.15 K

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Abstract:

Speed of sound,u, and density,ρ, of binary liquid mixtures of ethyl propionate with 1,2-dichlorobenzene/1,3-dichlorobenzene/1,2,4-trichlorobenzene have been measured at 303.15, 308.15, 313.15 and 318.15 K over the entire composition range. Speed of sound and density are used to estimate various thermo-acoustic parameters along with excess values of molar volume V_m^E, excess isentropic compressibility, κ_s^E, excess molar isentropic compressibility, $K_{s,m}^E$,and excess isobaric thermal expansion α_p^E. Redlich-Kister polynomials corroborated the correlation of extra parameters. The intermolecular interactions between the dissimilar molecules in the binary mixtures are discussed in relation to the observed changes of the aforementioned parameters with concentration and temperature.

Keywords: Thermo-acoustic, ethyl propionate, chlorobenzene, molar volume

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INTRODUCTION

In understanding the intermolecular interactions occurring among component molecules, volumetric and ultrasonic investigations of liquid mixtures are of considerable importance [1, 2]. Since a binary mixture is formed by the replacement of like contacts in the pure components by unlike contacts in the mixture, it may trigger inter or intra molecular changes in either one or both the components or this must be reflected in the excess molar volume. The physicochemical properties of aromatic hydrocarbons are of great significance in the selection of appropriate solvent for (i) gas and liquid

chromatography, (ii) dissolution of materials and (iii) their use in propellants and aerosols.

Ethyl propionate (EP) is highly hydrophobic molecule and it belongs to carboxylic acid ester. EP is generally deployed in the processing of food, flavour industry and a model of fatty acid ethyl esters used as first-generation biodiesel. EP is used in the production of some antimalarial drugs including pyrimethamine. 1,2-dichlorobenzene (1,2-DCB) is used as an intermediate for dyes and certain agricultural chemicals. 1,3-dichlorobenzene (1,3-DCB) is widely used in the manufacture of poly resin, used as a room deodorant blocks and moth control. 1,2,4-trichlorobenzene (1,2,4-TCB) is used in the manufacture of the herbicide, in some pesticides as a dye carrier in dielectric field, as an organic intermediate and a chemical manufacture solvent in lubricants [3].

In this paper, we report speed of sound,u, and density,ρ, of binary liquid mixtures of ethyl propionate with 1,2-dichlorobenzene/1,3-dichlorobenzene/1,2,4-trichlorobenzene at 303.15, 308.15, 313.15 and 318.15 K over the entire composition range. Ultrasonic velocity and density are used to estimate various thermo-acoustic parameters along with excess values of molar volume V_m^E, excess isentropic compressibility, κ_s^E, excess molar isentropic compressibility, $K_{s,m}^E$, and excess isobaric thermal expansion α_p^E. Redlich-Kister polynomials corroborated the correlation of extra parameters. The intermolecular interactions between the dissimilar molecules in the binary mixtures are discussed in relation to the observed changes of the aforementioned parameters with concentration and temperature.

MATERIALS AND METHODS

The purity of these solvents was ascertained by comparing the measured densities, and speeds of sound with the available literature [4-7] with the NIST ThermoLit data compiled in **Table 1**.

The measured values of speed of sound and density are presented in T**able 2**. The coefficients, A_i and corresponding standard deviations, σ where given in **Table 3**.

A detailed description and experimental procedure of the equipment used for measurement of density and speed of sound can be found elsewhere [8].

RESULTS AND DISCUSSION

All the formulas related to this manuscript are given elsewhere [8].

Table 1. Density, speed of sound and molar heat capacity data at different temperatures at 0.1 MPa obtained in this work and from available literature values.

T (K)	ρ (kg m^{-3})		u (m s^{-1})		Cp (J K^{-1} mol^{-1})
	Expt	Ref.	Expt	Ref.	
Ethyl propionate					
303.15	878.5	879.14 [4]	1135.6	1136 [4]	197.0 [4]
308.15	872.6	873.33 [4]	1114.4	1114 [4]	198.5 [4]
313.15	866.7	867.48 [4]	1093.3	1093 [4]	199.9 [4]
318.15	860.9	861.60 [4]	1072.2	1072 [4]	201.5 [4]
1,2-dichlorobenzene					
303.15	1295.0	1294.72 [5]	1263.0	1265 [5]	171.76 [7]
308.15	1289.3	1289.13 [5]	1243.0	1246 [5]	172.87
313.15	1283.7	1276.53 [6]	1222.0	1237 [6]	173.86 [6]
318.15	1278.1	-	1203.0	-	175.15
1,3-dichlorobenzene					
303.15	1277.7	1277.72 [5]	1235	1237 [5]	171.25 [7]
308.15	1272.3	1272.19 [5]	1221		172.36
313.15	1266.8		1206		173.24 [6]
318.15	1261.4		1192		174.65
1,2,4-trichlorobenzene					
303.15	1442.4	1442.48 [5]	1255.5	1256 [7]	195.92 [7]
308.15	1436.4	1436.45 [5]	1240.0		196.81
313.15	1430.5		1224.5		197.26 [7]
318.15	1424.5		1209.0		198.66

Table 2. Densities and Speeds of Sound as a Function of Mole Fraction of EP at Different Temperatures.

x_1	ρ (kg m^{-3})	u (m s^{-1})	ρ (kg m^{-3})	u (m s^{-1})	ρ (kg m^{-3})	u (m s^{-1})	ρ (kg m^{-3})	u (m s^{-1})
	303.15 K		308.15 K		313.15 K		318.15 K	
EP + 1,2-DCB								
0.0000	1295.0	1263.0	1289.3	1243.0	1283.7	1222.0	1278.1	1203.0
0.1007	1253.0	1250.2	1247.4	1230.1	1241.7	1209.0	1236.1	1189.8
0.1943	1214.0	1238.2	1208.4	1218.0	1202.7	1197.0	1197.0	1177.6
0.3017	1169.3	1224.6	1163.6	1204.2	1157.9	1183.2	1152.2	1163.5
0.4030	1127.2	1211.7	1121.4	1191.2	1115.7	1170.1	1110.0	1150.3
0.5047	1084.8	1198.7	1079.0	1178.1	1073.3	1157.0	1067.5	1137.0
0.6026	1044.0	1186.2	1038.2	1165.5	1032.4	1144.4	1026.7	1124.2

0.6977	1004.4	1174.1	998.6	1153.3	992.8	1132.2	987.0	1111.7
0.8065	959.1	1160.2	953.3	1139.3	947.4	1118.2	941.6	1097.5
0.9000	920.1	1148.3	914.3	1127.3	908.4	1106.2	902.6	1085.2
1.0000	878.5	1135.6	872.6	1114.4	866.7	1093.3	860.9	1072.2
EP + 1,3-DCB								
0.0000	1277.7	1235.0	1272.3	1221.0	1266.8	1206.0	1261.4	1192.0
0.1085	1234.4	1224.2	1228.9	1209.4	1223.4	1193.8	1218.0	1179.0
0.2124	1192.9	1213.9	1187.4	1198.4	1181.9	1182.1	1176.3	1166.6
0.3098	1154.1	1204.2	1148.5	1188.0	1142.9	1171.1	1137.3	1154.9
0.4212	1109.6	1193.1	1103.9	1176.1	1098.3	1158.5	1092.7	1141.5
0.5194	1070.4	1183.4	1064.7	1165.6	1059.0	1147.5	1053.4	1129.8
0.6143	1032.5	1173.9	1026.8	1155.5	1021.1	1136.8	1015.4	1118.4
0.7120	993.5	1164.2	987.7	1145.1	982.0	1125.8	976.2	1106.7
0.8128	953.3	1154.2	947.5	1134.4	941.7	1114.4	935.9	1094.6
0.9062	915.9	1144.9	910.1	1124.4	904.3	1103.9	898.4	1083.4
1.0000	878.5	1135.6	872.6	1114.4	866.7	1093.3	860.9	1072.2
EP + 1,2,4-TCB								
0.0000	1442.4	1255.5	1436.4	1240.0	1430.5	1224.5	1424.5	1209.0
0.0995	1386.3	1243.6	1380.4	1227.5	1374.4	1211.5	1368.4	1195.4
0.2095	1324.3	1230.4	1318.3	1213.7	1312.4	1197.0	1306.4	1180.3
0.3080	1268.7	1218.6	1262.8	1201.3	1256.8	1184.1	1250.9	1166.9
0.3975	1218.3	1207.8	1212.3	1190.1	1206.4	1172.3	1200.5	1154.6
0.5150	1152.0	1193.7	1146.1	1175.3	1140.1	1156.9	1134.2	1138.5
0.6003	1103.9	1183.5	1098.0	1164.6	1092.1	1145.7	1086.2	1126.9
0.7120	1040.9	1170.1	1035.0	1150.6	1029.1	1131.1	1023.2	1111.6
0.7997	991.5	1159.6	985.6	1139.6	979.7	1119.6	973.8	1099.6
0.8995	935.1	1147.6	929.3	1127.1	923.4	1106.5	917.5	1085.9
1.0000	878.5	1135.6	872.6	1114.4	866.7	1093.3	860.9	1072.2

Table 3. Coefficients A_j of R-K Equation along with Standard Deviations σ of Binary Mixture Properties.

Parameter	T (K)	A_0	A_1	A_2	σ
EP + 1,2-DCB					
$V_m^E \cdot 10^6$ / (m^3 mol^{-1})	303.15	-1.0466	-0.2031	-0.0392	0.0001
	308.15	-1.1637	-0.2270	-0.0438	0.0001
	313.15	-1.2847	-0.2523	-0.0488	0.0001
	318.15	-1.4089	-0.2783	-0.0543	0.0001

$\kappa_s^E \cdot 10^{10}$ / (m^2 N^{-1})	303.15	-2.0659	-0.3349	-0.0711	0.0002
	308.15	-2.2076	-0.3599	-0.0767	0.0002
	313.15	-2.3508	-0.3858	-0.0826	0.0002
	318.15	-2.5282	-0.4171	-0.0900	0.0003
$K_{s,m}^E \cdot 10^{14}$ /(m^5 N^{-1} mol^{-1})	303.15	-2.4404	-0.4471	-0.0974	0.0003
	308.15	-2.6280	-0.4890	-0.1065	0.0003
	313.15	-2.8202	-0.5332	-0.1175	0.0004
	318.15	-3.0552	-0.5865	-0.1309	0.0004
$\alpha_p^E \cdot 10^3$ / (K^{-1})	303.15	-9.1207	1.8828	-0.341	0.0002
	308.15	-10.0869	2.1038	-0.381	0.0004
	313.15	-11.0769	2.3360	-0.425	0.0004
	318.15	-12.0821	2.5771	-0.471	0.0005
EP + 1,3-DCB					
$V_m^E \cdot 10^6$ / (m^3 mol^{-1})	303.15	-0.4442	-0.0832	-0.0148	0.00004
	308.15	-0.5552	-0.1044	-0.0198	0.00005
	313.15	-0.6705	-0.1275	-0.0235	0.00007
	318.15	-0.7890	-0.1509	-0.0292	0.00008
$\kappa_s^E \cdot 10^{10}$/ (m^2 N^{-1})	303.15	-1.7741	-0.2734	-0.0557	0.0002
	308.15	-1.9347	-0.3019	-0.0620	0.0002
	313.15	-2.1012	-0.3333	-0.0686	0.0002
	318.15	-2.3008	-0.3697	-0.0773	0.0002
$K_{s,m}^E \cdot 10^{14}$ / (m^5 N^{-1} mol^{-1})	303.15	-2.0811	-0.3405	-0.0702	0.0002
	308.15	-2.2877	-0.3844	-0.0800	0.0002
	313.15	-2.5046	-0.4322	-0.0908	0.0003
	318.15	-2.7636	-0.4877	-0.1039	0.0003
$\alpha_p^E \cdot 10^3$ / (K^{-1})	303.15	-3.8389	0.7415	-0.128	0.0003
	308.15	-4.7751	0.9319	-0.167	0.0002
	313.15	-5.7358	1.1355	-0.202	0.0002
	318.15	-6.7146	1.3465	-0.242	0.0002
EP + 1,2,4-TCB					
$V_m^E \cdot 10^6$ / (m^3 mol^{-1})	303.15	4.6358	1.1489	0.2819	0.0010
	308.15	4.5319	1.1292	0.2787	0.0010

	313.15	4.4245	1.1077	0.2748	0.0010
	318.15	4.3122	1.0854	0.2701	0.0010
$\kappa_s^E \cdot 10^{10}$ / (m^2 N^{-1})	303.15	-2.3126	-0.5894	-0.1453	0.0005
	308.15	-2.4897	-0.6386	-0.1590	0.0006
	313.15	-2.6776	-0.6922	-0.1734	0.0006
	318.15	-2.8966	-0.7525	-0.1902	0.0007
$K_{s,m}^E \cdot 10^{14}$ / (m^5 N^{-1} mol^{-1})	303.15	-2.5196	-0.4295	-0.0779	0.0002
	308.15	-2.7465	-0.4826	-0.0910	0.0002
	313.15	-2.9893	-0.5422	-0.1053	0.0003
	318.15	-3.2732	-0.6101	-0.1228	0.0003
$\alpha_p^E \cdot 10^3$ / (K^{-1})	303.15	37.9014	-7.9978	2.348	0.002
	308.15	36.8607	-7.8760	2.311	0.001
	313.15	35.8046	-7.7337	2.264	0.001
	318.15	34.7143	-7.5929	2.207	0.001

In all the cases, for each system, the V_m^E over the whole mole fraction range is obviously increasing with increasing temperature from (303.15 to 318.15) K. The reasonable mixtures formed explanation for the fact is as follows. Ethyl propionate is a polar molecule, chlorobenzene is a non-polar molecule. The ethyl propionate and chlorobenzene not only have interaction of self- association between ethyl propionate molecule and chlorobenzene molecule. The kinetic energy of molecules also increase when temperature increase. This leads decrease of the interactions of molecule, so the contraction in volume decrease, that is V_m^E increase.

By comparison of the minimum values of V_m^E (**Fig. 1**) for the three mixtures containing a chlorobenzene at same temperature, it is shown that 1,3-dichlorobenzene is the most favorable one to form close packing with ethyl propionate.

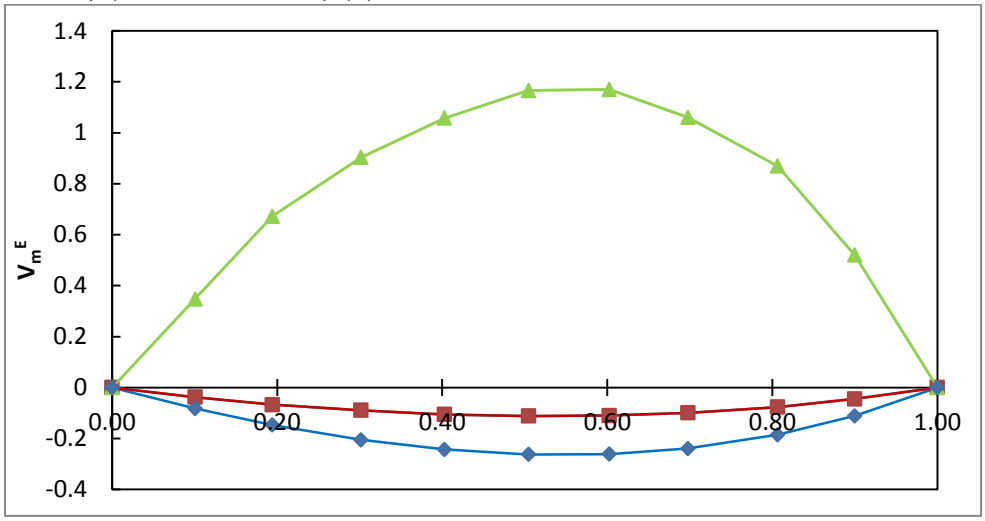

Figure 1: Variation of V_m^E with mole fraction of EP for EP + 1,2-DCB(♦)/ 1,3-DCB(■)/ 1,2,4-TCB(▲) at 303.15 K.

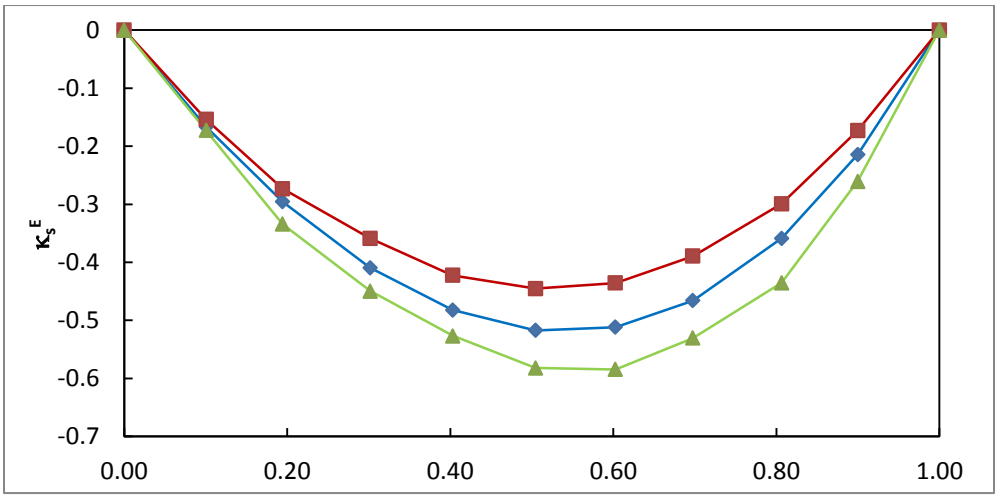

Figure 2: Variation of κ_s^E with mole fraction of EP for EP + 1,2-DCB(♦)/ 1,3-DCB(■)/ 1,2,4-TCB(▲) at 303.15 K.

A perusal of **Fig. 1, 2** indicates that V_m^E and κ_s^E values for these binary mixtures are negative over the entire composition range and investigated temperature range. The sign and magnitude of the volume changes that take place on mixing Ethyl propionate with chlorobenzenes is the result of several effects that operate in the same or in the opposite direction[1,2]. In general, the physical contributions comprise of dispersion forces and non-specific physical (weak) interactions, which lead to positive V_m^E and κ_s^E values. The chemical contributions involve breaking up of the associates present in the pure liquids, resulting in

positive V_m^E and κ_S^E values. The chemical contributions also comprise of specific interactions such as formation of H-bonding, charge transfer (donor-acceptor) complexes, and strong dipole-dipole interactions between the component molecules of the mixture, resulting in negative V_m^E and κ_S^E values. The structural contributions are due to the geometrical fitting (favorable/unfavorable) of the molecules of too different molecular sizes into each other's structures resulting in negative/positive V_m^E and κ_S^E values [9,10].

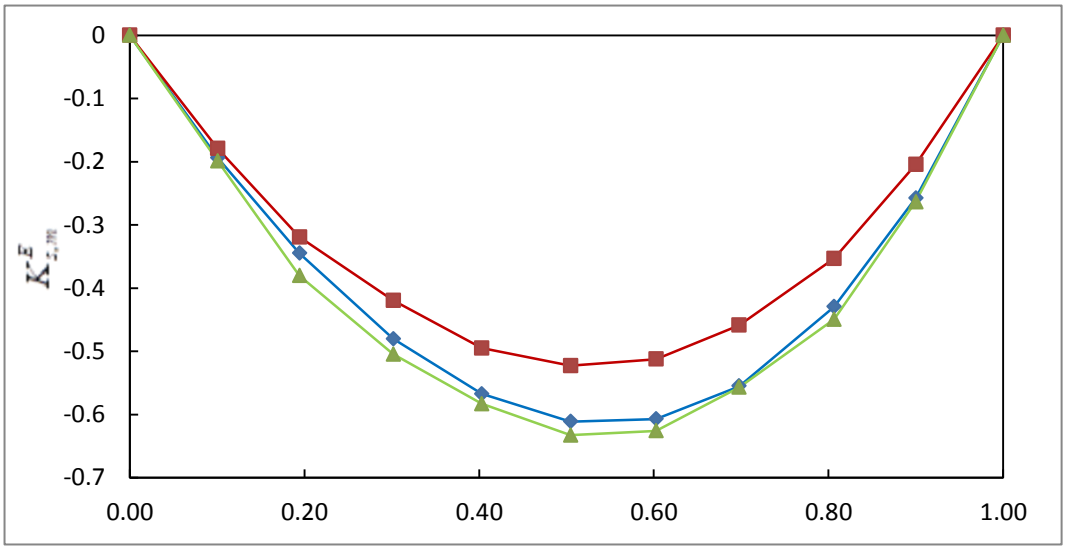

Figure 3: Variation of $K_{s,m}^E$ with mole fraction of EP for EP + 1,2-DCB(♦)/ 1,3-DCB(■)/ 1,2,4-TCB(▲) at 303.15 K.

The results presented in **Fig. 3** indicate that $K_{s,m}^E$ values are negative over the entire composition range and at each investigated temperature The observed negative values of $K_{s,m}^E$ for these mixtures indicate the presence of specific interactions between the dipoles of Ethyl propionate with chlorobenzene molecules with the formation of H-bonds between >COOH of Ethyl propionate and hydroxyl group of chlorobenzene molecules, leading to a decrease in compressibility of the mixture, which results in negative $K_{s,m}^E$ values [11].

The $K_{s,m}^E$ values decrease with increase in temperature ***(Fig. 3)*** for these mixtures. The decrease in $K_{s,m}^E$ is attributed to the closer packing of unlike molecules due to increased dipole -dipole interactions by availability of more chlorobenzene dipoles on breaking of hydrogen

bonds with rise in temperature, leading to a contraction in volume, and hence, a decrease in molar compressibility of the mixture.

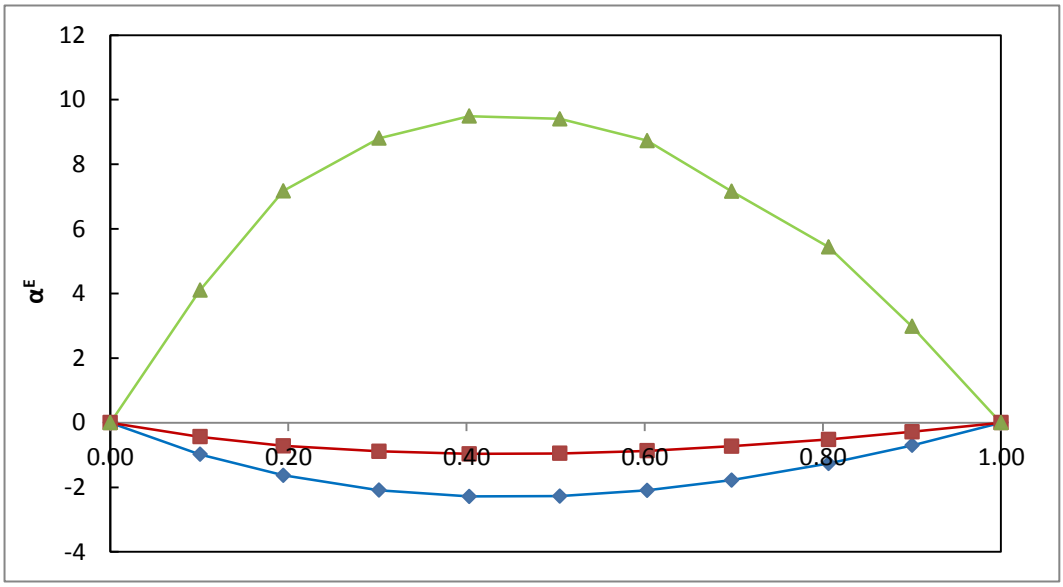

Figure 4: Variation of α^E with mole fraction of EP for EP + 1,2-DCB(♦)/ 1,3-DCB(■)/ 1,2,4-TCB(▲) at 303.15 K.

Excess thermal expansion coefficients α_p^E at 303.15 K are plotted in **Fig 4** with whole range of composition for all the three mixtures**.** Based on **Fig 4,** the excess thermal expansion coefficient (α_p^E) values for the mixture is negative for EP+1,2-DCB and EP+1,3-DCB whereas it is positive for EP+1,2,4-TCB. Generally, negative α_p^E values indicate the formation of new interactions between unlike molecules, while positive α_p^E values are attributed to self-association of components in the mixtures [12].

Conclusion:

In the present work excess volume and excess thermal expansion coefficient data of binary mixtures of EP with 1,2-DCB and 1,3-DCB are negative whereas with 1,2,4-TCB it is positive over the entire composition range at 303.15 to 318.15 K. This data reveals that weak intermolecular interactions are prevailing in liquid mixtures containing 1,2,4-TCB and strong interactions in liquid mixtures containing 1,2-DCB and 1,3-DCB. Further, negative κ_s^E and $K_{s,m}^E$ data in all the binary mixtures which arise due to changes of free volume in the real mixtures and presence of π-electrons in EP result in the formation of strong intermolecular complexes leading to negative excess isentropic compressibility.

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