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Volumetric, ultrasonic and viscometric studies of binary liquid mixures of N-ethylaniline + chlorobenzene, + Bromobeneze, + 1, 2-dichlorobenzene + 1, 3-dichlorobenzene+1, 2, 4-trichlorobenzene at 303.15 and 308.15 K

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Abstract−We measured densities (ρ), ultrasonic speeds (u) and viscosities (η) for binary binary mixtures of N-ethylaniline (N-EA) with chlorobenzene (CB), bromobenzene (BB), 1,2-dichlorobenzene (1,2-DCB), 1,3-dichlorobenzene (1,3-DCB), and 1,2,4-trichlorobenzene (1,2,4-TCB) and their pure liquids at 303.15 K and 308.15 K. These experimental data were used to calculate the excess volume (V^E), deviations in ultrasonic speeds (Δu), deviation in isentropic compressibility ($\Delta\kappa_s$), deviation in intermolecular free length (ΔL_f), deviation in acoustic impedance (ΔZ), deviation in viscosity ($\Delta\eta$) and excess Gibbs free energy of activation of viscous flow (G^{*E}). The variations of these properties with composition of binary mixtures suggest loss of dipolar association, difference in size and shape of the component molecules, dipole-dipole interactions and hydrogen bonding between unlike molecules. The viscosity data were correlated with Grunberg and Nissan, Katti and Chaudhri, and Hind et al. equations and the results were compared with the experimental results. The excess parameters were fitted to the Redlich-Kister polynomial equation using multi parametric nonlinear regression analysis to derive the binary coefficients and to estimate the standard deviation.

Keywords: Ultrasonic Speed, Viscosity, Excess Molar Volume, N-ethylaniline, Halobenzenes

INTRODUCTION

A detailed study of the thermodynamic, transport and dielectric properties of fluids and fluid mixtures is important not only for the solution problems concerning heat transfer, fluidity, and so forth, but also for our understanding of molecular interactions, and geometrical effects in such systems. Ultrasonic studies of binary mixtures have been preferred in many diversifying fields such as Brilliouin scattering spectroscopy and biomedical research. Furthermore, in the chemical industry, information on density and viscosity of the liquid mixtures is vital in different applications that include surface facilities, pipeline systems and mass transfer operations.

The present investigation is a continuation of our earlier research [1-4] on thermodynamic properties of binary liquid mixtures. The liquids here were chosen on the basis of their industrial importance. N-ethylaniline is chosen as polar solvent and self associated through hydrogen bonding of their amine group. The amino group in N-ethylaniline is an electron-donor, and the hydrogen atom in the -NH_2 group can also play the role of electron-acceptor center. N-ethylaniline is used as an intermediate to manufacture dyes, agrochemicals and in preparation of some organic compounds. Chlorine atom in chlorobenzene is an electron-withdrawing atom that tends to attract the π-electrons of the benzene ring, and thereby decreases the electron density of ring. As a result, the benzene ring in chlorobenzene becomes a relatively poor electron-donor towards the electron-seeking proton of any group. Chlorobenzene is more reactive because the chlorine atom is bonded with SP^2 hybridized carbon atom and consequently can be removed easily. So, the rate of reaction with chlorobenzene is faster. Bromobenzene is less reactive because of large size and low electronegativity. Hence the rate of reaction is slow. 1,2-chlorobenzene is used as intermediate for dyes and agricultural chemicals, whereas 1, 2, 4-trichlorobenzene is used as a solvent and as a dye carrier in the textile industry. The aim of this is to reveal new and interesting results on molecular interaction in N-ethylaniline+halogenated aromatic hydrocarbons; further, addition of chloro, bromo groups in benzene molecules and addition of second/third chloro groups in the benzene environment that may influence both the sign and magnitude of various thermodynamic functions in the present investigation.

Several researchers elucidated the density, viscosity and ultrasonic studies of binary mixtures of substituted benzenes with acetophenone [5], dimethylsulfoxide [6], and tetrahydrofuran [7]. However, no effort appears in terms of V^E, $\Delta\kappa_s$, and $\Delta\eta$. To characterize the type and magnitude of the molecular interactions between N-ethylaniline and substituted benzenes (chlorobenzene, bromobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene), we present here the excess molar volume (V^E), deviation in isentropic compressibility ($\Delta\kappa_s$), and deviation in viscosity ($\Delta\eta$) of N-ethylaniline with substituted benzenes at 303.15 K and 308.15 K. These results have been fitted to the Redlich-Kister polynomial equation using multi parametric nonlinear regression analysis to derive the binary coefficients and to estimate the standard deviation (σ).

EXPERIMENTAL

All the chemicals used were of analytical reagent grade from S.D.

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Table 1. Densities (ρ), and ultrasonic speed (u) data of pure components at T=298.15 K

Compoments	Density (ρ)/gm·cm^{-3}		Ultrasonic speed (u)/m·sec^{-1}	
	Experimental	Literature	Experimental	Literature
N-ethylaniline	0.95653	0.95650[a]	1495.2	1497.4*[b]
Bromobenzene	1.48148	1.48150*[c]	1135.4	1137.0*[c]
Chlorobenzene	1.09552	1.09550*[c]	1251.0	1249.0*[c]
1,2-Dichlorobenzene	1.30088	1.30090[d]	1266.0	1265.0*[d]
1,3-Dichlorobenzene	1.28283	1.28283[d]	1240.0	1238.0*[d]
1,2,4-Trichlorobenzene	1.44840	1.44841[d]	1257.0	1256.0*[d]

*303.15 K
[a]Reference [9]
[b]Reference [10]
[c]Reference [11]
[d]Reference [12]

Fine Chemicals Ltd., India and Merck and their purities were as follows: N-ethylaniline 99.5%, bromobenzene 99.5%, chlorobenzene 99.5%, 1,2-dichlorobenzene 99.5%, 1,3-dichlorobenzene 99.5%, 1,2,4-trichlorobenzene 99.6%. Prior to experimental measurements, all the liquids were purified as described in the literature [8]. The pure samples were attained by fractional distillation and the purity of chemicals was checked by comparing the measured densities, speed of sounds and viscosities, which were in good agreement with literature values [5,9-14] as can be seen in Table 1. The purity of the samples was further confirmed by GLC single sharp peaks. Before use, the chemicals were stored over 0.4 nm molecular sieves for about 72 hrs to remove water. The dissolved gases in organic liquids are often a source of bubble formation, which introduces an error in density measurements. To overcome this difficulty, all the liquids were degassed before use, mixed in desired proportions, and kept for few hours to attain thermal equilibrium before the experimental observations were taken.

MEASUREMENTS

All the binary liquid mixtures were prepared by weighing an amount of pure liquids in an electric balance (Afoset, ER-120A, India) with a precision of ±0.1 mg by syringing each component into airtight stopper bottles to minimize evaporation losses. The uncertainty of the mole fraction was $\pm 1\times 10^{-4}$. After mixing the sample, the bubble-free homogeneous sample was transferred into the U-tube of the densimeter through a syringe. The density measurements were performed with a Rudolph Research Analytical digital densimeter (DDH-2911 Model), equipped with a built-in solid-state thermostat and a resident program with accuracy of temperature of 303.15 K ±0.03 K. The uncertainty density measurement liquid mixtures were $\pm 5\times 10^{-5}$ gm cm^{-3}. Proper calibration at each temperature was achieved with doubly distilled, deionized water and with air as standards. A multi frequency ultrasonic interferometer (M-82 Model, Mittal Enterprise, New Delhi, India) operated at 2 MHz, was used to measure the ultrasonic velocities of the binary liquid mixtures at 303.15 K and 308.15 K by using a digital constant temperature water bath. The uncertainty in the measurement of ultrasonic sound velocity was ±0.2%. The temperature stability was maintained within ±0.02 K by circulating thermostated water bath around the cell with a circulating pump. To minimize the uncertainty of the measurement, several maxima were allowed to pass and their number (50) in the present study was counted. All maxima were recorded with the highest swing of the needle on the micrometer scale. The total distance d (cm) moved by the reflector was given by $d=n\lambda/2$, where λ is the wave length. The frequency (ν), of the crystal being accurately known (2.0 MHz), the speed of sound, u in m·sec^{-1} was calculated by using the relation $u=\nu\lambda$. The working of the interferometer was tested by making measurements for pure samples of benzene, toluene, chloroform and acetone and the measured sound velocities of these liquids are in good agreement, which was reported in the literature [15]. The viscosities of pure liquids and their mixtures were determined at atmospheric pressure and at temperature 303.15 K and 308.15 K by using a Ubbelohde viscometer, which was calibrated with benzene and doubly distilled water. The Ubbelohde viscometer bulb has a capacity of 15 ml and the capillary tube with a length of about 90 mm with 0.5 mm internal diameter. The viscometer was thoroughly cleaned and perfectly dried, filled with the sample liquid by fitting the viscometer to about 30° from the vertical, and its limbs were closed with Teflon caps to avoid evaporation. The viscometer was kept in a transparent walled bath with a thermal stability of ±0.01 K for about 20 minutes to obtain thermal equilibrium. An electronic digital stopwatch with an uncertainty ±0.01 s was used for flow time measurements. The viscosity values of pure liquids and mixtures were calculated using the relation:

$$\eta=(at-b/t)\rho \tag{1}$$

where a and b are the characteristic constants of the viscometer, ρ is the density and t represents the flow time. The uncertainty of viscosity thus estimated was found to be ±0.005 mPa·s.

THEORY AND CALCULATIONS

The experimental values of density (ρ), ultrasonic sound velocity (u) and viscosity (η) of pure liquids and their mixtures as function of mole fraction of N-ethylaniline at 303.15 and 308.15 K were used to calculate the parameters such as V^E, κ_s, $\Delta\kappa_s$, and $\Delta\eta$ from experimental data using the following expressions:

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

$$L_f=K/u(\rho)^{1/2} \tag{3}$$

$$Z=u\rho \tag{4}$$

$$\Delta L_f=L_f-[x_1 L_{f1}+x_2 L_{f2}] \tag{5}$$

$$\Delta Z=Z-[x_1 Z_1+x_2 Z_2] \tag{6}$$

$$V^E=[x_1M_1+x_2M_2]/\rho-[x_1M_1/\rho_1+x_2M_2/\rho_2] \tag{7}$$

$$\Delta\kappa_s=\kappa_s-[x_1 \kappa_{s1}+x_2 \kappa_{s2}] \tag{8}$$

$$\Delta\eta=\eta-[x_1 \eta_1+x_2 \eta_2] \tag{9}$$

$$\Delta u=u-[x_1 u_1+x_2 u_2] \tag{10}$$

where κ_{s1}, L_{f1}, Z_1, ρ_1, u_1, η_1, M_1, x_1, V_1, κ_{s2}, L_{f2}, Z_2, ρ_2, u_2, η_2, x_2, M_2, V_2, κ_s, L_f, Z, ρ, u, and η, are isentropic compressibility, intermolecular free length, acoustic impedance, density, ultrasonic speed, viscosity, molecular weight, mole fraction and volume of the components 1, components 2, and mixtures, respectively.

RESULTS AND DISCUSSION

1. Excess Molar Volume

Table 2 shows that the excess volumes for the systems N-ethylaniline+chlorobenzene, +bromobenzene, are negative, whereas for the binary mixtures of N-ethylaniline+1, 2-dichlorobenzene, +1, 3-dichlorobenzene, +1, 2, 4-trichlorobenzene, they are positive over the entire composition range at 303.15 K and 308.15 K. The excess

Table 2. Mole fraction of N-ethylaniline (x_1), density (ρ), ultrasonic sound velocity (u), excess volume (V^E), deviations in ultrasonic speeds (Δu), deviation in isentropic compressibility ($\Delta\kappa_s$), deviation in intermolecular free length (ΔL_f), deviation in acoustic impedance (ΔZ) of the binary mixtures at 303.15 K and 308.15 K

N-ethylaniline (1)+chlorobenzene (2)

303.15 K

x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	u/m·sec^{-1}	Δu/m·sec^{-1}	$\Delta\kappa_s$/Tpa^{-1}	$\Delta L_f\times10^{-9}$/m	$Z^E\times10^{-3}$/kgm^{-2}s^{-1}
0.0000	1.09552	0.0000	1251.0	0.0000	0.000	0.000	0.000
0.0629	1.08594	−0.1055	1268.0	1.6398	−3.220	−1.006	2.726
0.1159	1.07754	−0.1667	1282.2	2.8972	−5.448	−1.702	4.531
0.1959	1.06478	−0.2140	1303.6	4.7612	−8.196	−2.561	6.663
0.2558	1.05541	−0.2382	1319.4	5.9336	−9.758	−3.049	7.909
0.3298	1.04405	−0.2551	1338.6	7.0628	−11.10	−3.468	8.995
0.3968	1.03405	−0.2673	1355.6	7.7014	−11.77	−3.678	9.593
0.4856	1.02111	−0.2696	1377.6	8.0165	−11.90	−3.718	9.750
0.5625	1.01026	−0.2675	1396.1	7.7375	−11.35	−3.546	9.366
0.6359	1.00016	−0.2577	1413.4	7.1132	−10.36	−3.238	8.629
0.7025	0.99119	−0.2404	1428.7	6.1495	−9.024	−2.820	7.542
0.7839	0.98052	−0.2146	1447.1	4.6716	−7.023	−2.195	5.971
0.8592	0.97081	−0.1718	1463.9	3.0834	−4.822	−1.507	4.188
0.9215	0.96282	−0.1132	1477.7	1.6697	−2.765	−0.864	2.435
1.0000	0.95274	0.0000	1495.2	0.0000	0.000	0.000	0.000

N-ethyl aniline (1)+chlorobenzene (2)

308.15 K

x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	u/m·sec^{-1}	Δu/m·sec^{-1}	$\Delta\kappa_s$/Tpa^{-1}	$\Delta L_f\times10^{-9}$/m	$Z^E\times10^{-3}$/kgm^{-2}s^{-1}
0.0000	1.08772	0.0000	1225.2	0.000	0.000	0.000	0.000
0.0629	1.07831	−0.1216	1244.0	2.735	−4.917	−1.552	4.239
0.1159	1.07019	−0.1859	1259.9	5.099	−8.545	−2.698	7.359
0.1959	1.05791	−0.2450	1283.7	8.467	−13.07	−4.127	11.34
0.2558	1.04883	−0.2724	1301.3	10.76	−15.77	−4.980	13.85
0.3298	1.03778	−0.2896	1322.4	12.96	−18.06	−5.703	16.07
0.3968	1.02802	−0.2991	1340.8	14.25	−19.18	−6.057	17.28
0.4856	1.01542	−0.3018	1364.3	15.07	−19.50	−6.158	17.89
0.5625	1.00479	−0.2931	1383.6	14.73	−18.61	−5.875	17.28
0.6359	0.99499	−0.2888	1401.1	13.49	−16.87	−5.326	15.88
0.7025	0.98629	−0.2775	1416.4	11.78	−14.69	−4.639	14.01
0.7839	0.97584	−0.2473	1434.4	8.991	−11.32	−3.573	10.94
0.8592	0.96635	−0.2034	1450.6	5.960	−7.695	−2.430	7.594
0.9215	0.95847	−0.1354	1463.8	3.248	−4.362	−1.377	4.354
1.0000	0.94845	0.0000	1480.6	0.000	0.000	0.000	0.000

Table 2. Continued

N-ethyl aniline (1)+bromobenzene (2)

303.15 K

x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	u/m·sec^{-1}	Δu/m·sec^{-1}	$\Delta\kappa_s$/Tpa^{-1}	$\Delta L_f\times10^{-9}$/m	$Z^E\times10^{-3}$/kgm^{-2}s^{-1}
0.0000	1.48148	0.0000	1135.4	0.000	0.000	0.000	0.000
0.0714	1.43777	−0.0756	1160.2	−0.889	−3.056	−0.958	4.480
0.1264	1.40474	−0.1180	1179.3	−1.578	−4.921	−1.543	7.149
0.1965	1.36345	−0.1603	1203.8	−2.300	−6.873	−2.155	9.909
0.2605	1.32653	−0.1847	1226.3	−2.827	−8.236	−2.582	11.79
0.3365	1.28372	−0.2050	1253.0	−3.472	−9.245	−2.898	13.13
0.3956	1.25121	−0.2167	1273.9	−3.836	−9.720	−3.047	13.77
0.4958	1.19754	−0.2232	1309.6	−4.188	−9.895	−3.102	13.95
0.5606	1.16381	−0.2223	1332.8	−4.303	−9.566	−2.999	13.46
0.6429	1.12203	−0.2147	1362.5	−4.215	−8.734	−2.738	12.29
0.7152	1.08626	−0.2007	1388.8	−3.929	−7.615	−2.387	10.73
0.7825	1.05365	−0.1730	1413.6	−3.343	−6.313	−1.979	8.904
0.8628	1.01568	−0.1325	1443.4	−2.435	−4.345	−1.362	6.171
0.9205	0.98890	−0.0846	1465.1	−1.495	−2.695	−0.845	3.832
1.0000	0.95274	0.0000	1495.2	0.000	0.000	0.000	0.000

N-ethyl aniline (1)+bromobenzene (2)

308.15 K

x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	u/m·sec^{-1}	Δu/m·sec^{-1}	$\Delta\kappa_s$/Tpa^{-1}	$\Delta L_f\times10^{-9}$/m	$Z^E\times10^{-3}$/kgm^{-2}s^{-1}
0.0000	1.41569	0.0000	1124.6	0.000	0.000	0.000	0.000
0.0714	1.37886	−0.0967	1149.4	−0.618	−4.023	−1.270	6.186
0.1264	1.35075	−0.1518	1168.5	−1.098	−6.503	−2.053	10.01
0.1965	1.31532	−0.2024	1192.8	−1.754	−8.917	−2.816	13.73
0.2605	1.28340	−0.2324	1215.1	−2.238	−10.58	−3.341	16.30
0.3365	1.24611	−0.2556	1241.7	−2.694	−11.93	−3.767	18.41
0.3956	1.21760	−0.2674	1262.4	−3.033	−12.49	−3.943	19.31
0.4958	1.17019	−0.2719	1297.8	−3.304	−12.69	−4.007	19.70
0.5606	1.14017	−0.2677	1320.9	−3.273	−12.36	−3.903	19.25
0.6429	1.10276	−0.2553	1350.4	−3.072	−11.38	−3.594	17.83
0.7152	1.07053	−0.2364	1376.5	−2.711	−10.05	−3.172	15.82
0.7825	1.04096	−0.2013	1401.0	−2.170	−8.400	−2.652	13.26
0.8628	1.00635	−0.1530	1430.3	−1.456	−5.870	−1.853	9.340
0.9205	0.98179	−0.0971	1451.4	−0.898	−3.615	−1.141	5.764
1.0000	0.94845	0.0000	1480.6	0.000	0.000	0.000	0.000

N-ethyl aniline (1)+1,2-dichlorobenzene (2)

303.15 K

x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	u/m·sec^{-1}	Δu/m·sec^{-1}	$\Delta\kappa_s$/Tpa^{-1}	$\Delta L_f\times10^{-9}$/m	$Z^E\times10^{-3}$/kgm^{-2}s^{-1}
0.0000	1.29924	0.0000	1266.0	0.000	0.000	0.000	0.000
0.0789	1.26816	0.0581	1293.0	8.916	−7.717	−2.411	12.27
0.1156	1.25395	0.0822	1304.8	12.34	−10.57	−3.302	16.78
0.1659	1.23472	0.1125	1320.3	16.27	−13.84	−4.323	21.91
0.2569	1.20066	0.1561	1346.5	21.61	−18.09	−5.654	28.45
0.3287	1.17442	0.1810	1365.8	24.42	−20.24	−6.324	31.60
0.3968	1.15005	0.1946	1383.0	26.05	−21.35	−6.673	33.10
0.4925	1.11661	0.1984	1405.6	26.71	−21.65	−6.765	33.17
0.5421	1.09963	0.1940	1416.6	26.35	−21.24	−6.637	32.32
0.6325	1.06927	0.1754	1435.6	24.63	−19.65	−6.142	29.55
0.6897	1.05044	0.1565	1446.8	22.72	−18.03	−5.634	26.88

Table 2. Continued

N-ethyl aniline (1)+1,2-dichlorobenzene (2)

303.15 K

x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	u/m·sec^{-1}	Δu/m·sec^{-1}	$\Delta\kappa_s$/Tpa^{-1}	$\Delta L_f\times10^{-9}$/m	$Z^E\times10^{-3}$/kgm^{-2}s^{-1}
0.7659	1.02578	0.1246	1460.7	19.15	−15.10	−4.719	22.25
0.8425	1.00145	0.0868	1473.5	14.39	−11.27	−3.523	16.40
0.9121	0.97972	0.0487	1483.9	8.846	−6.892	−2.154	9.905
1.0000	0.95274	0.0000	1495.2	0.000	0.000	0.000	0.000

N-ethyl aniline(1) +1,2-dichlorobenzene (2)

308.15 K

x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	u/m·sec^{-1}	Δu/m·sec^{-1}	$\Delta\kappa_s$/Tpa^{-1}	$\Delta L_f\times10^{-9}$/m	$Z^E\times10^{-3}$/kgm^{-2}s^{-1}
0.0000	1.28927	0.0000	1251.0	0.000	0.000	0.000	0.000
0.0789	1.25901	0.0376	1279.0	9.885	−8.910	−2.813	13.86
0.1156	1.24514	0.0545	1291.3	13.76	−12.27	−3.875	19.09
0.1659	1.22627	0.0837	1307.3	18.21	−16.02	−5.059	24.83
0.2569	1.19283	0.1255	1334.3	24.32	−20.96	−6.619	32.31
0.3287	1.16701	0.1534	1354.0	27.53	−23.40	−7.388	35.82
0.3968	1.14307	0.1647	1371.4	29.29	−24.64	−7.781	37.50
0.4925	1.11016	0.1698	1394.0	29.92	−24.85	−7.848	37.42
0.5421	1.09345	0.1651	1405.0	29.53	−24.38	−7.699	36.50
0.6325	1.06356	0.1460	1423.6	27.38	−22.41	−7.074	33.15
0.6897	1.04501	0.1272	1434.5	25.14	−20.48	−6.467	30.06
0.7659	1.02072	0.0940	1447.9	21.05	−17.07	−5.389	24.79
0.8425	0.99671	0.0591	1460.0	15.56	−12.59	−3.975	18.07
0.9121	0.97521	0.0298	1469.9	9.482	−7.651	−2.416	10.85
1.0000	0.94845	0.0000	1480.6	0.000	0.000	0.000	0.000

N-ethyl aniline (1)+1,3-dichlorobenzene (2)

303.15 K

x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	u/m·sec^{-1}	Δu/m·sec^{-1}	$\Delta\kappa_s$/Tpa^{-1}	$\Delta L_f\times10^{-9}$/m	$Z^E\times10^{-3}$/kgm^{-2}s^{-1}
0.0000	1.27715	0.0000	1240.0	0.000	0.000	0.000	0.000
0.0725	1.25070	0.0608	1265.4	6.898	−7.016	−2.192	10.51
0.1256	1.23164	0.1013	1283.3	11.24	−11.22	−3.508	16.88
0.1956	1.20695	0.1451	1306.0	16.08	−15.69	−4.905	23.74
0.2687	1.18165	0.1821	1328.4	19.82	−18.98	−5.932	28.80
0.3369	1.15849	0.2071	1348.4	22.42	−21.09	−6.590	32.05
0.4056	1.13559	0.2218	1367.5	23.99	−22.22	−6.943	33.80
0.4856	1.10943	0.2276	1388.5	24.57	−22.40	−7.001	34.05
0.5598	1.08564	0.2216	1406.8	23.93	−21.56	−6.737	32.69
0.6235	1.06557	0.2074	1421.7	22.58	−20.15	−6.297	30.47
0.6925	1.04418	0.1834	1436.9	20.17	−17.87	−5.584	26.91
0.7759	1.01878	0.1443	1454.2	16.19	−14.23	−4.448	21.31
0.8596	0.99376	0.0953	1470.3	10.93	−9.584	−2.995	14.25
0.9125	0.97817	0.0610	1480.0	7.130	−6.242	−1.951	9.231
1.0000	0.95274	0.0000	1495.2	0.000	0.000	0.000	0.000

volume data of all the binary systems can be explained qualitatively by taking into consideration the following factors: (i) Chemical or specific interaction, which includes charge-transfer force, formation of hydrogen bonding, dipole-dipole interaction and other complex forming interactions; (ii) Loss of dipolar association and differences in size and shape; (iii) Steric hindrance due to branching of chains, and (iv) Physical interaction consisting of dispersion forces or weak dipole-dipole interactions. The first effect leads to contraction in volume, making negative V^E values in liquid mixtures, while the remaining effects lead to expansion in volume resulting in positive V^E values. The actual volumes of V^E depend on the resultant of these opposing contributions. The experimental results suggest that the

Table 2. Continued

N-ethylaniline (1)+1,3-dichlorobenzene (2)

308.15 K

x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	u/m·sec^{-1}	Δu/m·sec^{-1}	$\Delta\kappa_s$/Tpa^{-1}	$\Delta L_f \times 10^{-9}$/m	$Z^E \times 10^{-3}$/kgm^{-2}s^{-1}
0.0000	1.27219	0.0000	1229.0	0.000	0.000	0.000	0.000
0.0725	1.24589	0.0509	1252.6	5.359	−5.990	−1.891	8.626
0.1256	1.22693	0.0848	1270.1	9.499	−10.21	−3.223	14.80
0.1956	1.20233	0.1236	1292.9	14.69	−15.13	−4.778	22.12
0.2687	1.17712	0.1555	1316.1	19.50	−19.35	−6.110	28.48
0.3369	1.15402	0.1781	1336.7	22.94	−22.14	−6.992	32.71
0.4056	1.13116	0.1926	1356.3	25.25	−23.83	−7.524	35.26
0.4856	1.10505	0.1978	1377.5	26.32	−24.34	−7.687	36.01
0.5598	1.08129	0.1931	1395.4	25.55	−23.36	−7.377	34.46
0.6235	1.06124	0.1810	1409.6	23.73	−21.58	−6.813	31.69
0.6925	1.03986	0.1608	1423.9	20.67	−18.78	−5.929	27.41
0.7759	1.01447	0.1269	1439.8	15.58	−14.29	−4.514	20.67
0.8596	0.98946	0.0836	1454.9	9.625	−9.041	−2.855	12.93
0.9125	0.97387	0.0539	1464.4	5.815	−5.585	−1.763	7.926
1.0000	0.94845	0.0000	1480.6	0.000	0.000	0.000	0.000

N-ethyl aniline (1)+1,2,4-trichlorobenzene (2)

303.15 K

x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	u/m·sec^{-1}	Δu/m·sec^{-1}	$\Delta\kappa_s$/Tpa^{-1}	$\Delta L_f \times 10^{-9}$/m	$Z^E \times 10^{-3}$/kgm^{-2}s^{-1}
0.0000	1.44215	0.0000	1257.0	0.000	0.000	0.000	0.000
0.0875	1.39785	0.0947	1285.9	8.057	−8.895	−2.780	18.68
0.1559	1.36352	0.1507	1307.3	13.16	−14.50	−4.531	30.27
0.2286	1.32728	0.1950	1329.0	17.54	−19.29	−6.028	39.93
0.2938	1.29502	0.2181	1347.6	20.61	−22.65	−7.077	46.45
0.3656	1.25957	0.2426	1367.2	23.11	−25.32	−7.914	51.24
0.4225	1.23164	0.2502	1382.1	24.46	−26.75	−8.359	53.50
0.4952	1.19609	0.2514	1400.2	25.24	−27.59	−8.621	54.24
0.5659	1.16165	0.2441	1416.8	25.00	−27.34	−8.543	52.75
0.6359	1.12767	0.2289	1432.3	23.82	−26.07	−8.147	49.26
0.7025	1.09545	0.2063	1446.1	21.76	−23.85	−7.453	44.09
0.7812	1.05750	0.1702	1461.2	18.11	−19.89	−6.216	35.73
0.8525	1.02325	0.1257	1473.6	13.53	−14.92	−4.664	26.06
0.9199	0.99096	0.0760	1484.3	8.179	−9.000	−2.812	15.25
1.0000	0.95274	0.0000	1495.2	0.000	0.000	0.000	0.000

N-ethyl aniline (1)+1,2,4-trichlorobenzene (2)

308.15 K

x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	u/m·sec^{-1}	Δu/m·sec^{-1}	$\Delta\kappa_s$/Tpa^{-1}	$\Delta L_f \times 10^{-9}$/m	$Z^E \times 10^{-3}$/kgm^{-2}s^{-1}
0.0000	1.43655	0.0000	1248.0	0.000	0.000	0.000	0.000
0.0875	1.39275	0.0583	1273.8	5.447	−7.406	−2.339	15.27
0.1559	1.35861	0.1030	1294.2	9.938	−12.80	−4.042	26.07
0.2286	1.32245	0.1465	1315.5	14.33	−17.76	−5.608	35.69
0.2938	1.29015	0.1800	1334.2	17.86	−21.51	−6.791	42.66
0.3656	1.25475	0.2073	1353.6	20.56	−24.41	−7.706	47.67
0.4225	1.22682	0.2215	1368.3	22.03	−25.95	−8.193	50.00
0.4952	1.19129	0.2296	1386.1	22.92	−26.88	−8.486	50.84
0.5659	1.15692	0.2242	1402.1	22.47	−26.51	−8.371	49.18
0.6359	1.12303	0.2088	1416.8	20.89	−24.97	−7.886	45.37
0.7025	1.09092	0.1836	1429.8	18.40	−22.45	−7.088	39.93

Table 2. Continued

N-ethyl aniline (1)+1,2,4-trichlorobenzene (2)							
308.15 K							
x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	u/m·sec^{-1}	Δu/m·sec^{-1}	$\Delta\kappa_s$/Tpa^{-1}	$\Delta L_f\times10^{-9}$/m	$Z^E\times10^{-3}$/kgm^{-2}s^{-1}
0.7812	1.05311	0.1431	1444.1	14.39	−18.18	−5.741	31.51
0.8525	1.01895	0.0994	1456.3	10.01	−13.19	−4.166	22.31
0.9199	0.98672	0.0539	1467.4	5.431	−7.574	−2.392	12.52
1.0000	0.94845	0.0000	1480.6	0.000	0.000	0.000	0.000

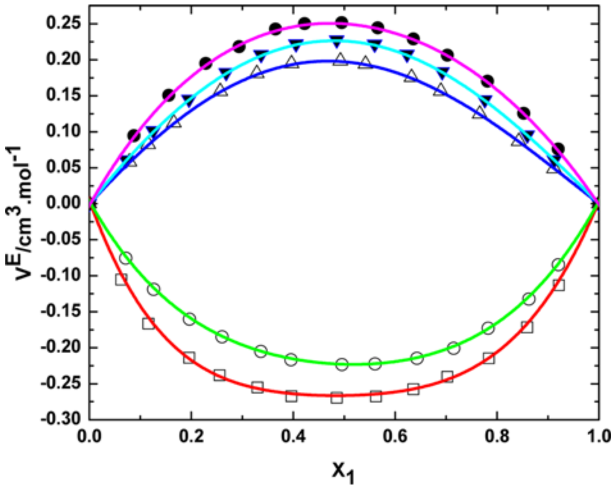

Fig. 1. Variation of excess molar volume (V^E) with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with chlorobenzene (□), bromobenzene (○), 1,2-dichlorobebeze (△), 1,3-dichlorobenzene (▼) and 1,2,4-trichlorobenzene (●) at 303.15 K.

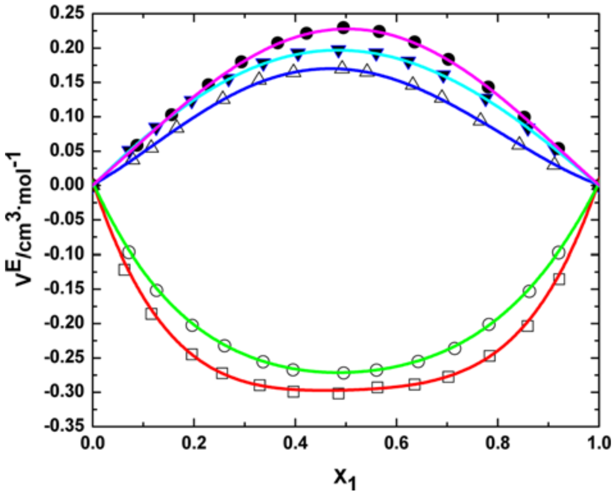

Fig. 2. Variation of excess molar volume (V^E) with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with chlorobenzene (□), bromobenzene (○), 1,2-dichlorobebeze (△), 1,3-dichlorobenzene (▼) and 1,2,4-trichlorobenzene (●) at 308.15 K.

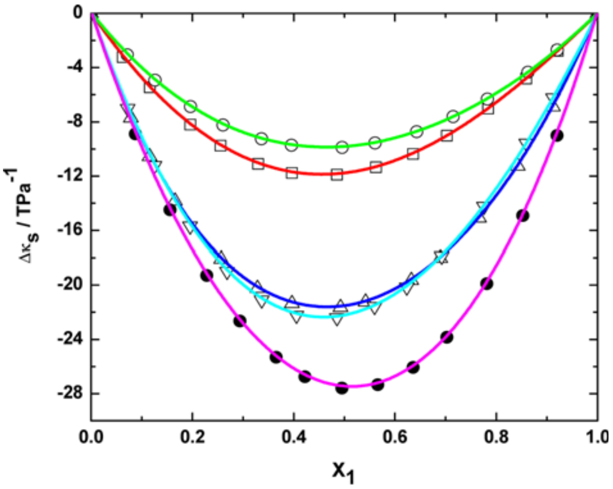

Fig. 3. Deviation in isentropic compressibility ($\Delta\kappa_s$), with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with chlorobenzene (□), bromobenzene (○), 1,2-dichlorobebeze (△), 1,3-dichlorobenzene (▽) and 1,2,4-trichlorobenzene (●) at 303.15 K.

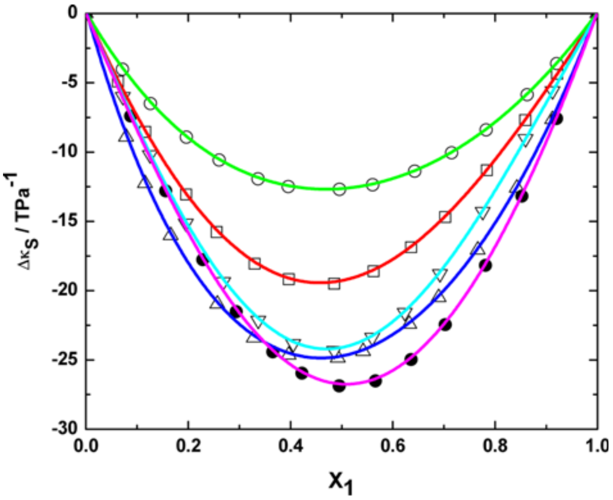

Fig. 4. Deviation in isentropic compressibility ($\Delta\kappa_s$), with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with chlorobenzene (□), bromobenzene (○), 1,2-dichlorobebeze (△), 1,3-dichlorobenzene (▽) and 1,2,4-trichlorobenzene (●) at 308.15 K.

former effect is dominant in the present investigation for binary mixtures of N-ethylaniline with chlorobenzene, +bromobenzene and other effects are dominant for remaining binary mixtures.

An examination of curves in Figs. 1 and 2 suggests that decrease in negative values of V^E with increase in number of chloro groups in chlrobenzene molecule reveals that dipole-dipole interactions are becoming weaker from 1,2-dichlorobenzene to 1,2,4-trichlorobenzene.

- The negative V^E value of chlorobenzene is more than that of bromobenzene due to strong dipole-dipole interaction.

Algebraic values of excess volumes for the systems of N-ethylaniline with chlorobenzenes fall in the order:

1, 2-dichlorobenzene<1, 3-dichlorobenzene<1, 2, 4-trichlorobenzene.

The observed positive V^E values suggest that the volume expansion factors dominate the volume contraction factors. This contention is supported by the positive excess volumes data for the mixtures of acetophenone with 1, 2-dichloroethane and 1, 2-dibromoethane with aliphatic ketones [16,17]. When a halogen atom is introduced into the aromatic ring, it causes a change in the π-electron density around the aromatic ring because of positive mesomeric and positive electromeric effects. (+T effect>–I effect). Further, substitution of second and third chloro groups in benzene molecule increases the distance of closet approach of the N-ethylaniline and dichloro, trichlorobenzene molecule resulting decrease is interaction between component molecules. The effect on the π-electron density due to increase in the number of chlorine atoms from chlorobenzene to di/trichlorobenzene is relatively small, which may be attributed to decrease in V^E. The difference in V^E values observed between dichloro

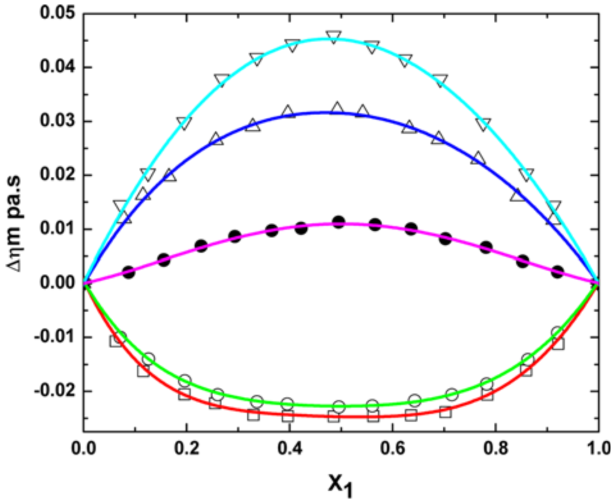

Fig. 5. Deviation of viscosity $\Delta\eta$ with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with chlorobenzene (□), bromobenzene (○), 1,2-dichlorobebeze (△), 1,3-dichlorobenzene (▽) and 1,2,4-trichlorobenzene (●) at 303.15 K.

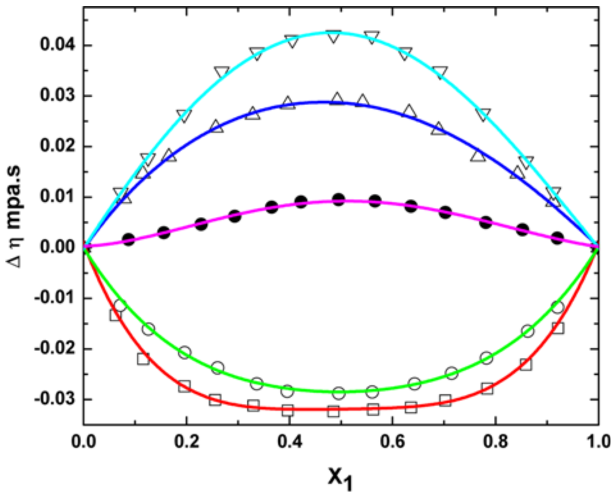

Fig. 6. Deviation of viscosity $\Delta\eta$ with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with chlorobenzene (□), bromobenzene (○), 1,2-dichlorobebeze (△), 1,3-dichlorobenzene (▽) and 1,2,4-trichlorobenzene (●) at 308.15 K.

Table 3. Mole fraction of N-ethylaniline (x_1), viscosity (η), deviation in viscosities ($\Delta\eta$), excess Gibbs free energy of activation of viscous flow (G^{*E}), Grunberg-Nissan interaction parameters (d), Katti-Chaudhri interaction parameters (W_{vis}/RT), and Hind interaction parameters (H_{12}) at 303.15 K and 308.15 K

N-ethyl aniline (1)+chlorobenzene (2)						
303.15 K						
x_1	η/mPa·s	$\Delta\eta$/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}
0.0000	0.713	0.000	0.000			
0.0629	0.767	−0.011	0.186	0.124	0.127	1.137
0.1159	0.816	−0.016	0.349	0.133	0.137	1.148
0.1959	0.894	−0.021	0.573	0.141	0.146	1.162
0.2558	0.954	−0.022	0.702	0.143	0.148	1.169
0.3298	1.028	−0.024	0.801	0.140	0.146	1.172
0.3968	1.096	−0.025	0.857	0.138	0.144	1.176
0.4856	1.188	−0.025	0.866	0.133	0.139	1.178
0.5625	1.267	−0.025	0.820	0.128	0.134	1.177
0.6359	1.342	−0.024	0.736	0.122	0.128	1.175
0.7025	1.412	−0.024	0.631	0.116	0.121	1.170
0.7839	1.499	−0.021	0.484	0.110	0.115	1.167
0.8592	1.581	−0.016	0.325	0.103	0.108	1.161
0.9215	1.650	−0.011	0.179	0.095	0.099	1.150
1.0000	1.742	0.000	0.000			
N-ethyl aniline(1) +chlorobenzene (2)						
308.15 K						
x_1	η/mPa·s	$\Delta\eta$/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}
0.0000	0.678	0.000	0.000			
0.0629	0.720	−0.013	0.088	0.057	0.059	1.005
0.1159	0.758	−0.022	0.173	0.064	0.067	1.011
0.1959	0.823	−0.027	0.354	0.085	0.089	1.031
0.2558	0.873	−0.030	0.460	0.091	0.095	1.039
0.3298	0.937	−0.031	0.567	0.097	0.101	1.047
0.3968	0.995	−0.032	0.617	0.097	0.102	1.051
0.4856	1.073	−0.032	0.637	0.096	0.101	1.053
0.5625	1.141	−0.032	0.609	0.093	0.098	1.053
0.6359	1.206	−0.032	0.543	0.088	0.093	1.050
0.7025	1.266	−0.030	0.463	0.083	0.088	1.046
0.7839	1.340	−0.028	0.337	0.075	0.079	1.036
0.8592	1.411	−0.023	0.208	0.065	0.068	1.023
0.9215	1.473	−0.016	0.106	0.055	0.058	1.008
1.0000	1.558	0.000	0.000			

and trichlorobenzenes is probably due to the difference in their shapes, which leads to different alignments in the liquid mixtures. Further, the electron donor-acceptor interactions in it are lower than those of 1, 2-dichlorobenzene and 1, 3-dichlorobenzene. Hence, the above order may be justified [6,7].

2. Isentropic Compressibility (κ_s)

Generally, negative values of Δu indicate dispersion forces due to weak interactions, whereas positive values of Δu indicate strong interactions [18,19]. The sign and magnitude of Δu play an important role in describing the molecular rearrangements among the component molecules in the mixtures and lead to intermolecular interactions between the molecules. Table 2 shows that the values of Δu are positive for N-ethylaniline+chlorobenzene, +1,2-di chlorobenzene, +1,3-dichlorobenzene, and 1,2,4-trichlorobenzene, whereas for the mixtures of N-ethylaniline+bromobenzene is negative over the entire composition ranges at 303.15 K and 308.15 K.

Table 2 also shows that the deviation in isentropic compressibility ($\Delta\kappa_s$) and deviation in intermolecular free length (ΔL_f) are negative in all the binary systems over the entire range of composition. According to Sri Devi et al. [20] the negative excess values are due to the closely packed molecules, which accounts for the existence of strong molecular interaction, whereas positive excess values cause weak interaction between unlike molecules. The sign of deviation in isentropic compressibility ($\Delta\kappa_s$) and deviation in intermolecular free length (ΔL_f) plays a vital role in assessing the compactness due to molecular interaction in liquid mixtures through hydrogen-bonding, charge transfer, dipole-dipole interactions and dipole-induced dipole interactions, interstitial accommodation and orientational ordering [21] leading to more compact structure making negative excess isentropic compressibility and excess intermolecular free length val-

Table 3. Continued

N-ethylaniline (1)+bromobenzene (2)

303.15 K

x_1	η/mPa·s	$\Delta\eta$/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}
0.0000	1.014	0.000	0.000			
0.0714	1.056	−0.010	0.026	0.013	0.016	1.303
0.1264	1.092	−0.014	0.071	0.022	0.026	1.315
0.1965	1.139	−0.018	0.121	0.027	0.031	1.321
0.2605	1.183	−0.021	0.160	0.030	0.033	1.324
0.3365	1.237	−0.022	0.202	0.032	0.036	1.329
0.3956	1.280	-0.022	0.224	0.034	0.038	1.331
0.4958	1.352	−0.023	0.234	0.034	0.038	1.332
0.5606	1.399	−0.023	0.227	0.033	0.037	1.332
0.6429	1.460	−0.022	0.203	0.032	0.036	1.331
0.7152	1.514	−0.021	0.167	0.029	0.033	1.327
0.7825	1.565	−0.019	0.128	0.027	0.030	1.323
0.8628	1.628	−0.014	0.080	0.024	0.027	1.318
0.9205	1.675	−0.009	0.046	0.023	0.025	1.316
1.0000	1.742	0.000	0.000			

N-ethyl aniline (1)+bromobenzene (2)

308.15 K

x_1	η/mPa·s	$\Delta\eta$/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}
0.0000	0.964	0.000	0.000			
0.0714	0.995	−0.011	0.030	0.001	0.000	1.175
0.1264	1.023	−0.016	0.040	0.002	0.002	1.188
0.1965	1.060	−0.021	0.005	0.003	0.004	1.195
0.2605	1.095	−0.024	0.025	0.005	0.005	1.199
0.3365	1.137	−0.027	0.039	0.007	0.007	1.201
0.3956	1.171	−0.028	0.048	0.008	0.008	1.202
0.4958	1.229	−0.029	0.062	0.009	0.010	1.203
0.5606	1.268	−0.028	0.061	0.009	0.010	1.203
0.6429	1.319	−0.027	0.056	0.009	0.010	1.202
0.7152	1.364	−0.025	0.042	0.008	0.008	1.200
0.7825	1.407	−0.022	0.028	0.006	0.006	1.197
0.8628	1.460	−0.017	0.009	0.003	0.003	1.191
0.9205	1.499	−0.012	0.003	0.001	0.001	1.181
1.0000	1.558	0.000	0.000			

Table 3. Continued

N-ethyl aniline (1)+1,2-dichlorobenzene (2)

303.15 K

x_1	η/mPa·s	$\Delta\eta$/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}
0.0000	1.234	0.000	0.000			
0.0789	1.286	0.012	0.163	0.084	0.090	1.57
0.1156	1.309	0.016	0.222	0.081	0.087	1.568
0.1659	1.338	0.020	0.277	0.074	0.081	1.559
0.2569	1.391	0.026	0.366	0.071	0.077	1.557
0.3287	1.430	0.029	0.402	0.067	0.073	1.554
0.3968	1.467	0.032	0.427	0.066	0.072	1.554
0.4925	1.516	0.032	0.428	0.063	0.069	1.552
0.5421	1.541	0.032	0.417	0.062	0.067	1.552
0.6325	1.584	0.029	0.374	0.059	0.065	1.55
0.6897	1.611	0.027	0.341	0.058	0.064	1.55
0.7659	1.646	0.023	0.284	0.058	0.064	1.552
0.8425	1.678	0.016	0.199	0.055	0.060	1.548
0.9121	1.709	0.012	0.131	0.061	0.066	1.561
1.0000	1.742	0.000	0.000			

N-ethyl aniline (1)+1,2-dichlorobenzene (2)

308.15 K

x_1	η/mPa·s	$\Delta\eta$/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}
0.0000	1.148	0.000	0.000			
0.0789	1.190	0.009	0.139	0.071	0.076	1.419
0.1156	1.210	0.014	0.203	0.073	0.078	1.424
0.1659	1.234	0.018	0.255	0.068	0.073	1.418
0.2569	1.277	0.023	0.334	0.064	0.069	1.415
0.3287	1.309	0.026	0.369	0.061	0.066	1.412
0.3968	1.339	0.028	0.392	0.059	0.065	1.412
0.4925	1.379	0.029	0.395	0.057	0.062	1.411
0.5421	1.399	0.028	0.386	0.056	0.061	1.411
0.6325	1.434	0.026	0.351	0.055	0.060	1.410
0.6897	1.454	0.023	0.308	0.052	0.057	1.407
0.7659	1.480	0.018	0.242	0.049	0.053	1.403
0.8425	1.508	0.014	0.184	0.051	0.055	1.408
0.9121	1.531	0.009	0.111	0.051	0.055	1.409
1.0000	1.558	0.000	0.000			

ues. Negative values of deviation in isentropic compressibility ($\Delta\kappa_s$) and deviation in intermolecular free length (ΔL_f) in the present investigation suggest that dipole-dipole interactions are prevailing between unlike molecules in the liquid mixtures.

Algebraic values of of $\Delta\kappa_s$ for the systems of N-ethylaniline with chlorobenzenes fall in the order:

bromobenzene<Chlorobenzene<1,2-dichlorobenzene≈1,3-dichlorobenzene<1,2,4-trichlorobenzeneuene. An examination of negative $\Delta\kappa_s$ values in Figs. 3 and 4 suggests that dipole-dipole interaction in ortho position becomes more than the meta and para isomers due to which polar character will be more in ortho isomer.

- That the negative $\Delta\kappa_s$ value of 1, 2, 4-trichlorobenzene is less than that of dichlorobenzene may be due to least steric hindrance.

3. Deviation in Viscosity

According to Fort and Moore [22], the deviation in viscosities tends to become more positive as the strength of the interaction increases. The deviation in viscosity variation gives a qualitative estimation of the strength of the intermolecular interactions. The deviation in viscosities [23] may be generally explained by considering the following factors. (i) The difference in size and shape of the component molecules and the loss of dipolar association in pure component may contribute to a decrease in viscosity, and (ii) specific interactions between unlike components such as hydrogen bond formation and charge transfer complexes may cause an increase in viscosity in mixtures than in pure components. The former effect produces negative deviation in viscosity, and the latter effect produces positive deviation in excess viscosity. Hence, such a negative deviation of viscosity lends further additional support for the existence of weak magnitude of dispersive forces present in the components of the mixtures.

Table 3. Continued

N-ethyl aniline(1) +1,3-dichlorobenzene (2)

303.15 K

x_1	η/mPa·s	$\Delta\eta$/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}
0.0000	0.949	0.000	0.000			
0.0725	1.021	0.015	0.324	0.188	0.194	1.453
0.1256	1.069	0.020	0.478	0.169	0.175	1.438
0.1956	1.134	0.030	0.663	0.164	0.169	1.440
0.2687	1.200	0.038	0.800	0.158	0.164	1.442
0.3369	1.258	0.042	0.866	0.150	0.156	1.439
0.4056	1.315	0.044	0.896	0.144	0.149	1.437
0.4856	1.380	0.046	0.893	0.138	0.144	1.437
0.5598	1.437	0.044	0.842	0.132	0.137	1.435
0.6235	1.485	0.042	0.777	0.128	0.133	1.434
0.6925	1.536	0.038	0.686	0.124	0.129	1.434
0.7759	1.594	0.030	0.533	0.118	0.123	1.431
0.8596	1.651	0.020	0.356	0.114	0.119	1.430
0.9125	1.687	0.014	0.237	0.115	0.119	1.436
1.0000	1.742	0.000	0.000			

N-ethyl aniline (1)+1,3-dichlorobenzene (2)

308.15 K

x_1	η/mPa·s	$\Delta\eta$/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}
0.0000	0.895	0.000	0.000			
0.0725	0.954	0.011	0.268	0.153	0.158	1.308
0.1256	0.996	0.018	0.424	0.147	0.153	1.307
0.1956	1.051	0.026	0.594	0.144	0.149	1.310
0.2687	1.108	0.035	0.735	0.143	0.148	1.315
0.3369	1.157	0.039	0.798	0.136	0.141	1.313
0.4056	1.205	0.041	0.828	0.131	0.136	1.312
0.4856	1.259	0.042	0.824	0.125	0.130	1.311
0.5598	1.308	0.042	0.790	0.122	0.127	1.311
0.6235	1.347	0.039	0.723	0.117	0.122	1.309
0.6925	1.389	0.035	0.637	0.113	0.118	1.308
0.7759	1.436	0.027	0.490	0.107	0.111	1.303
0.8596	1.482	0.017	0.319	0.100	0.105	1.297
0.9125	1.511	0.011	0.205	0.097	0.102	1.295
1.0000	1.558	0.000	0.000			

Table 3. Continued

N-ethyl aniline(1) +1,2,4 trichlorobenzene (2)

303.15 K

x_1	η/mPa·s	$\Delta\eta$/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}
0.0000	1.785	0.000	0.000			
0.0875	1.784	0.002	0.021	0.006	0.011	1.776
0.1559	1.783	0.004	0.040	0.008	0.012	1.78
0.2286	1.782	0.007	0.059	0.010	0.013	1.783
0.2938	1.781	0.009	0.072	0.010	0.014	1.784
0.3656	1.779	0.010	0.081	0.010	0.014	1.784
0.4225	1.777	0.010	0.084	0.010	0.014	1.784
0.4952	1.775	0.011	0.091	0.011	0.015	1.786
0.5659	1.772	0.011	0.088	0.011	0.014	1.786
0.6359	1.768	0.010	0.082	0.011	0.014	1.785
0.7025	1.763	0.008	0.069	0.010	0.013	1.783
0.7812	1.758	0.007	0.056	0.010	0.013	1.783
0.8525	1.752	0.004	0.036	0.008	0.012	1.78
0.9199	1.748	0.002	0.020	0.007	0.011	1.778
1.0000	1.742	0.000	0.000			

N-ethyl aniline(1) +1,2,4-trichlorobenzene (2)

308.15 K

x_1	η/mPa·s	$\Delta\eta$/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}
0.0000	1.622	0.000	0.000			
0.0875	1.618	0.002	0.017	0.006	0.008	1.600
0.1559	1.615	0.003	0.030	0.006	0.009	1.601
0.2286	1.612	0.005	0.046	0.007	0.010	1.603
0.2938	1.609	0.006	0.060	0.008	0.011	1.605
0.3656	1.607	0.008	0.075	0.010	0.013	1.607
0.4225	1.604	0.009	0.084	0.010	0.014	1.609
0.4952	1.600	0.009	0.088	0.011	0.014	1.609
0.5659	1.595	0.009	0.085	0.011	0.014	1.609
0.6359	1.589	0.008	0.077	0.010	0.013	1.608
0.7025	1.584	0.007	0.066	0.010	0.013	1.607
0.7812	1.577	0.005	0.049	0.008	0.011	1.605
0.8525	1.571	0.004	0.035	0.008	0.011	1.604
0.9199	1.565	0.002	0.019	0.007	0.010	1.603
1.0000	1.558	0.000	0.000			

Figs. 5 and 6 show that a deviation in viscosity data is positive for mixtures of N-ethylaniline with 1,2-dichlorobenzene, +1,3-dichlorobenzene, +1,2,4-trichlorobenzene and is negative for the systems containing bromobenzene and chlorobenzene over the entire composition ranges at 303.15 K and 308.15 K. In the present investigation, the positive $\Delta\eta$ values are due to the presence of specific interactions between component molecules [23,24], while the negative $\Delta\eta$ values suggest that dispersion forces are dominant in mixtures. The existence of dispersion forces indicates that the component molecules have different molecule sizes and shapes.

The excess Gibbs free energy of activation of viscous flow (G^{*E}) is obtained by the equation,

$$G^{*E}=RT\left[\ln \eta V-(x_1 \ln\eta_1 V_1+x_2 \ln\eta_2 V_2)\right] \tag{11}$$

where V_1, V_2 and V are the molar volumes of the component 1 and component 2 and molar volume of the mixture, respectively. R and T terms are gas constant and Absolute temperature, respectively.

Grunberg and Nissan [25] proposed the following equation for the measurement of viscosity of liquid mixtures:

$$\ln \eta=x_1 \ln \eta_1+x_2 \ln \eta_2+x_1x_2d_{12} \tag{12}$$

where d_{12} is a parameter proportional to interchange energy, which

Table 4. Coefficients of Redlich-Kister equation and standard deviation ó of the syste

Binary mixtures	T/K		a_0	a_1	a_2	σ
N-EA+bromobenzene	303.15	V^E/cm^3·mol^{-1}	−0.895	−0.025	−0.358	0.001
		Δu/m·sec^{-1}	−16.99	−4.33	−0.327	0.041
		$\Delta\kappa_s$/TPa^{-1}	−39.39	5.407	−2.545	0.023
		$\Delta\eta$/mPa·s	−0.090	0.007	−0.062	0.001
N-EA+chlorobenzene	303.15	V^E/cm^3·mol^{-1}	−1.054	0.080	−0.826	0.005
		Δu/m·sec^{-1}	32.015	−2.712	−9.118	0.022
		$\Delta\kappa_s$/TPa^{-1}	20.671	−17.175	−5.543	0.040
		$\Delta\eta$/mPa·s	−0.096	0.009	−0.092	0.001
N-EA+1,2dichlorobenzene	303.15	V^E/cm^3·mol^{-1}	0.794	−0.116	−0.131	0.001
		Δu/m·sec^{-1}	−86.36	11.486	13.748	0.043
		$\Delta\kappa_s$/TPa^{-1}	−11.39	0.521	−6.606	0.018
		$\Delta\eta$/mPa·s	0.124	−0.013	0.035	0.001
N-EA+1,3dichlorobenzene	303.15	V^E/cm^3·mol^{-1}	0.909	−0.088	−0.107	0.001
		Δu/m·sec^{-1}	98.216	−7.989	−3.295	0.037
		$\Delta\kappa_s$/TPa^{-1}	−89.28	15.323	−2.500	0.034
		$\Delta\eta$/mPa·s	0.179	−0.016	0.012	0.001
N-EA+1,2,4-trichlorobenzene	303.15	V^E/cm^3·mol^{-1}	1.003	−0.099	0.150	0.002
		Δu/m·sec^{-1}	100.65	5.844	7.067	0.088
		$\Delta\kappa_s$/TPa^{-1}	−110.22	−6.152	−9.024	0.032
		$\Delta\eta$/mPa·s	0.044	0.001	−0.023	0.001
N-EA+bromobenzene	308.15	V^E/cm^3·mol^{-1}	−1.088	0.056	−0.429	0.002
		Δu/m·sec^{-1}	−13.141	−1.577	3.389	0.025
		$\Delta\kappa_s$/TPa^{-1}	−50.772	6.207	−5.970	0.028
		$\Delta\eta$/mPa·s	−0.111	0.003	−0.066	0.001
N-EA+chlorobenzene	308.15	V^E/cm^3·mol^{-1}	−1.177	0.053	−1.039	0.004
		Δu/m·sec^{-1}	60.30	−1.471	−19.78	0.031
		$\Delta\kappa_s$/TPa^{-1}	−77.557	13.945	8.041	0.049
		$\Delta\eta$/mPa·s	−0.126	0.003	−0.131	0.001
N-EA+1,2dichlorobenzene	308.15	V^E/cm^3·mol^{-1}	0.683	−0.101	−0.352	0.002
		Δu/m·sec^{-1}	119.80	−10.59	10.59	0.033
		$\Delta\kappa_s$/TPa^{-1}	−99.300	15.718	−13.892	0.058
		$\Delta\eta$/mPa·s	0.114	−0.016	0.012	0.001
N-EA+1,3dichlorobenzene	308.15	V^E/cm^3·mol^{-1}	0.791	−0.054	−0.109	0.001
		Δu/m·sec^{-1}	105.16	−5.582	−41.021	0.031
		$\Delta\kappa_s$/TPa^{-1}	−97.138	12.962	24.986	0.081
		$\Delta\eta$/mPa·s	0.170	−0.015	−0.031	0.001
N-EA+1,2,4-trichlorobenzene	308.15	V^E/cm^3·mol^{-1}	0.917	0.008	−0.269	0.001
		Δu/m·sec^{-1}	91.72	3.380	−29.671	0.064
		$\Delta\kappa_s$/TPa^{-1}	−107.66	−5.703	14.029	0.067
		$\Delta\eta$/mPa·s	0.036	0.003	−0.021	0.001

reflects the non-ideality of the system.

Katti and Chaudhri [26] proposed the following equation:

$$\ln \eta V = x_1 \ln V_1 \eta_1 + x_2 \ln V_2 \eta_2 + x_1 x_2 W_{vis}/RT \qquad (13)$$

where W_{vis}/RT is an interaction term.

Hind et al. [27] suggested an equation for the viscosity of binary liquid mixtures as

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 H_{12} \qquad (14)$$

where H_{12} is Hind interaction parameter, and above mentioned computed values are also presented in Table 3.

According to Reed and Taylor [24], positive deviation in G^{*E} may be due to specific interactions like hydrogen bonding and charge-transfer, whereas the negative deviation may be ascribed to dispersion forces with systems. The interaction parameter d_{12} in the Grunberg and Nissan equation is a measure of the strength of interaction between the mixed components. In the present investigation, positive values of G^{*E} and d_{12} are due to the strong specific interactions between component molecules. According to Kalra et al. [28], large and positive d_{12} values indicate strong specific interaction; small

Table 5. Experimental and calculated values of viscosity (η) for the binary mixtures of N-ethylaniline (x_1) and chloro benzene, bromo benzene, 1,2 di chloro benzene, 1,3-di chloro benzene and 1,2,4-tri chloro benzene at temperatures 303.15 K and 308.15 K using Grunberg and Nissan (ηGN), Katti and Chaudhri (ηKC) and (çH) equations including standard deviation (SD)

N-EA+chloro benzene								
	303.15 K				308.15 K			
X_1	η Expt	η GN	η KC	η H	η Expt	η GN	η KC	η H
0.0000	1.014	1.014	1.014	1.014	0.964	0.964	0.964	0.964
0.0629	1.056	1.058	1.061	1.094	0.995	1.013	1.001	1.030
0.1159	1.092	1.093	1.096	1.153	1.023	1.051	1.029	1.078
0.1959	1.139	1.139	1.139	1.224	1.06	1.098	1.063	1.136
0.2558	1.183	1.182	1.182	1.285	1.095	1.142	1.097	1.186
0.3298	1.237	1.234	1.234	1.354	1.137	1.192	1.139	1.242
0.3968	1.28	1.275	1.273	1.404	1.171	1.231	1.170	1.283
0.4856	1.352	1.347	1.348	1.481	1.229	1.295	1.231	1.346
0.5625	1.399	1.395	1.393	1.527	1.268	1.335	1.266	1.383
0.6359	1.46	1.457	1.457	1.579	1.319	1.383	1.319	1.426
0.7025	1.514	1.513	1.515	1.621	1.364	1.424	1.367	1.460
0.7839	1.565	1.565	1.564	1.656	1.407	1.459	1.407	1.489
0.8592	1.628	1.630	1.630	1.692	1.46	1.499	1.463	1.518
0.9215	1.675	1.676	1.676	1.715	1.499	1.525	1.502	1.536
1.0000	1.742	1.742	1.742	1.742	1.558	1.558	1.558	1.558
SD		0.003	0.001	0.094		0.048	0.000	0.085

N-EA+bromo benzene								
	303.15 K				308.15 K			
X_1	η Expt	η GN	η KC	η H	η Expt	η GN	η KC	η H
0.0000	1.014	1.014	1.014	1.014	0.964	0.964	0.964	0.964
0.0629	1.056	1.058	1.061	1.094	0.995	1.013	1.001	1.030
0.1159	1.092	1.093	1.096	1.153	1.023	1.051	1.029	1.078
0.1959	1.139	1.139	1.139	1.224	1.06	1.098	1.063	1.136
0.2558	1.183	1.182	1.182	1.285	1.095	1.142	1.097	1.186
0.3298	1.237	1.234	1.234	1.354	1.137	1.192	1.139	1.242
0.3968	1.28	1.275	1.273	1.404	1.171	1.231	1.170	1.283
0.4856	1.352	1.347	1.348	1.481	1.229	1.295	1.231	1.346
0.5625	1.399	1.395	1.393	1.527	1.268	1.335	1.266	1.383
0.6359	1.46	1.457	1.457	1.579	1.319	1.383	1.319	1.426
0.7025	1.514	1.513	1.515	1.621	1.364	1.424	1.367	1.460
0.7839	1.565	1.565	1.564	1.656	1.407	1.459	1.407	1.489
0.8592	1.628	1.630	1.630	1.692	1.46	1.499	1.463	1.518
0.9215	1.675	1.676	1.676	1.715	1.499	1.525	1.502	1.536
1.0000	1.742	1.742	1.742	1.742	1.558	1.558	1.558	1.558
SD		0.003	0.001	0.094		0.048	0.000	0.085

Table 5. Continued

N-EA+1,2-di chloro benzene

	303.15 K				308.15 K			
X_1	η Expt	η GN	η KC	η H	η Expt	η GN	η KC	η H
0.0000	1.234	1.234	1.234	1.234	1.148	1.148	1.148	1.148
0.0789	1.286	1.282	1.288	1.330	1.190	1.198	1.193	1.230
0.1156	1.309	1.304	1.306	1.371	1.210	1.221	1.207	1.266
0.1659	1.338	1.334	1.327	1.424	1.234	1.252	1.224	1.311
0.2569	1.391	1.388	1.391	1.510	1.277	1.304	1.277	1.385
0.3287	1.430	1.429	1.431	1.570	1.309	1.344	1.310	1.435
0.3968	1.467	1.467	1.470	1.618	1.339	1.378	1.341	1.476
0.4925	1.516	1.519	1.524	1.675	1.379	1.423	1.385	1.522
0.5421	1.541	1.545	1.541	1.699	1.399	1.444	1.397	1.541
0.6325	1.584	1.590	1.591	1.733	1.434	1.479	1.439	1.567
0.6897	1.611	1.617	1.615	1.748	1.454	1.498	1.457	1.578
0.7659	1.646	1.651	1.648	1.760	1.480	1.519	1.483	1.586
0.8425	1.678	1.684	1.680	1.763	1.508	1.537	1.509	1.585
0.9121	1.709	1.711	1.709	1.759	1.531	1.548	1.532	1.577
1.0000	1.742	1.742	1.742	1.742	1.558	1.558	1.558	1.558
SD		0.004	0.002	0.115		0.032	0.003	0.104

N-EA+1,3 tri chloro benzene

	303.15 K				308.15 K			
X_1	η Expt	η GN	η KC	η H	η Expt	η GN	η KC	η H
0.0000	0.949	0.949	0.949	0.949	0.895	0.895	0.895	0.895
0.0789	1.021	1.014	1.016	1.058	0.954	0.964	0.952	0.989
0.1156	1.069	1.062	1.064	1.133	0.996	1.014	0.993	1.054
0.1659	1.134	1.125	1.125	1.224	1.051	1.079	1.044	1.133
0.2569	1.200	1.191	1.194	1.312	1.108	1.146	1.102	1.209
0.3287	1.258	1.253	1.254	1.387	1.157	1.207	1.152	1.273
0.3968	1.315	1.313	1.315	1.455	1.205	1.265	1.203	1.330
0.4925	1.380	1.383	1.382	1.525	1.259	1.328	1.258	1.389
0.5421	1.437	1.445	1.443	1.581	1.308	1.381	1.309	1.436
0.6325	1.485	1.496	1.492	1.623	1.347	1.423	1.349	1.470
0.6897	1.536	1.549	1.545	1.661	1.389	1.462	1.394	1.501
0.7659	1.594	1.609	1.606	1.697	1.436	1.501	1.445	1.529
0.8425	1.651	1.664	1.664	1.723	1.482	1.531	1.493	1.548
0.9121	1.687	1.695	1.693	1.734	1.511	1.545	1.516	1.555
1.0000	1.742	1.742	1.742	1.742	1.558	1.558	1.558	1.558
SD		0.009	0.012	0.106		0.052	0.009	0.095

positive values indicated weak specific interaction and large negative values indicated no specific interaction. The experimental and theoretical values of viscosity of the liquid mixtures calculated using Eqs. (12)-(14) including standard deviation are presented in Table 5. All the empirical relations gave a reasonable fit, but the viscosity values calculated using Grunberg and Nissan and Katti-Chaudhri relation are in good agreement with the experimental values.

The variation of V^E, Δu, $\Delta\kappa_s$ and $\Delta\eta$ with mole fraction was fitted to the Redlich-Kister polynomial equation [29] of the type

$$Y^E=x_1x_2[a_0+a_1(x_1-x_2)+a_2(x_1-x_2)^2] \qquad (15)$$

where Y^E is V^E or Δu or $\Delta\kappa_s$ or $\Delta\eta$. The values of a_0, a_1 and a_2 are the coefficients of the polynomial equation, and the corresponding standard deviations (σ) obtained by the method of least-squares with equal weights assigned to each point are calculated. The standard deviation (σ) is defined as:

$$\sigma(Y^E)=[\sum(Y^E_{obs}-Y^E_{cal})^2/(n-m)]^{1/2} \qquad (16)$$

where n is the total number of experimental points and m is the number of coefficients. The values of a_0, a_1 and a_2 are the coefficients determined by a multiple-regression analysis on the least square method and summarized along with the standard deviations between the experimental and fitted values of V^E, Δu, $\Delta\kappa_s$, and $\Delta\eta$ are presented in Table 4. Finally, it can be concluded that the expressions

Table 5. Continued

N-EA+1,2,4-tri chloro benzene								
	303.15 K				308.15 K			
X_1	η Expt	η GN	η KC	η H	η Expt	η GN	η KC	η H
0.0000	1.785	1.785	1.785	1.785	1.622	1.622	1.622	1.622
0.0875	1.784	1.784	1.795	1.842	1.618	1.615	1.628	1.671
0.1559	1.783	1.784	1.800	1.878	1.615	1.610	1.631	1.701
0.2286	1.782	1.782	1.795	1.909	1.612	1.605	1.625	1.727
0.2938	1.781	1.781	1.794	1.930	1.609	1.600	1.623	1.744
0.3656	1.779	1.778	1.791	1.945	1.607	1.595	1.618	1.756
0.4225	1.777	1.776	1.785	1.952	1.604	1.592	1.611	1.761
0.4952	1.775	1.774	1.775	1.954	1.6	1.587	1.601	1.760
0.5659	1.772	1.770	1.770	1.947	1.595	1.582	1.594	1.752
0.6359	1.768	1.767	1.765	1.933	1.589	1.578	1.588	1.738
0.7025	1.763	1.763	1.762	1.913	1.584	1.574	1.583	1.719
0.7812	1.758	1.758	1.756	1.881	1.577	1.570	1.577	1.688
0.8525	1.752	1.753	1.751	1.844	1.571	1.566	1.570	1.653
0.9199	1.748	1.748	1.748	1.801	1.565	1.562	1.565	1.613
1.0000	1.742	1.742	1.742	1.742	1.558	1.558	1.558	1.558
SD		0.001	0.002	0.133		0.009	0.000	0.120

used for interpolating the experimental data measured in this work are good results as can be seen by inspecting the (σ) values obtained.

CONCLUSIONS

The deviation pattern of the thermodynamic properties for binary mixtures of N-ethylaniline with mono-halo benzenes is different from that of dichloro and trichlorobenzenes. The variation of these properties shows that the addition of second or third chlorogroup on benzene ring has influenced the sign and magnitude of excess volume and viscosity to a significant extent.

A comparison between V^E and $\Delta\kappa_s$ shows that the two quantities do not have same sign over the whole range. This supports the contention of Kaulgud that V^E and $\Delta\kappa_s$ are dependent of different factors. According to his theory a greater knowledge of expansion and contraction in volume is not sufficient to predict the nature of ultrasonic speed and compressibility deviations correctly, but the magnitude and sign of excess entropy has to be taken into account. The interaction parameters calculated from different viscosity theoretical equations indicated the presence of specific molecular interactions between the components.

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