6.1 Introduction

The study of physical properties such as densities, speeds of sound and viscosities of solutions is very important, especially for the chemical design and for the optimization of chemical processes. The data will provide the information about the behavior of solutions and the types of interactions that are present. The study of such properties plays a vital role in many industrially relevant processes such as organic synthesis, ion extraction systems, adsorption of solvents, mass transfer phenomena, etc.

The liquids are chosen in the present study on the basis of their industrial importance. 3-chloroaniline is a polar solvent and self associated through hydrogen bonding of its amine group. The amino group in 3-chloroaniline is an electron donor and also plays as proton-acceptor. 3-chloroaniline is used as an intermediate in the production of a number of products such as agricultural chemicals, azo dyes and pigments, bactericide or biocide and pharmaceuticals. Aryl halides have a special kind of structure and are nucleophilic in nature and so these are used extensively for synthesis. Commercial use of chlorobenzene is an intermediate in the production of commodities such as herbicides, dye stuffs and rubber. Bromobenzene is an important compound in the preparation of Grignard reagent and also an ingredient in the manufacture of phenylcyclidine [1, 2]. The largest end use for nitrobenzene is in the production of aniline, p-aminophenol, nigrosine dyes, dyestuffs and resins. The aim of the present work is to know the effect of aromatization and the influence of different substituents in the aromatic ring on excess volume, deviation in viscosity and excess isentropic compressibility values. A thorough survey of literature reveals that there are no data available showing detailed physical properties like density, speed of sound and viscosity, etc. for the binary mixtures of 3-chloroaniline with Chloro/Bromo/Nitro-Benzene. Hence, this research work is undertaken pertaining to these binary blends. The data found in this work may be helpful in selecting proper compositions of halo benzenes or nitrobenzene with 3-chloroaniline for suitable applications in industrial processes.

6.2 Density and excess volume data of binary mixtures of 3-chloroaniline with mono substituted benzene derivatives (bromobenzene, chlorobenzene and nitrobenzene) at T= (303.15 - 318.15) K

Excess molar volume (V^E) is one of the important parameter which provides useful and ample information about what type of molecular interactions are prevailing between pure liquids and their mixtures.

In the present investigation, excess volume data (V^E) for the binary mixtures of 3-chloroaniline with mono substituted benzene derivatives (bromobenzene, chlorobenzene and nitrobenzene) were calculated from the measured density (ρ) of pure liquids and their mixtures over the entire composition range at temperature from 303.15 K to 318.15 K. The excess volumes (V^E) data of all the binary mixtures were computed from the experimentally determined density data by using the equation (3.2.1) in chapter III.

The V^E data of all the binary mixtures of 3-chloroaniline with bromobenzene, chlorobenzene and nitrobenzene were given in Tables 6.2.1 - 6.2.3 and also these were graphically represented in Figs. from 6.2.1 to 6.2.4

The negative V^E values indicated the presence of specific interactions such as hydrogen bond interaction between the mixing components, interstitial accommodation among the mixing components and dipole-dipole or dipole-dipole induced interaction leading to electron donor-acceptor complexes [3]. Because of the comparable molar volumes of the components, interstitial accommodation of the mixing components would not be a good explanation for negative V^E values. There was a little ability for hydrogen bond interaction (N-H…π) between 3-chloroaniline and substituted benzene derivatives [4]. Furthermore, there was possibility of electron donor-acceptor interactions between the electronegative nitrogen atom of 3-chloroaniline and substituted benzene derivatives. In such electron donor-acceptor interactions, 3-chloroaniline acts as an electron donor and the substituted benzene derivatives act as electron acceptor [5]. Excess molar volumes

(V^E) for these binary systems may be attributed to dipole-induced dipole interactions between the components of the mixtures resulting the formation of electron donor-acceptor complexes [3].

When hydrogen atom of the benzene was replaced by halo atom / nitro group, charge in the σ bond was transferred away from the ring to the halogen atom / nitro group (inductive effect) leaving a positive charge in the ring.

However, although the halogen atom / nitro group was in this way a σ bond acceptor, it was also n-π donor in a donor-acceptor action (dative conjugation) [6, 7]. As result of these two opposite effects, there might be a net transfer of negative charge from the ring to the halogenated atom as well as an enhancement of the acceptor character of the aromatic ring. Therefore, the interaction between the aromatic ring and the 3-chloroaniline must be increased when a halo atom / nitro group was attached to the ring. V^E data in the Tables 6.2.1 - 6.2.3 for the binary systems of chlorobenzene and bromobenzene showed more negative V^E values for the former than the latter. This could be explained as follows: chlorobenzene was more reactive than bromobenzene because the chlorine atom was bonded with sp^3 hybridized carbon atom and thereby it could be removed very easily. Hence, the rate of reaction of chlorobenzene became faster [8-10] when compared with bromobenzene. The experimental results in the present investigation supported this contention. Chlorine atom in chlorobenzene is an electron withdrawing atom, and tries to attract the π-electrons of the benzene ring and so the electron density of the aromatic ring decreases. As a result, the benzene ring in chlorobenzene becomes relatively poor electron donor towards electron seeking proton of any group [11]. Hence chlorobenzene interacts strongly with 3-chloroaniline leading to more V^E values. Further, bromobenzene is less reactive when compared to chlorobenzene because of its double bond character between carbon and bromine atom and also it may be attributed to its heavier size. Further, the less negative V^E of bromobenzene when compared to chlorobenzene may be postulated in terms of the presence of vacant 3d-orbital in bromine

atom of bromobenzene and so the latter can act as an electron acceptor towards π-electrons of aromatic compounds [12, 13]. The more negative V^E data for the binary system of 3-chloroaniline with nitrobenzene than to chlorobenzene and bromobenzene binary blends may be due to high dipole moment and dielectric constant. Nitrobenzene is supposed to be a relatively complex molecule and its non-ideality arises due to rotation of nitro group freely along the C-N axis where it gives more flexibility to the interaction arising due to the two highly polar N→O bonds [8]. Further, the more negative V^E data for the mixture 3-chloroaniline with nitrobenzene when compared to other mixtures of present investigation may also due to the following reasons: i) Nitro group withdraw the electron cloud from the benzene ring while chloro and bromo groups release the electron cloud to the benzene ring and ii) viscous nature of nitrobenzene [4].

The values of V^E with respect to non-common component fall in the order:

Nitrobenzene < chlorobenzene < bromobenzene

The above order indicates that the electron accepting ability decreases with increasing electron withdrawing halo/group in the substituted benzene derivatives [14]. Hence the said order is justified.

The increase in V^E values with increasing temperature may be due to factors (i) declustering of components at higher temperature, (ii) weakening of dipole-dipole interactions due to decreases in polarizabilities [15], and (iii) increase in kinetic energy at higher temperature.

The V^E composition profiles for the binary mixtures of 3-chloroaniline with mono substituted benzene derivatives are fitted to Redlich - Kister polynomial equation (eq. 3.2.2).The values of the parameters obtained by method of least – squares and were given in Table 6.2.4 along with standard deviation σ (V^E) values at T= (303.15-318.15) K. The standard deviations were calculated using the eq. (3.2.3). Finally, it can be concluded that the expressions used for interpolating the experimental data measured in this work give good results, as can be seen by inspecting the (σ) values obtained.

Table 6.2.1: Mole fraction of 3-chloroaniline(x_1), density (ρ) and excess molar volume (V^E) data for the binary mixture of 3-chloroaniline with bromobenzene at T= (303.15-318.15) K

	303.15 K		308.15 K		313.15 K		318.15 K	
x_1	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}
0.0000	1.48152	0.0000	1.47536	0.0000	1.46802	0.0000	1.46136	0.0000
0.0902	1.45714	-0.0369	1.45119	-0.0409	1.44419	-0.0473	1.43777	-0.0526
0.1842	1.43171	-0.0751	1.42593	-0.0807	1.41921	-0.0888	1.41299	-0.0951
0.2789	1.40600	-0.1083	1.40036	-0.1132	1.39388	-0.1204	1.38782	-0.1252
0.3759	1.37947	-0.1297	1.37399	-0.1352	1.36775	-0.1405	1.36185	-0.1429
0.4745	1.35234	-0.1396	1.34699	-0.1436	1.34099	-0.1474	1.33526	-0.1479
0.5763	1.32409	-0.1327	1.31891	-0.1369	1.31318	-0.1405	1.30762	-0.1403
0.6782	1.29562	-0.1098	1.29063	-0.1158	1.28516	-0.1203	1.27981	-0.1207
0.7852	1.26562	-0.0762	1.26078	-0.0815	1.25560	-0.0872	1.25046	-0.0890
0.8914	1.23579	-0.0374	1.23109	-0.0406	1.22616	-0.0459	1.22122	-0.0484
1.0000	1.20532	0.0000	1.20075	0.0000	1.19602	0.0000	1.19125	0.0000

Table 6.2.2: Mole fraction of 3-chloroaniline (x_1), density (ρ) and excess molar volume (V^E) data for the binary mixture of 3-chloroaniline with chlorobenzene at T= (303.15-318.15) K

	303.15 K		308.15 K		313.15 K		318.15 K	
x_1	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}
0.0000	1.09554	0.0000	1.08972	0.0000	1.08471	0.0000	1.07945	0.0000
0.0895	1.10611	-0.0443	1.10043	-0.0483	1.09550	-0.0542	1.09031	-0.0588
0.1802	1.11669	-0.0820	1.11115	-0.0889	1.10627	-0.0986	1.10112	-0.1032
0.2935	1.12974	-0.1189	1.12432	-0.1257	1.11945	-0.1340	1.11434	-0.1375
0.3821	1.13977	-0.1376	1.13443	-0.1425	1.12956	-0.1483	1.12449	-0.1514
0.4956	1.15234	-0.1433	1.14715	-0.1480	1.14229	-0.1517	1.13726	-0.1545
0.5823	1.16175	-0.1348	1.15668	-0.1404	1.15183	-0.1433	1.14685	-0.1458
0.6923	1.17348	-0.1118	1.16855	-0.1174	1.16377	-0.1226	1.15887	-0.1270
0.8012	1.18488	-0.0773	1.18009	-0.0824	1.17535	-0.0880	1.17053	-0.0943
0.8856	1.19358	-0.0437	1.18891	-0.0492	1.18421	-0.0553	1.17942	-0.0599
1.0000	1.20532	0.0000	1.20075	0.0000	1.19602	0.0000	1.19125	0.0000

Table 6.2.3: Mole fraction of 3-chloroaniline(x_1), density (ρ) and excess molar volume (V^E) data for the binary mixture of 3-chloroaniline with nitrobenzene at T= (303.15-318.15) K

	303.15 K		308.15 K		313.15 K		318.15 K	
x_1	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}	ρ/ g·cm^{-3}	V^E/ cm^3·mol^{-1}
0.0000	1.19345	0.0000	1.18829	0.0000	1.18369	0.0000	1.17732	0.0000
0.0812	1.19497	-0.0464	1.18992	-0.0520	1.18537	-0.0572	1.17919	-0.0631
0.1725	1.19657	-0.0889	1.19159	-0.0964	1.18704	-0.1032	1.18100	-0.1091
0.2623	1.19801	-0.1201	1.19307	-0.1267	1.18849	-0.1329	1.18258	-0.1373
0.3725	1.19959	-0.1430	1.19469	-0.1476	1.19008	-0.1522	1.18435	-0.1566
0.4854	1.20100	-0.1489	1.19616	-0.1524	1.19152	-0.1560	1.18597	-0.1611
0.5896	1.20212	-0.1393	1.19735	-0.1433	1.19270	-0.1474	1.18732	-0.1525
0.6785	1.20296	-0.1209	1.19825	-0.1262	1.19361	-0.1316	1.18837	-0.1367
0.7825	1.20381	-0.0891	1.19918	-0.0960	1.19455	-0.1028	1.18950	-0.1094
0.8905	1.20459	-0.0474	1.20003	-0.0537	1.19537	-0.0599	1.19049	-0.0657
1.0000	1.20532	0.0000	1.20075	0.0000	1.19602	0.0000	1.19125	0.0000

Table 6.2.4: Values of the parameters of computed from Redlish - Kister equation 3.2.2 and standard deviation, σ (V^E) at T = (303.15 -318.15) K

System	a_0	a_1	a_2	σ (V^E)
		$cm^3 \cdot mol^{-1}$		
303.15 K				
3-chloroaniline				
bromobenzene	-0.555	0.051	0.216	0.001
chlorobenzene	-0.571	0.071	0.134	0.001
nitrobenzene	-0.594	0.087	0.064	0.001
308.15 K				
3-chloroaniline				
bromobenzene	-0.574	0.056	0.180	0.001
chlorobenzene	-0.591	0.0714	0.085	0.001
nitrobenzene	-0.608	0.089	-0.021	0.001
313.15 K				
3-chloroaniline				
bromobenzene	-0.588	0.068	0.099	0.001
chlorobenzene	-0.608	0.083	0.004	0.001
nitrobenzene	-0.623	0.088	-0.101	0.001
318.15 K				
3-chloroaniline				
bromobenzene	-0.589	0.089	0.031	0.001
chlorobenzene	-0.617	0.081	-0.062	0.001
nitrobenzene	-0.636	0.089	-0.179	0.001

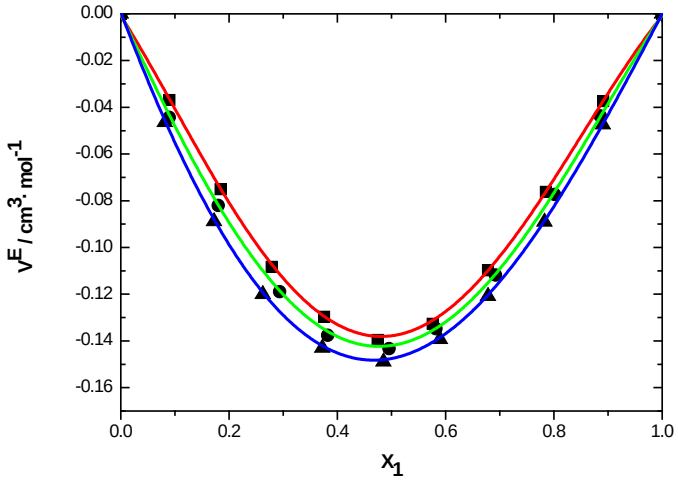

Fig.6.2.1: Variation of excess molar volume (V^E) with mole fraction (x_1) of 3-chloroaniline for the binary liquid mixtures of 3-chloroaniline with bromobenzene (■), chlorobenzene (●) and nitrobenzene (▲) at 303.15 K

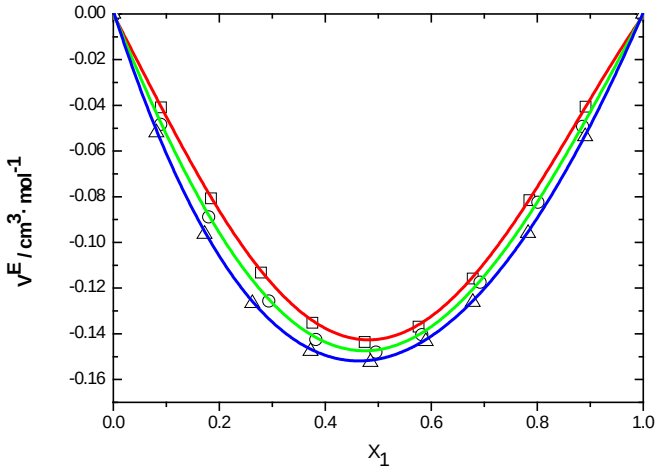

Fig.6.2.2: Variation of excess molar volume (V^E) with mole fraction (x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene (□), chlorobenzene (○) and nitrobenzene (Δ) at 308.15 K

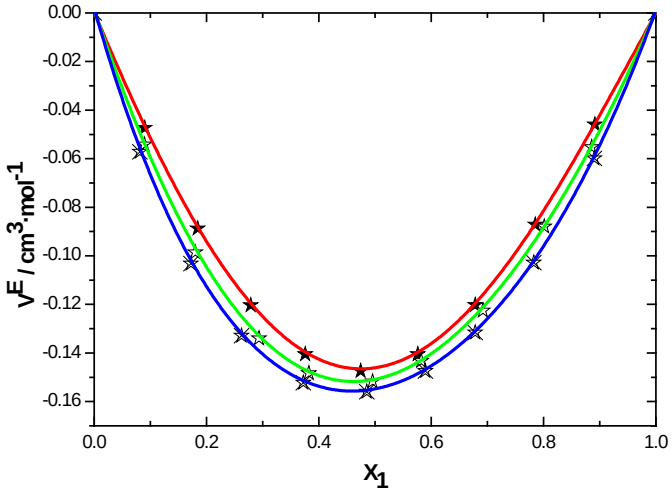

Fig.6.2.3: Variation of excess molar volume (V^E) with mole fraction (x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene (★) chlorobenzene (☆) and nitrobenzene (✯) at 313.15 K

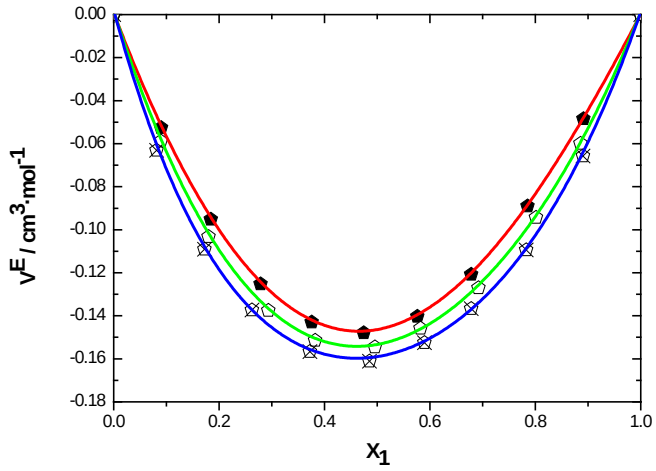

Fig.6.2.4: Variation of excess molar volume (V^E) with mole fraction (x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene (⬟),chlorobenzene (⬠) and nitrobenzene (⊠) at 318.15 K

6.3 Isentropic compressibility (κ_s) and excess isentropic compressibility (κ_s^E) data of binary mixtures of 3-chloroaniline with mono substituted benzene derivatives at T= (303.15 - 318.15) K

In the present study speed of sound (u) data of pure liquids and their binary mixtures formed by mixing 3-chloroaniline with mono substituted benzene derivatives were measured over the entire composition range at T= (303.15 - 318.15) K. Moreover, the measured speed of sound (u), and density (ρ) data were used to compute isentropic compressibilities (κ_s) and excess isentropic compressibilities (κ_s^E) by adopting the equations from 3.3.1 to 3.3.5 of chapter III.

The mole fraction of 3-chloroaniline (x_1), speed of sound (u), isentropic compressibility (κ_s), and excess isentropic compressibility (κ_s^E) were included in Tables 6.3.1-6.3.3 and also the κ_s^E data were graphically represented in Figs. 6.3.1- 6.3.4

A perusal of curves in Figs. 6.3.1- 6.3.4 revealed that excess isentropic compressibility (κ_s^E) was negative over the entire composition range for the binary mixtures of 3-chloroaniline with mono substituted benzene derivatives at T= (303.15-318.15) K. The observed values of κ_s^E can be qualitatively explained by considering the factors (i) disruption of associated structures / molecular order in the pure liquids, (ii) the formation of weak bonds by dipole-induced dipole interaction between unlike molecules, and (iii) free volume changes from mixing of components of different sizes. The first factor contributes positive κ_s^E values, whereas the remaining two factors led to negative κ_s^E values [16]. The resultant negative values of κ_s^E for the binaries indicate the dominance of net combination of factors (ii) and (iii), and that binaries are less compressible than their ideal mixtures.

The values of κ_s^E for the binary mixtures of 3-chloroaniline with mono substituted benzene derivatives are in the following order: Nitrobenzene < chlorobenzene < bromobenzene

The above order suggests that the extent of interactions between unlike molecules decreases with polarizability [15, 17] value and proper dipole alignment of the components. The negative values of κ_s^E increase with increasing temperature and this suggests that specific interactions increase due to the enhanced thermal energy. Comelli et al. [18] have also reported similar behavior for κ_s^E.

The dependence of κ_s^E data on composition was correlated by the Redlich - Kister polynomial equation (3.3.6) of chapter III. The values of all the binary parameters along with standard deviation σ (κ_s^E) were given in Table 6.3.7 and the adjustable parameters of the functions are determined by using the least-square equation (3.3.7) of chapter III

The experimental density (ρ) and speed of sound (u) data were used to calculate the values of acoustic impedance, (Z) and intermolecular free length (L_f). The values of Δu, ΔZ, and ΔL_f were evaluated by adopting the equation 3.3.8 of chapter III.

Generally, negative values of Δu indicate dispersion forces due to weak interactions whereas positive values of Δu indicate strong interactions. The sign and magnitude of Δu play an important role in describing the molecular rearrangements among the component molecules in the mixtures and leads to intermolecular interactions between the molecules.

An examination of data in Tables 6.3.4 - 6.3.6 reveals that deviation in speed of sound *(*Δu) values are negative for 3-chloroaniline + bromobenzene / chlorobenzene and positive for 3-chloroaniline+nitrobenzene mixtures over the entire composition range and at all investigated temperatures. In general, the positive deviation in Δu indicate the presence of significant interactions and negative deviations in Δu indicate weak interactions between the unlike molecules in the mixtures.

An examination of data in Tables 6.3.4 - 6.3.6 reveals that ΔZ values are negative for 3-chloroaniline + bromobenzene / chlorobenzene and positive for 3-chloroaniline + nitrobenzene mixtures over the entire composition range and at all investigated temperatures. The observed negative Δu and ΔZ values suggest the presence of weak interaction between unlike molecules whereas the positive Δu and ΔZ values for 3-

chloroaniline + nitrobenzene mixture suggest the presence of specific interaction between 3-chloroaniline + nitrobenzene molecules in these mixtures. The deviation in intermolecular free length is negative for all the binary mixtures at T=(303.15-318.15) K. The negative deviation of the intermolecular free length indicates the presence of strong dipole-dipole interactions between unlike molecules in the binary liquid mixtures.

Table 6.3.1: Mole fraction of 3-chloroaniline(x_1), speed of sound (u) isentropic compressibility (κ_s) and excess isentropic compressibility (κ_s^E) data for the binary mixture of 3-chloroaniline with bromobenzene at T= (303.15-318.15) K

	303.15 K			308.15 K			313.15 K			318.15 K		
	u	κ_s	κ_s^E	u	κ_s	κ_s^E	u	κ_s	κ_s^E	u	κ_s	κ_s^E
x_1	/m·s^{-1}	/TPa^{-1}	/ TPa^{-1}	/m·s^{-1}	/TPa^{-1}	/ TPa^{-1}	/m·s^{-1}	/TPa^{-1}	/ TPa^{-1}	/m·s^{-1}	/TPa^{-1}	/ TPa^{-1}
0.0000	1136.0	5.230	0.000	1122.0	5.384	0.000	1109.0	5.539	0.000	1099.0	5.666	0.000
0.0902	1162.5	5.078	-0.574	1148.3	5.226	-0.650	1134.9	5.376	-0.729	1124.6	5.500	-0.790
0.1842	1191.5	4.920	-1.071	1177.1	5.062	-1.174	1163.0	5.209	-1.271	1152.3	5.330	-1.345
0.2789	1222.1	4.762	-1.456	1207.4	4.898	-1.560	1192.8	5.043	-1.641	1181.7	5.160	-1.706
0.3759	1255.1	4.602	-1.717	1240.2	4.732	-1.817	1224.9	4.873	-1.874	1213.3	4.988	-1.930
0.4745	1290.5	4.440	-1.837	1275.4	4.564	-1.941	1259.3	4.703	-1.982	1247.3	4.814	-2.044
0.5763	1329.2	4.275	-1.802	1313.8	4.392	-1.925	1296.9	4.527	-1.967	1284.5	4.635	-2.054
0.6782	1370.2	4.111	-1.607	1354.7	4.222	-1.754	1336.9	4.353	-1.815	1324.0	4.458	-1.937
0.7852	1416.0	3.940	-1.231	1400.3	4.045	-1.392	1381.6	4.173	-1.474	1368.0	4.273	-1.624
0.8914	1464.5	3.773	-0.697	1448.6	3.871	-0.826	1428.7	3.995	-0.903	1414.5	4.093	-1.031
1.0000	1517.5	3.603	0.000	1501.2	3.695	0.000	1480.0	3.817	0.000	1464.8	3.912	0.000

Table 6.3.2: Mole fraction of 3-chloroaniline(x_1), speed of sound (u) isentropic compressibility (κ_s) and excess isentropic compressibility (κ_s^E) data for the binary mixture of 3-chloroaniline with chlorobenzene at T=(303.15-318.15) K

	303.15 K			308.15 K			313.15 K			318.15 k		
	u	κ_s	κ_s^E	u	κ_s	κ_s^E	u	κ_s	κ_s^E	u	κ_s	κ_s^E
x_1	/m·s^{-1}	/TPa^{-1}	/ TPa^{-1}	/m·s^{-1}	/TPa^{-1}	/ TPa^{-1}	/m·s^{-1}	/TPa^{-1}	/ TPa^{-1}	/m·s^{-1}	/TPa^{-1}	/ TPa^{-1}
0.0000	1248.2	5.859	0.000	1226.0	6.105	0.000	1206.2	6.336	0.000	1181.0	6.642	0.000
0.0895	1265.6	5.645	-0.661	1243.5	5.877	-0.721	1223.6	6.097	-0.785	1198.7	6.383	-0.799
0.1802	1284.1	5.431	-1.169	1262.3	5.648	-1.268	1242.2	5.858	-1.309	1217.7	6.125	-1.301
0.2935	1308.9	5.167	-1.603	1287.4	5.367	-1.733	1267.1	5.564	-1.700	1243.1	5.807	-1.679
0.3821	1329.6	4.963	-1.806	1308.4	5.149	-1.930	1288.0	5.337	-1.865	1264.5	5.561	-1.835
0.4956	1358.1	4.705	-1.905	1337.4	4.874	-2.043	1316.8	5.049	-1.951	1294.2	5.250	-1.940
0.5823	1381.5	4.510	-1.862	1361.3	4.666	-2.005	1340.5	4.831	-1.934	1318.8	5.013	-1.947
0.6923	1413.3	4.266	-1.655	1393.9	4.404	-1.817	1373.1	4.558	-1.790	1352.6	4.717	-1.838
0.8012	1447.5	4.028	-1.268	1429.0	4.150	-1.408	1408.2	4.290	-1.458	1389.2	4.427	-1.522
0.8856	1476.0	3.846	-0.826	1458.3	3.955	-0.927	1437.5	4.086	-1.006	1419.9	4.205	-1.113
1.0000	1517.5	3.603	0.000	1501.2	3.695	0.000	1480.3	3.816	0.000	1464.8	3.912	0.000

Table 6.3.3: Mole fraction of 3-chloroaniline(x_1), speed of sound (u) isentropic compressibility (κ_s) and excess isentropic compressibility (κ_s^E) data for the binary mixture of 3-chloroaniline with nitrobenzene at T= (303.15-318.15) K

	303.15 K			308.15 K			313.15 K			318.15 K		
	u	κ_s	κ_s^E	u	κ_s	κ_s^E	u	κ_s	κ_s^E	u	κ_s	κ_s^E
x_1	/m·s^{-1}	/TPa^{-1}	/ TPa^{-1}	/m·s^{-1}	/TPa^{-1}	/ TPa^{-1}	/m·s^{-1}	/TPa^{-1}	/ TPa^{-1}	/m·s^{-1}	/TPa^{-1}	/ TPa^{-1}
0.0000	1438.0	4.052	0.000	1420.0	4.174	0.000	1402.0	4.298	0.000	1385.0	4.428	0.000
0.0812	1445.0	4.008	-0.687	1427.2	4.126	-0.787	1409.1	4.249	-0.883	1392.1	4.376	-0.898
0.1725	1452.6	3.961	-1.235	1435.0	4.075	-1.387	1416.6	4.198	-1.508	1399.7	4.322	-1.516
0.2623	1460.0	3.916	-1.595	1442.5	4.028	-1.762	1423.8	4.150	-1.863	1407.0	4.272	-1.859
0.3725	1468.9	3.863	-1.853	1451.6	3.972	-2.014	1432.6	4.094	-2.103	1415.8	4.212	-2.072
0.4854	1478.0	3.812	-1.951	1460.9	3.917	-2.105	1441.5	4.039	-2.195	1424.9	4.153	-2.167
0.5896	1486.4	3.765	-1.910	1469.4	3.868	-2.064	1449.8	3.989	-2.178	1433.4	4.099	-2.183
0.6785	1493.5	3.727	-1.769	1476.7	3.827	-1.925	1456.8	3.947	-2.048	1440.7	4.054	-2.117
0.7825	1501.6	3.684	-1.451	1485.0	3.781	-1.603	1465.0	3.901	-1.767	1449.1	4.004	-1.866
0.8905	1509.8	3.642	-0.893	1493.4	3.737	-1.005	1473.0	3.856	-1.156	1457.3	3.955	-1.248
1.0000	1517.5	3.603	0.000	1501.2	3.695	0.000	1480.3	3.816	0.000	1464.8	3.912	0.000

Table 6.3.4: Mole fraction of 3-chloroaniline(x_1), deviation in speed of sound (Δu), deviation in intermolecular free length (ΔL_f) and deviation in acoustic impedance (ΔZ) data for the binary mixture of 3-chloroaniline with bromobenzene at T= (303.15 -318.15) K

	303.15 K			308.15 K			313.15 K			318.15 K		
	Δu	$\Delta L_f \times 10^{-9}$	$\Delta Z \times 10^{-3}$	Δu	$\Delta L_f \times 10^{-9}$	$\Delta Z \times 10^{-3}$	Δu	$\Delta L_f \times 10^{-9}$	$\Delta Z \times 10^{-3}$	Δu	$\Delta L_f \times 10^{-9}$	$\Delta Z \times 10^{-3}$
x_1	/ $m \cdot s^{-1}$	/m	/ $kgm^{-2}s^{-1}$	/ $m \cdot s^{-1}$	/m	/ $kgm^{-2}s^{-1}$	/ $m \cdot s^{-1}$	/m	/ $kgm^{-2}s^{-1}$	/ $m \cdot s^{-1}$	/m	/ $kgm^{-2}s^{-1}$
0.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.0902	-7.890	-1.739	-2.221	-7.859	-1.974	-2.171	-7.590	-2.256	-1.880	-7.435	-2.475	-1.702
0.1842	-14.81	-3.246	-4.082	-14.79	-3.563	-4.063	-14.31	-3.926	-3.620	-14.03	-4.206	-3.362
0.2789	-20.33	-4.412	-5.513	-20.32	-4.730	-5.570	-19.69	-5.063	-5.066	-19.32	-5.326	-4.790
0.3759	-24.32	-5.205	-6.559	-24.34	-5.510	-6.670	-23.61	-5.778	-6.153	-23.17	-6.020	-5.875
0.4745	-26.54	-5.570	-7.149	-26.56	-5.887	-7.293	-25.77	-6.111	-6.773	-25.27	-6.374	-6.480
0.5763	-26.70	-5.464	-7.257	-26.70	-5.841	-7.360	-25.89	-6.068	-6.832	-25.35	-6.409	-6.494
0.6782	-24.52	-4.872	-6.788	-24.48	-5.326	-6.787	-23.70	-5.602	-6.243	-23.13	-6.053	-5.842
0.7852	-19.52	-3.734	-5.533	-19.41	-4.233	-5.422	-18.74	-4.558	-4.895	-18.21	-5.085	-4.454
0.8914	-11.55	-2.113	-3.371	-11.41	-2.515	-3.216	-10.97	-2.795	-2.822	-10.59	-3.236	-2.459
1.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 6.3.5: Mole fraction of 3-chloroaniline(x_1), deviation in speed of sound (Δu), deviation in intermolecular free length (ΔL_f) and deviation in acoustic impedance (ΔZ) data for the binary mixture of 3-chloroaniline with chlorobenzene at T= (303.15 -318.15) K

	303.15 K			308.15 K			313.15 K			318.15 K		
	Δu	$\Delta L_f \times 10^{-9}$	$\Delta Z \times 10^{-3}$	Δu	$\Delta L_f \times 10^{-9}$	$\Delta Z \times 10^{-3}$	Δu	$\Delta L_f \times 10^{-9}$	$\Delta Z \times 10^{-3}$	Δu	$\Delta L_f \times 10^{-9}$	$\Delta Z \times 10^{-3}$
x_1	/ $m \cdot s^{-1}$	/m	/ $kgm^{-2}s^{-1}$	/ $m \cdot s^{-1}$	/m	/ $kgm^{-2}s^{-1}$	/ $m \cdot s^{-1}$	/m	/ $kgm^{-2}s^{-1}$	/ $m \cdot s^{-1}$	/m	/ $kgm^{-2}s^{-1}$
0.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.0895	-6.748	-3.792	-8.926	-7.120	-4.033	-9.361	-7.124	-4.449	-9.278	-7.697	-4.711	-9.943
0.1802	-12.59	-6.771	-16.65	-13.30	-7.177	-17.49	-13.38	-7.698	-17.42	-14.47	-8.053	-18.74
0.2935	-18.33	-9.372	-24.22	-19.38	-9.913	-25.50	-19.57	-10.35	-25.57	-21.19	-10.81	-27.56
0.3821	-21.48	-10.60	-28.38	-22.74	-11.14	-29.97	-22.98	-11.55	-30.11	-24.91	-12.05	-32.51
0.4956	-23.56	-11.18	-31.23	-24.98	-11.77	-33.02	-25.26	-12.13	-33.25	-27.43	-12.72	-35.95
0.5823	-23.54	-10.89	-31.32	-24.98	-11.50	-33.13	-25.26	-11.90	-33.36	-27.46	-12.56	-36.11
0.6923	-21.32	-9.600	-28.53	-22.62	-10.25	-30.16	-22.86	-10.71	-30.31	-24.90	-11.41	-32.83
0.8012	-16.47	-7.262	-22.20	-17.49	-7.807	-23.47	-17.59	-8.376	-23.46	-19.22	-8.990	-25.43
0.8856	-10.73	-4.677	-14.59	-11.42	-5.062	-15.40	-11.42	-5.574	-15.28	-12.42	-6.177	-16.49
1.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 6.3.6: Mole fraction of 3-chloroaniline(x_1), deviation in speed of sound (Δu), deviation in intermolecular free length (ΔL_f) and deviation in acoustic impedance (ΔZ) data for the binary mixture of 3-chloroaniline with nitrobenzene at T= (303.15 -318.15) K

	303.15 K			308.15 K			313.15 K			318.15 K		
	Δu	$\Delta L_f \times 10^{-9}$	$\Delta Z \times 10^{-3}$	Δu	$\Delta L_f \times 10^{-9}$	$\Delta Z \times 10^{-3}$	Δu	$\Delta L_f \times 10^{-9}$	$\Delta Z \times 10^{-3}$	Δu	$\Delta L_f \times 10^{-9}$	$\Delta Z \times 10^{-3}$
x_1	/ m·s^{-1}	/m	/ kgm^{-2}s^{-1}	/ m·s^{-1}	/m	/ kgm^{-2}s^{-1}	/ m·s^{-1}	/m	/ kgm^{-2}s^{-1}	/ m·s^{-1}	/m	/ kgm^{-2}s^{-1}
0.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.0857	0.537	-2.423	1.379	0.596	-2.769	1.518	0.697	-3.104	1.705	0.599	-3.207	1.648
0.1749	0.912	-4.387	2.513	0.989	-4.923	2.683	1.110	-5.361	2.905	0.937	-5.489	2.733
0.2679	1.133	-5.698	3.283	1.202	-6.300	3.417	1.289	-6.691	3.579	1.063	-6.808	3.304
0.3619	1.299	-6.650	3.862	1.342	-7.247	3.921	1.419	-7.614	4.038	1.114	-7.663	3.659
0.4597	1.419	-7.012	4.111	1.447	-7.593	4.131	1.532	-7.968	4.241	1.213	-8.036	3.852
0.5607	1.502	-6.853	4.063	1.535	-7.431	4.102	1.660	-7.881	4.268	1.397	-8.049	3.952
0.6649	1.523	-6.324	3.794	1.573	-6.900	3.883	1.704	-7.369	4.084	1.573	-7.733	3.933
0.7726	1.410	-5.153	3.144	1.486	-5.700	3.306	1.689	-6.284	3.625	1.640	-6.720	3.612
0.8835	0.987	-3.144	1.958	1.060	-3.537	2.128	1.264	-4.056	2.452	1.278	-4.422	2.526
1.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 6.3.7: Values of the parameters of computed from Redlish - Kister equation 3.3. 6 and standard deviation, $\sigma(\kappa_s^{E})$ at T = (303.15-318.15) K

System	b_0	b_1	b_2	$\sigma(\kappa_s^{E})$
		TPa^{-1}		
303.15 K				
3-chloroaniline				
bromobenzene	-7.359	-0.089	0.114	0.001
chlorobenzene	-7.585	-0.012	-1.035	0.001
nitrobenzene	-7.811	-0.087	-2.094	0.001
308.15 K				
3-chloroaniline				
bromobenzene	-7.805	-0.407	-0.667	0.001
chlorobenzene	-8.195	-0.256	-1.307	0.007
nitrobenzene	-8.426	-0.026	-3.054	0.001
313.15 K				
3-chloroaniline				
bromobenzene	-7.963	-0.344	-1.789	0.001
chlorobenzene	-8.357	-0.333	-3.121	0.001
nitrobenzene	-8.750	-0.279	-4.695	0.009
318.15 K				
3-chloroaniline				
bromobenzene	-8.228	-0.749	-2.996	0.001
chlorobenzene	-8.549	-0.840	-4.143	0.015
nitrobenzene	-8.791	-0.791	-5.706	0.001

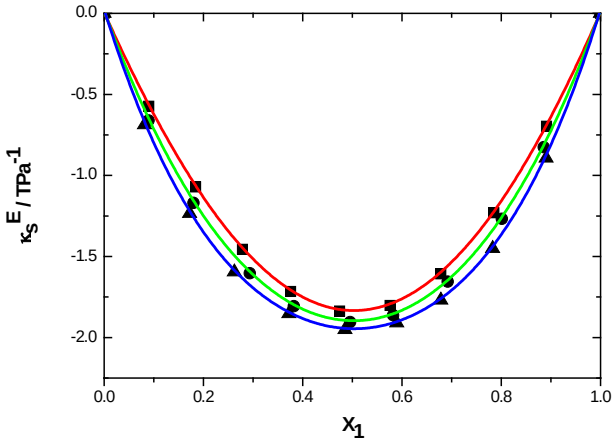

Fig.6.3.1: Excess isentropic compressibility (κ_s^E) with mole fraction (x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene (■), chlorobenzene (●) and nitrobenzene (▲) at 303.15 K

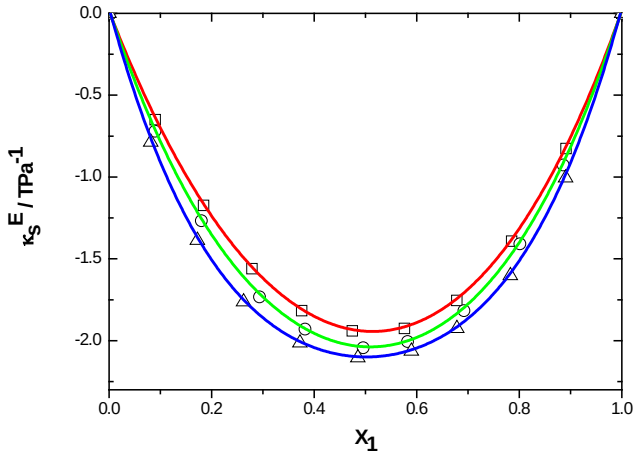

Fig.6.3.2: Excess isentropic compressibility (κ_s^E) with mole fraction (x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene (□), chlorobenzene (○) and nitrobenzene (Δ) at 308.15 K

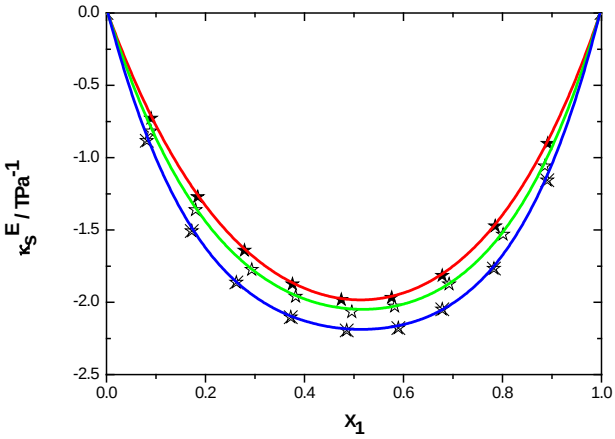

Fig.6.3.3: Excess isentropic compressibility (κ_s^E) with mole fraction (x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene (★) chlorobenzene (☆) and nitrobenzene (⛤) at 313.15 K

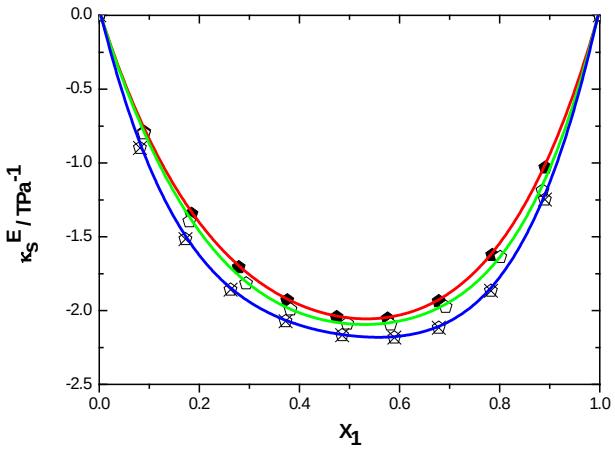

Fig.6.3.4: Excess isentropic compressibility (κ_s^E) with mole fraction(x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene (⬟),chlorobenzene (⬠) and nitrobenzene (⊠) at 318.15 K

6.4 Viscosity (η), deviation in viscosity (Δη) and excess Gibbs energy of activation of viscous flow (G^{*E}) of binary mixtures of 3-chloroaniline with mono substituted benzene derivatives at T= (303.15 - 318.15) K

Deviation in viscosity (Δη), excess Gibbs energy of activation of viscous flow (G^{*E}) of the mixtures were calculated using equations (3.4.1 and 3.4.4) respectively. The viscosity deviation data of the liquid mixtures were graphically given in Figures 6.4.1-6.4.4 and viscosity deviation data were given in Tables 6.4.1- 6.4.3.

The sign and magnitude of Δη depend on the combined effect of the factors such as molecular size, shape and intermolecular forces. The data presented in Figures 6.4.1 - 6.4.4 reveal that deviation in viscosity is positive for all the binary systems over the entire composition range at T = (303.15 - 318.15) K.

The sign and magnitude of Δη depend on the combined effect of the factors such as molecular size, shape and intermolecular forces [19]. The positive data for all the binary systems suggests that the viscosity of the mixture is higher than that of the pure components and hence the fluidity of the mixture is low. This indicates the presence of specific interaction such as the formation of charge-transfer complex between unlike molecules [3]. The positive values of deviation in viscosity increase with increasing temperature for all the binary systems. The viscosity deviation values are found to be opposite to the sign of excess molar volumes for all binary mixtures, which is in agreement with the view proposed by Brocos et al [20, 21].

The dependence of Δη data on composition was correlated by the Redlich - Kister polynomial equation (3.4.2) of chapter III. The values of all the binary parameters along with standard deviation σ (Δη) were given in Table 6.4.7 and the adjustable parameters of the functions are determined by using the least-square equation (3.4.3) of chapter III

The variation of excess Gibbs energy of activation of viscous flow (G^{*E}) with mole fraction of 3-chloroaniline with mono substituted benzene derivatives at all investigated temperatures were depicted in Figs. 6.4.5 - 6.4.8 and also data represented in Tables 6.4.1- 6.4.3.

According to Reed and Taylor [22] and Palepu et al. [23], the G^{*E} parameter may be considered as a reliable criterion to detect or exclude the presence of interaction between unlike molecules. According to these authors, the magnitude of the positive G^{*E} values is an excellent indication of the strength of specific interactions. An examination of curves in Figs. 6.4.5 - 6.4.8 and Tables 6.4.1- 6.4.3 suggests that the excess Gibbs energy of activation of viscous flow for all the binary systems are positive over the entire composition range at all investigated temperatures. The positive values of excess Gibbs energy of activation of viscous flow for the binary systems investigated suggest that the dipole-induced interactions between the components of the mixtures are resulting in the formation of electron donor-acceptor complexes.

Table 6.4.1: Mole fraction of 3-chloroaniline(x_1), viscosity (η) deviation in viscosity ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow (G^{*E}) data for the binary mixture of 3-chloroaniline with bromobenzene at T= (303.15-318.15) K

	303.15 K			308.15 K			313.15 K			318.15 K		
	η	$\Delta\eta$	G^{*E}	η	$\Delta\eta$	G^{*E}	η	$\Delta\eta$	G^{*E}	η	$\Delta\eta$	G^{*E}
x_1	/ mPa·s	/ mPa·s	/ J·˙mol^{-1}	/ mPa·s	/ mPa·s	/ J·˙mol^{-1}	/ mPa·s	/ mPa·s	/ J·˙mol^{-1}	/ mPa·s	/ mPa·s	/ J·˙mol^{-1}
0.0000	0.982	0.000	0.000	0.953	0.000	0.000	0.892	0.000	0.000	0.848	0.000	0.000
0.0902	1.3640	0.087	4.878	1.3066	0.093	4.792	1.2233	0.102	4.986	1.1553	0.111	5.069
0.1842	1.7405	0.156	7.504	1.6502	0.165	7.373	1.5326	0.173	7.515	1.4367	0.188	7.634
0.2789	2.1011	0.206	8.727	1.9757	0.217	8.581	1.8256	0.226	8.726	1.6923	0.238	8.759
0.3759	2.4536	0.241	9.041	2.2910	0.252	8.900	2.1041	0.258	9.013	1.9340	0.269	9.022
0.4745	2.7955	0.260	8.688	2.5928	0.269	8.552	2.3723	0.276	8.682	2.1646	0.285	8.689
0.5763	3.1308	0.262	7.794	2.8879	0.270	7.690	2.6325	0.278	7.833	2.3884	0.287	7.882
0.6782	3.4464	0.244	6.470	3.1663	0.254	6.429	2.8755	0.262	6.580	2.5952	0.273	6.673
0.7852	3.7517	0.199	4.686	3.4274	0.206	4.668	3.1052	0.220	4.858	2.7856	0.230	4.978
0.8914	4.0220	0.122	2.550	3.6573	0.129	2.574	3.2934	0.139	2.703	2.9336	0.147	2.815
1.0000	4.2554	0.000	0.000	3.8420	0.000	0.000	3.4302	0.000	0.000	3.0224	0.000	0.000

Table 6.4.2: Mole fraction of 3-chloroaniline(x_1), viscosity (η) deviation in viscosity ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow (G^{*E}) data for the binary mixtures of 3-chloroaniline with chlorobenzene at T= (303.15-318.15) K

	303.15 K			308.15 K			313.15 K			318.15 K		
	η	$\Delta\eta$	G^{*E}	η	$\Delta\eta$	G^{*E}	η	$\Delta\eta$	G^{*E}	η	$\Delta\eta$	G^{*E}
x_1	/ mPa·s	/ mPa·s	/ J·˙mol^{-1}	/ mPa·s	/ mPa·s	/ J·˙mol^{-1}	/ mPa·s	/ mPa·s	/ J·˙mol^{-1}	/ mPa·s	/ mPa·s	/ J·˙mol^{-1}
0.0000	0.712	0.000	0.000	0.675	0.000	0.000	0.634	0.000	0.000	0.6020	0.000	0.000
0.0895	1.1257	0.097	7.409	1.0586	0.100	7.435	0.9961	0.112	7.717	0.9397	0.121	7.846
0.1802	1.5164	0.166	10.78	1.4177	0.172	10.83	1.3216	0.184	11.04	1.2381	0.200	11.21
0.2935	1.9751	0.223	12.31	1.8355	0.231	12.37	1.6965	0.242	12.53	1.5696	0.257	12.63
0.3821	2.3170	0.251	12.33	2.1446	0.259	12.40	1.9725	0.270	12.56	1.8085	0.282	12.59
0.4956	2.7376	0.269	11.43	2.5221	0.278	11.51	2.3065	0.287	11.66	2.0977	0.296	11.68
0.5823	3.0458	0.271	10.23	2.7969	0.278	10.31	2.5480	0.286	10.45	2.3077	0.296	10.52
0.6923	3.4174	0.252	8.210	3.1256	0.258	8.290	2.8386	0.269	8.462	2.5567	0.279	8.569
0.8012	3.7561	0.205	5.723	3.4214	0.209	5.795	3.0972	0.223	5.984	2.7731	0.232	6.108
0.8856	3.9909	0.141	3.484	3.6227	0.143	3.536	3.2639	0.154	3.676	2.9082	0.163	3.802
1.0000	4.2554	0.000	0.000	3.8420	0.000	0.000	3.4302	0.000	0.000	3.0224	0.000	0.000

Table 6.4.3: Mole fraction of 3-chloroaniline(x_1), viscosity (η) deviation in viscosity ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow (G^{*E}) data for the binary mixtures of 3-chloroaniline with nitrobenzene at T= (303.15-318.15) K

	303.15 K			308.15 K			313.15 K			318.15 K		
	η	$\Delta\eta$	G^{*E}	η	$\Delta\eta$	G^{*E}	η	$\Delta\eta$	G^{*E}	η	$\Delta\eta$	G^{*E}
x_1	/ mPa·s	/ mPa·s	/ J·˙mol^{-1}	/ mPa·s	/ mPa·s	/ J·˙mol^{-1}	/ mPa·s	/ mPa·s	/ J·˙mol^{-1}	/ mPa·s	/ mPa·s	/ J·˙mol^{-1}
0.0000	1.627	0.000	0.000	1.498	0.000	0.000	1.388	0.000	0.000	1.2750	0.000	0.000
0.0812	1.9381	0.098	2.402	1.7870	0.099	2.516	1.6661	0.112	2.793	1.5417	0.125	3.115
0.1725	2.2529	0.172	3.953	2.0785	0.176	4.153	1.9345	0.194	4.499	1.7872	0.211	4.906
0.2623	2.5370	0.221	4.753	2.3401	0.227	5.006	2.1673	0.244	5.325	1.9919	0.259	5.707
0.3725	2.8629	0.257	5.119	2.6374	0.266	5.401	2.4266	0.278	5.662	2.2184	0.292	6.031
0.4854	3.1789	0.276	5.022	2.9219	0.286	5.301	2.6738	0.295	5.529	2.4304	0.307	5.869
0.5896	3.4561	0.279	4.612	3.1679	0.288	4.866	2.8888	0.297	5.096	2.6146	0.309	5.430
0.6785	3.6787	0.268	4.042	3.3625	0.274	4.260	3.0591	0.285	4.504	2.7549	0.294	4.795
0.7825	3.9147	0.231	3.108	3.5652	0.233	3.269	3.2336	0.248	3.518	2.9016	0.259	3.812
0.8905	4.1171	0.149	1.787	3.7340	0.149	1.876	3.3687	0.162	2.069	3.0043	0.173	2.296
1.0000	4.2554	0.000	0.000	3.8420	0.000	0.000	3.4302	0.000	0.000	3.0224	0.000	0.000

Table 6.4.4: Values of the parameters of computed from Redlish - Kister equation 3.4.2 and standard deviation σ (Δη) at T = (303.15-318.15) K

System	c_0	c_1	c_2	σ (Δη)
		mPa·s[1]		
303.15 K				
3-chloroaniline				
bromobenzene	1.049	0.131	0.177	0.001
chlorobenzene	1.078	0.144	0.340	0.001
nitrobenzene	1.109	0.162	0.482	0.001
308.15 K				
3-chloroaniline				
bromobenzene	1.086	0.126	0.229	0.001
chlorobenzene	1.111	0.131	0.334	0.001
nitrobenzene	1.149	0.149	0.425	0.001
313.15 K				
3-chloroaniline				
bromobenzene	1.109	0.137	0.356	0.001
chlorobenzene	1.143	0.126	0.479	0.001
nitrobenzene	1.183	0.133	0.618	0.001
318.15 K				
3-chloroaniline				
bromobenzene	1.147	0.122	0.456	0.001
chlorobenzene	1.186	0.104	0.572	0.001
nitrobenzene	1.225	0.108	0.759	0.001

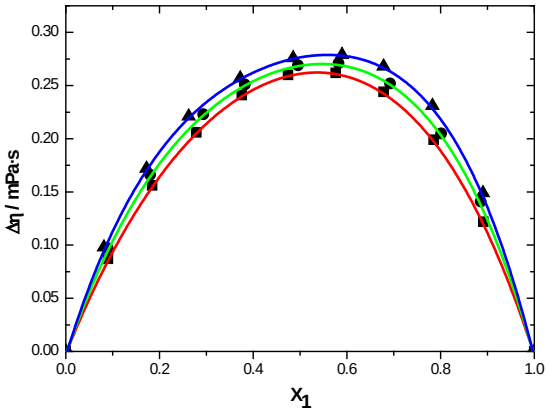

Fig.6.4.1: Variation of deviation in viscosity (Δη) with mole fraction (x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene (■), chlorobenzene (●) and nitrobenzene (▲) at 303.15K

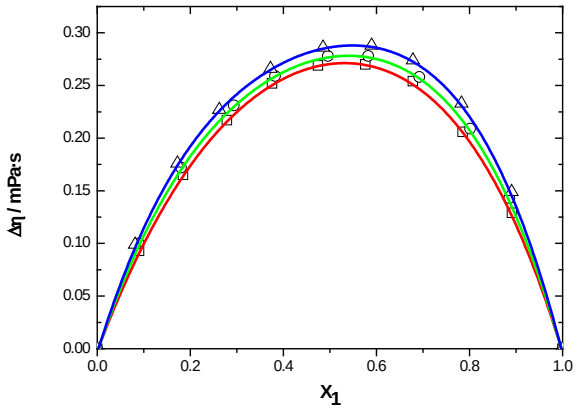

Fig.6.4.2: Variation of deviation in viscosity (Δη) with mole fraction (x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene (□), chlorobenzene (○) and nitrobenzene (Δ) at 308.15 K

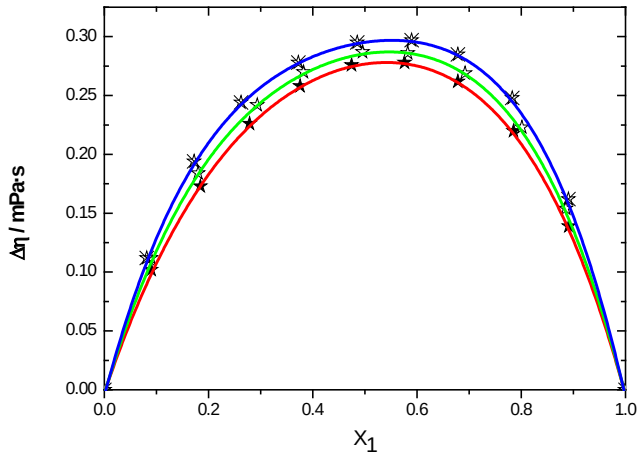

Fig.6.4.3: Variation of deviation in viscosity (Δη) with mole fraction (x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene (★) chlorobenzene (☆) and nitrobenzene (※) at 313.15 K

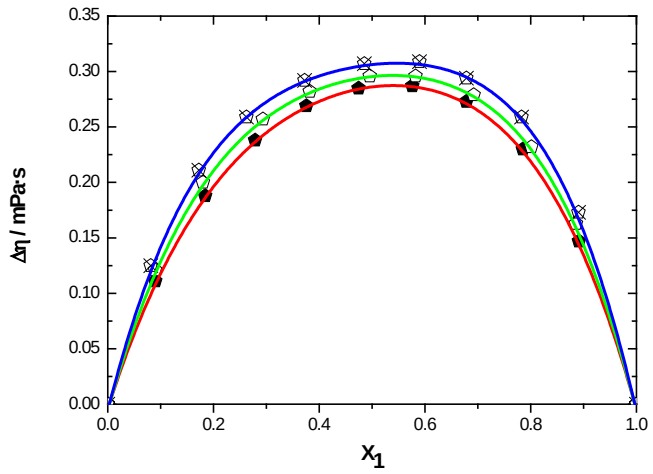

Fig.6.4.4: Variation of deviation in viscosity (Δη) with mole fraction (x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene(⬟), chlorobenzene (⬠) and nitrobenzene (⊠) at 318.15 K

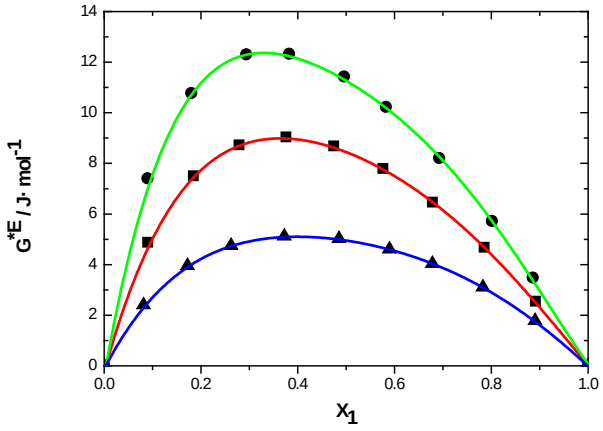

Fig.6.4.5: Excess Gibbs energy of activation of viscous flow (G^{*E}) with mole fraction (x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene (■), chlorobenzene (●) and nitrobenzene (▲) at 303.15 K

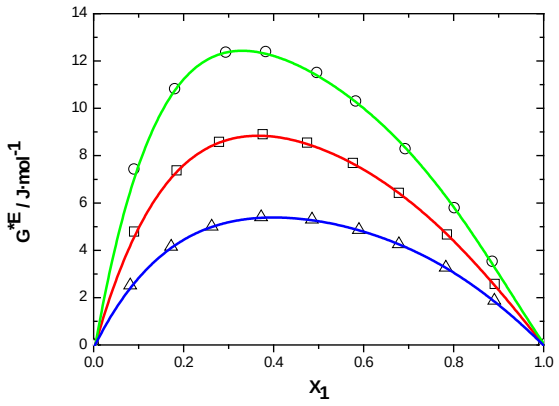

Fig.6.4.6: Excess Gibbs energy of activation of viscous flow (G^{*E}) with mole fraction (x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene (□), chlorobenzene (○) and nitrobenzene (Δ) at 308.15 K

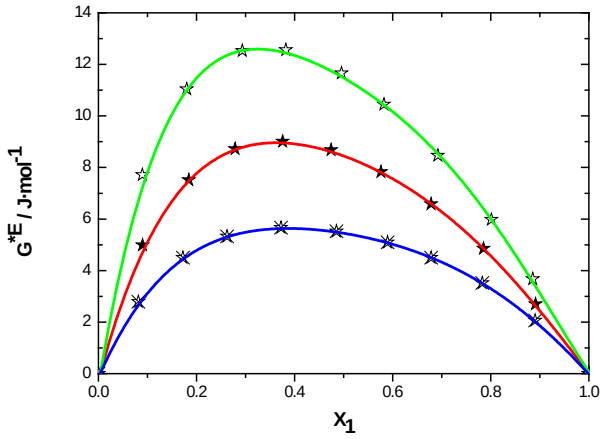

Fig.6.4.7: Excess Gibbs energy of activation of viscous flow (G^{*E}) with mole fraction (x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene (★), chlorobenzene (☆) and nitrobenzene (⛌) at 313.15 K

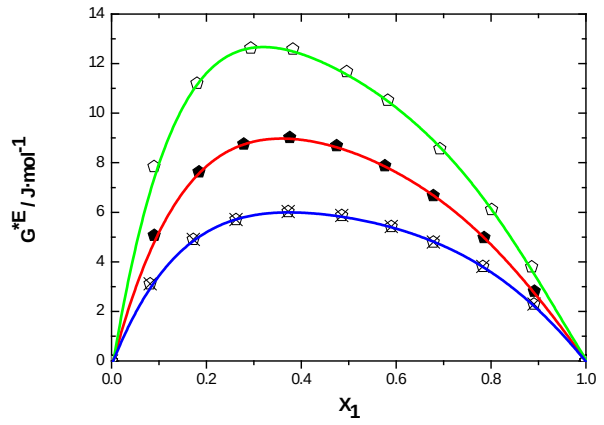

Fig.6.4.8: Excess Gibbs energy of activation of viscous flow (G^{*E}) with mole fraction (x_1) of 3-chloroaniline in the binary liquid mixtures of 3-chloroaniline with bromobenzene (⬟), chlorobenzene (⬠) and nitrobenzene (⛝) at 318.15 K

6.5 Viscosity Models and Interaction Parameters

Knowledge of the viscosity of pure liquids and respective mixtures and study of the viscosity calculation methods are important for practical and theoretical purposes [24]. In the present work, three typical semi-empirical relations were used to correlate the experimental viscosity data of the investigated binary systems. Grunberg and Nissan interaction parameter (d_{12}), Katti and Chaudhri interaction parameter (W_{vis}/RT), Hind interaction parameter (H_{12}), Tamura and Kurata (T_{12}) and Heric and Brewer (Δ_{12}) were calculated using equations (3.4.1 - 3.4.5) respectively.

Values of Grunberg and Nissan interaction parameter (d_{12}), Katti and Chaudhri interaction parameter (W_{vis}/RT) and Hind interaction parameter (H_{12}), Tamura and Kurata (T_{12}) and Heric and Brewer (Δ_{12}) were given in Tables 6.5.1- 6.5.3

From Tables 6.5.1- 6.5.3 it can be seen that the interaction parameter d_{12} is positive for binary systems. Fort and Moore [25] reported that for any binary liquid mixture, a positive value of d_{12} indicates the presence of specific interactions and a negative value of d_{12} indicates the presence of weak interactions between the unlike molecules. The values of d_{12} are positive for all binary systems indicating the presence of specific interaction between the two components of the binary mixtures.

It can be seen from Tables 6.5.1- 6.5.3 that interaction parameter are positive for all binary mixtures over the entire range of composition at T = (303.15 - 318.15) K. Interaction parameter W_{vis}/RT shows almost the same trend as that of d_{12}. In fact, one could say that the parameters d_{12} and W_{vis}/RT exhibit almost similar behavior, which is not unlikely in view of logarithmic nature of both equations.

It can be seen from Tables 6.5.1- 6.5.3 that interaction parameter are positive for all binary mixtures over the entire range of composition, suggesting the dipole - dipole interactions between mono substituted benzene derivatives and 3-chloroaniline molecules in the binary liquid mixtures.

The values of interaction parameters Tamura and Kurata (T_{12}) and Hind et al (H_{12}) do not differ appreciably from each other. It can be seen from Tables 6.5.1- 6.5.3 that interaction parameters are positive for all binary mixtures over the entire range of composition at T= (303.15 - 318.15) K. The positive values may be attributed to the electron donor-acceptor interactions resulting in the formation of complexes between the component molecules. This is in agreement with the view put forward by Fort and Moore [25] in regard to the nature of parameters T_{12} and H_{12}.

Table 6.5.1: Mole fraction of 3-chloroaniline (x_1), Grunberg and Nissan (d_{12}), Katti and Chaudhri (W_{vis}/RT), Hind.et al (H_{12}), Tamura and Kurata (T_{12}) and Heric Brower (Δ_{12}) data for binary mixture of 3-chloroaniline with bromobenzene at T= (303.15-318.15) K

	303.15 K					308.15 K				
x_1	d_{12}	W_{vis}/RT	H_{12}	T_{12}	Δ_{12}.	d_{12}	W_{vis}/RT	H_{12}	T_{12}	Δ_{12}.
0.0000										
0.0902	2.392	2.388	3.147	3.149	2.413	2.313	2.308	2.964	2.966	2.333
0.1842	2.011	2.007	3.136	3.137	2.032	1.945	1.940	2.947	2.948	1.965
0.2789	1.749	1.743	3.131	3.132	1.769	1.692	1.687	2.937	2.938	1.713
0.3759	1.554	1.548	3.133	3.134	1.575	1.505	1.500	2.935	2.936	1.526
0.4745	1.405	1.400	3.141	3.142	1.427	1.361	1.356	2.937	2.938	1.382
0.5763	1.288	1.282	3.156	3.157	1.309	1.250	1.245	2.950	2.952	1.272
0.6782	1.196	1.191	3.179	3.179	1.218	1.169	1.164	2.979	2.980	1.191
0.7852	1.121	1.116	3.210	3.211	1.143	1.099	1.094	3.008	3.009	1.121
0.8914	1.062	1.059	3.249	3.250	1.085	1.055	1.051	3.064	3.065	1.078
1.0000										
	313.15 K					318.15 K				
0.0000										
0.0902	2.369	2.363	2.785	2.787	2.389	2.371	2.365	2.612	2.615	2.391
0.1842	1.951	1.945	2.737	2.739	1.971	1.951	1.945	2.561	2.564	1.971
0.2789	1.693	1.688	2.722	2.724	1.714	1.673	1.667	2.527	2.529	1.694
0.3759	1.500	1.494	2.711	2.713	1.521	1.478	1.472	2.508	2.510	1.499
0.4745	1.360	1.354	2.714	2.716	1.381	1.340	1.334	2.506	2.508	1.361
0.5763	1.253	1.248	2.730	2.731	1.275	1.241	1.236	2.523	2.525	1.263
0.6782	1.178	1.173	2.762	2.763	1.200	1.176	1.171	2.559	2.561	1.198
0.7852	1.125	1.120	2.814	2.815	1.148	1.135	1.130	2.618	2.619	1.157
0.8914	1.091	1.086	2.878	2.879	1.113	1.118	1.113	2.696	2.697	1.141
1.0000										

Table 6.5.2: Mole fraction of 3-chloroaniline (x_1), Grunberg and Nissan (d_{12}), Katti and Chaudhri (W_{vis}/RT), Hind.et.al (H_{12}), Tamura and Kurata (T_{12}) and Heric Brower (Δ_{12}) data for binary mixture of 3-chloroaniline with chlorobenzene at T= (303.15-318.15) K.

	303.15 K					308.15 K				
x_1	d_{12}	W_{vis}/RT	H_{12}	T_{12}	Δ_{12}.	d_{12}	W_{vis}/RT	H_{12}	T_{12}	Δ_{12}.
0.0000										
0.0895	3.658	3.653	3.076	3.043	3.666	3.612	3.607	2.873	2.844	3.620
0.1802	2.937	2.932	3.045	3.014	2.945	2.902	2.896	2.841	2.813	2.910
0.2935	2.390	2.385	3.022	2.993	2.398	2.363	2.358	2.816	2.790	2.371
0.3821	2.104	2.099	3.015	2.988	2.112	2.082	2.076	2.808	2.784	2.090
0.4956	1.843	1.838	3.023	2.997	1.851	1.825	1.820	2.814	2.792	1.833
0.5823	1.695	1.691	3.040	3.015	1.703	1.681	1.676	2.830	2.809	1.689
0.6923	1.553	1.548	3.076	3.053	1.561	1.543	1.538	2.864	2.845	1.551
0.8012	1.448	1.444	3.128	3.108	1.456	1.443	1.438	2.914	2.898	1.450
0.8856	1.385	1.382	3.179	3.161	1.393	1.384	1.379	2.964	2.950	1.391
1.0000										
	313.15 K					318.15 K				
0.0000										
0.0895	3.689	3.683	2.718	2.691	3.698	3.693	3.686	2.555	2.531	3.701
0.1802	2.913	2.907	2.654	2.630	2.921	2.913	2.906	2.489	2.467	2.921
0.2935	2.357	2.351	2.615	2.593	2.365	2.338	2.332	2.432	2.413	2.346
0.3821	2.075	2.069	2.604	2.583	2.083	2.048	2.042	2.409	2.391	2.056
0.4956	1.819	1.814	2.606	2.587	1.827	1.795	1.789	2.405	2.389	1.803
0.5823	1.677	1.672	2.620	2.602	1.685	1.662	1.656	2.421	2.407	1.670
0.6923	1.550	1.545	2.663	2.647	1.558	1.545	1.540	2.467	2.455	1.553
0.8012	1.466	1.461	2.732	2.719	1.474	1.473	1.468	2.540	2.530	1.481
0.8856	1.416	1.411	2.790	2.779	1.424	1.442	1.437	2.615	2.607	1.449
1.0000										

Table 6.5.3: Mole fraction of 3-chloroaniline (x_1), Grunberg and Nissan (d_{12}), Katti and Chaudhri (W_{vis}/RT), Hind.et al (H_{12}), Tamura and Kurata (T_{12}) and Heric Brower (Δ_{12}) data for binary mixture of 3-chloroaniline with nitrobenzene at T= (303.15-318.15) K.

	303.15 K					308.15 K				
x_1	d_{12}	W_{vis}/RT	H_{12}	T_{12}	Δ_{12}.	d_{12}	W_{vis}/RT	H_{12}	T_{12}	Δ_{12}.
0.0000										
0.0812	1.299	1.293	3.596	3.572	1.300	1.340	1.333	3.331	3.310	1.340
0.1725	1.118	1.113	3.545	3.523	1.119	1.156	1.150	3.287	3.267	1.157
0.2623	0.993	0.987	3.511	3.491	0.993	1.029	1.023	3.257	3.239	1.029
0.3725	0.885	0.880	3.491	3.472	0.886	0.919	0.913	3.239	3.223	0.920
0.4854	0.813	0.808	3.494	3.477	0.814	0.844	0.839	3.243	3.228	0.845
0.5896	0.771	0.766	3.519	3.503	0.772	0.800	0.795	3.265	3.251	0.801
0.6785	0.749	0.745	3.556	3.542	0.750	0.777	0.772	3.298	3.286	0.778
0.7825	0.738	0.734	3.620	3.608	0.739	0.764	0.759	3.354	3.345	0.765
0.8905	0.741	0.737	3.708	3.699	0.741	0.765	0.760	3.432	3.425	0.766
1.0000										
	313.15 K					318.15 K				
0.0000										
0.0812	1.463	1.456	3.162	3.141	1.464	1.606	1.598	2.985	2.966	1.607
0.1725	1.233	1.226	3.090	3.071	1.233	1.323	1.316	2.887	2.871	1.324
0.2623	1.077	1.070	3.039	3.022	1.077	1.136	1.129	2.817	2.802	1.136
0.3725	0.948	0.942	3.004	2.989	0.949	0.994	0.988	2.774	2.762	0.995
0.4854	0.867	0.861	2.999	2.986	0.867	0.905	0.900	2.764	2.753	0.906
0.5896	0.825	0.819	3.022	3.011	0.825	0.865	0.859	2.788	2.779	0.865
0.6785	0.809	0.803	3.063	3.054	0.809	0.847	0.842	2.823	2.816	0.848
0.7825	0.809	0.804	3.136	3.129	0.810	0.863	0.858	2.910	2.905	0.864
0.8905	0.831	0.825	3.241	3.236	0.831	0.908	0.902	3.037	3.035	0.908
1.0000										

6.6 Conclusion:

Experimental data of density, speed of sound and viscosity are reported for binary mixtures of 3-chloroaniline with mono substituted benzene derivatives (chlorobenzene, bromobenzene, and nitrobenzene) over the entire range of mole fraction at T= (303.15 - 318.15) K. Calculated excess molar volume, excess isentropic compressibility, deviation in viscosity and excess Gibbs energy of activation of viscous flow are fitted with Redlich-Kister polynomial equation. The results are analyzed in terms of the molecular interactions through the dipole-induce-dipole interactions between the components of the mixtures, resulting in the formation of electron donor-acceptor complexes.

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