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Study of thermodynamic and transport properties of N-methylaniline with substituted chlorobenzenes at different temperatures

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ABSTRACT

Measurement of densities (ρ), ultrasonic speeds (u) and viscosities (η) has been carried out for binary mixtures of N-methylaniline (N-MA) 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 and 308.15) K. These experimental data have been 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 various thermodynamic properties with composition of binary mixtures suggest that loss of dipolar association, difference in size and shape of the component molecules, dipole-dipole interactions and hydrogen bonding between unlike molecules are involved in the molecular interactions between the components. The viscosity data have been correlated using three equations: Grunberg and Nissan, Katti and Chaudhri, and Hind et al. 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. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Ultrasonic speed;
Viscosity;
Excess properties;
N-ethylaniline;
Substituted chlorobenzenes.

INTRODUCTION

In binary liquid mixtures, the molecular interaction between dissimilar molecules is influenced by structural arrangement along with shape and size of the molecules. This paper deals with our investigations of thermodynamic and transport properties of binary liquid mixtures and is in continuation of our previous studies^[1-4]. The liquids were chosen in the present investigation on the basis of their industrial importance. N-methylaniline is

chosen as polar solvent and self associated through hydrogen bonding of their amine group. The amino group in N-methylaniline is an electron-donor and the hydrogen atom in the $-NH_2$ group can also play the role of electron-acceptor centers. N-methylaniline 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, tends to attract to π - electrons of the benzene ring and thereby decreases the electron density of ring.

As a result, the benzene ring in chlorobenzene becomes relatively poor electron-donor towards the electron-seeking proton of any group. Chlorobenzene is more reactive because the chlorine atom is bonded with SP² 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 electro negativity. 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 work is to reveal new and interesting results on molecular interaction in N-methylaniline + 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.

The variation of excess molar volume, isentropic compressibility and viscosity with changing composition of the mixtures has been investigations by various workers^[5-7]. In order to characterize the type and magnitude of the molecular interactions between N-methylaniline and substituted benzenes (chlorobenzene, bromobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene), we present here the ex-

cess molar volume (V^E), deviation in isentropic compressibility ($\Delta\kappa_s$) and deviation in viscosity ($\Delta\eta$) of N-methylaniline with substituted benzenes at (303.15 and 308.15) K. These results have been fitted to the Redlich - Kister polynomial equation using multi parametric nonlinear regression analysis to estimate the binary coefficients and standard deviation (σ).

EXPERIMENTAL

All the chemicals used in the present work were of analytical reagent grade procured from S.D. Fine Chemicals Ltd., India and Merck and their purities were as follows: N-methylaniline 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 purity samples were attained by fractional distillation and the purity of chemicals was checked by comparing the measured densities and viscosities, which were in good agreement with literature values^[9-12] as can be seen in TABLE 1. The purity of the samples were further confirmed by GLC single sharp peaks. Before use, the chemicals were stored over 0.4nm molecular sieves for about 72 hrs to remove water and were later degassed.

TABLE 1 : Densities (ρ), and ultrasonic speed (u) data of pure components at $T = 298.15$ K

components	Density(ρ) /gm.cm ⁻³		Ultrasonic speed (u) /m.sec ⁻¹	
	Experimental	Literature	Experimental	Literature
N-methylaniline	0.98167	0.98170 ^a	1551.0	1548.3* ^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]

MEASUREMENTS

All the binary liquid mixtures are 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 air tight 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 $303.15 \text{ K} \pm 0.03 \text{ K}$. The uncertainty in

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density measurement of liquid mixtures is $\pm 5 \times 10^{-5}$ 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 is $\pm 0.2\%$. The temperature stability is maintained within ± 0.02 K by circulating thermo stated water bath around the cell with a circulating pump. In order to minimize the uncertainty of the measurement, several maxima are allowed to pass and their number (50) in the present study is counted. All maxima are recorded with the highest swing of the needle on the micrometer scale. The total distance *d* (cm) moved by the reflector is given by $d = n\lambda/2$, where λ is the wave length. The frequency, *v*, of the crystal being accurately known (2.0 MHz), the speed of sound, *u* in m.sec⁻¹ is calculated by using the relation $u = v\lambda$. 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^[13]. 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 an Ubbelohde viscometer, which was calibrated with benzene and doubly distilled water. The Ubbelohde viscometer bulb has a capacity of 15ml and the capillary tube with a length of about 90mm with 0.5 mm internal diameter. The viscometer thoroughly cleaned and perfectly dried, is filled with the sample liquid by fitting the viscometer to about 30° from the vertical and its limbs are closed with Teflon caps to avoid the evaporation. The viscometer is 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 are calculated using the relation:

$$\eta = (at - b/t)\rho \quad (1)$$

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-methylaniline 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:

$$V^E = [x_1M_1 + x_2M_2]/\rho - [x_1M_1/\rho_1 + x_2M_2/\rho_2] \quad (2)$$

$$\kappa_s = u^{-2}\rho^{-1} \quad (3)$$

$$\Delta\kappa_s = \kappa_s - [x_1\kappa_{s1} + x_2\kappa_{s2}] \quad (4)$$

$$\Delta\eta = \eta - [x_1\eta_1 + x_2\eta_2] \quad (5)$$

In the above equations, M_1 , M_2 , κ_{s1} , κ_{s2} , η_1 , η_2 , u_1 , u_2 , ρ_1 , ρ_2 , ρ , κ_s , η , and *u* represent molecular weight, isentropic compressibility, viscosity, ultrasonic sound velocity and density data of component 1, component 2, the mixture respectively.

RESULTS AND DISCUSSION

Excess molar volume

An examination of data in the TABLE 2 suggests that the excess volume data for the systems N-methylaniline + chlorobenzene, + bromobenzene, are negative whereas for the binary mixtures of N-methylaniline + 1, 2-dichlorobenzene, + 1, 3-dichlorobenzene, + 1, 2, 4-trichlorobenzene are positive over the entire composition range at (303.15 and 308.15) K. The excess volume data of all the binary systems can be explained qualitatively by taking into consideration the following factors: 1. Chemical or specific interaction, which includes charge-transfer force, forming hydrogen bonding, dipole-dipole interaction and other complex forming interactions. 2. Loss of dipolar association and differences in size and shape 3. Steric hindrance due to branching of chains 4. Physical interaction consisting dispersion forces or weak dipole-dipole interactions. The former 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

TABLE 2 : Mole fraction of N-methylaniline (x_1), density (ρ), ultrasonic speed (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-methylaniline(1) + chlorobenzene (2)							
303.15 K							
x_1	$\rho/\text{gm.cm}^{-3}$	$V^E/\text{cm}^3.\text{mol}^{-1}$	$u/\text{m.sec}^{-1}$	$\Delta u/\text{m.sec}^{-1}$	$\Delta\kappa_s/\text{TPa}^{-1}$	$\Delta L_f \times 10^{-9}/\text{m}$	$\Delta Z \times 10^{-3}/\text{kgm}^{-2}\text{s}^{-1}$
0.0000	1.09582	0.0000	1251.0	0.000	0.000	0.000	0.000
0.0719	1.08764	-0.0787	1272.3	0.921	-3.727	-1.165	2.413
0.1242	1.08161	-0.1244	1288.6	1.310	-6.666	-2.083	4.762
0.2059	1.07211	-0.1809	1314.9	2.170	-11.13	-3.478	8.887
0.2641	1.06528	-0.2095	1334.1	4.830	-13.93	-4.353	11.79
0.3338	1.05708	-0.2354	1356.9	6.792	-16.59	-5.185	14.87
0.4016	1.04907	-0.2505	1378.8	8.331	-18.26	-5.706	17.08
0.4914	1.03845	-0.2586	1406.8	8.364	-18.89	-5.902	18.40
0.5725	1.02884	-0.2532	1430.8	8.050	-17.88	-5.588	17.77
0.6459	1.02013	-0.2378	1451.5	6.711	-15.78	-4.931	15.71
0.7125	1.01222	-0.2154	1469.5	4.772	-13.07	-4.083	12.79
0.7899	1.00302	-0.1791	1490.1	2.142	-9.313	-2.910	8.641
0.8492	0.99594	-0.1407	1506.0	1.280	-6.269	-1.959	5.316
0.9125	0.98836	-0.0902	1523.8	0.982	-3.194	-0.998	2.200
1.0000	0.97781	0.0000	1551.0	0.000	0.000	0.000	0.00
N-methyl aniline(1) + chlorobenzene (2)							
308.15 K							
x_1	$\rho/\text{gm.cm}^{-3}$	$V^E/\text{cm}^3.\text{mol}^{-1}$	$u/\text{m.sec}^{-1}$	$\Delta u/\text{m.sec}^{-1}$	$\Delta\kappa_s/\text{TPa}^{-1}$	$\Delta L_f \times 10^{-9}/\text{m}$	$\Delta Z \times 10^{-3}/\text{kgm}^{-2}\text{s}^{-1}$
0.0000	1.08772	0.0000	1225.2	0.000	0.000	0.000	0.000
0.0719	1.08026	-0.1180	1246.7	0.683	-4.224	-1.334	2.541
0.1242	1.07459	-0.1771	1263.3	1.698	-7.463	-2.356	4.844
0.2059	1.06546	-0.2366	1290.1	2.618	-12.30	-3.883	8.755
0.2641	1.05882	-0.2604	1309.6	3.846	-15.29	-4.828	11.47
0.3338	1.0508	-0.2762	1332.9	5.623	-18.05	-5.700	14.24
0.4016	1.04298	-0.2832	1355.3	6.086	-19.80	-6.251	16.28
0.4914	1.03265	-0.2849	1383.9	6.996	-20.37	-6.431	17.41
0.5725	1.02337	-0.2815	1408.6	6.632	-19.23	-6.073	16.77
0.6459	1.01500	-0.2729	1430.0	5.346	-16.99	-5.365	14.88
0.7125	1.00741	-0.2586	1448.7	3.480	-14.09	-4.450	12.15
0.7899	0.99855	-0.2290	1470.1	2.979	-10.07	-3.179	8.232
0.8492	0.99169	-0.1920	1486.7	1.723	-6.795	-2.146	5.080
0.9125	0.98424	-0.1317	1505.3	0.678	-3.492	-1.103	2.128
1.0000	0.97362	0.0000	1534.0	0.000	0.000	0.000	0.000
N-methyl aniline(1) + bromobenzene (2)							
303.15 K							
x_1	$\rho/\text{gm.cm}^{-3}$	$V^E/\text{cm}^3.\text{mol}^{-1}$	$u/\text{m.sec}^{-1}$	$\Delta u/\text{m.sec}^{-1}$	$\Delta\kappa_s/\text{TPa}^{-1}$	$\Delta L_f \times 10^{-9}/\text{m}$	$\Delta Z \times 10^{-3}/\text{kgm}^{-2}\text{s}^{-1}$
0.0000	1.48142	0.0000	1135.4	0.000	0.000	0.000	0.000
0.0614	1.4503	-0.0576	1156.9	-4.068	-2.367	-0.742	5.932
0.1364	1.41221	-0.1124	1184.9	-7.208	-5.821	-1.825	13.86
0.1865	1.38675	-0.1412	1204.5	-8.419	-8.215	-2.575	19.17

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x_1	$\rho/\text{gm.cm}^{-3}$	$V^E/\text{cm}^3.\text{mol}^{-1}$	$u/\text{m.sec}^{-1}$	$\Delta u/\text{m.sec}^{-1}$	$\Delta\kappa_s/\text{TPa}^{-1}$	$\Delta L_f \times 10^{-9}/\text{m}$	$\Delta Z \times 10^{-3}/\text{kgm}^{-2}\text{s}^{-1}$
0.2505	1.35422	-0.1692	1230.3	-9.248	-11.07	-3.471	25.48
0.3215	1.31817	-0.1916	1259.5	-9.515	-13.74	-4.307	31.41
0.3806	1.28819	-0.2026	1284.0	-9.547	-15.30	-4.798	35.03
0.4898	1.23293	-0.2088	1329.4	-9.541	-16.46	-5.162	38.10
0.5606	1.19721	-0.2034	1358.6	-9.745	-15.91	-4.987	37.31
0.6512	1.15165	-0.1870	1395.8	-10.24	-13.80	-4.325	33.19
0.7202	1.11706	-0.1662	1424.1	-10.61	-11.29	-3.538	27.95
0.7945	1.07992	-0.1353	1455.2	-10.43	-8.064	-2.528	20.88
0.8718	1.04141	-0.0940	1488.8	-8.920	-4.541	-1.424	12.66
0.9225	1.01622	-0.0611	1512.2	-6.621	-2.425	-0.760	7.294
1.0000	0.97781	0.0000	1551.0	0.000	0.000	0.000	0.000

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

308.15 K

x_1	$\rho/\text{gm.cm}^{-3}$	$V^E/\text{cm}^3.\text{mol}^{-1}$	$u/\text{m.sec}^{-1}$	$\Delta u/\text{m.sec}^{-1}$	$\Delta\kappa_s/\text{TPa}^{-1}$	$\Delta L_f \times 10^{-9}/\text{m}$	$\Delta Z \times 10^{-3}/\text{kgm}^{-2}\text{s}^{-1}$
0.0000	1.41569	0.0000	1124.6	0.000	0.000	0.000	0.000
0.0614	1.38980	-0.0845	1146.0	-3.787	-3.104	-0.980	6.607
0.1364	1.35767	-0.1536	1173.6	-6.812	-7.129	-2.251	14.76
0.1865	1.33597	-0.1836	1192.9	-8.063	-9.735	-3.074	19.96
0.2505	1.30804	-0.2078	1218.2	-8.995	-12.75	-4.026	26.00
0.3215	1.27686	-0.2218	1246.8	-9.472	-15.43	-4.873	31.52
0.3806	1.25080	-0.2269	1270.8	-9.618	-17.01	-5.370	34.94
0.4898	1.20249	-0.2281	1315.4	-9.724	-18.12	-5.721	37.94
0.5606	1.17108	-0.2247	1344.2	-9.910	-17.51	-5.528	37.33
0.6512	1.13080	-0.2165	1381.0	-10.20	-15.35	-4.848	33.73
0.7202	1.10003	-0.2043	1409.1	-10.35	-12.78	-4.037	28.94
0.7945	1.06676	-0.1800	1439.9	-10.02	-9.388	-2.964	22.19
0.8718	1.03196	-0.1375	1473.1	-8.395	-5.581	-1.762	14.03
0.9225	1.00900	-0.0958	1496.1	-6.172	-3.154	-0.996	8.394
1.0000	0.97362	0.0000	1534.0	0.000	0.000	0.000	0.000

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

303.15 K

x_1	$\rho/\text{gm.cm}^{-3}$	$V^E/\text{cm}^3.\text{mol}^{-1}$	$u/\text{m.sec}^{-1}$	$\Delta u/\text{m.sec}^{-1}$	$\Delta\kappa_s/\text{TPa}^{-1}$	$\Delta L_f \times 10^{-9}/\text{m}$	$\Delta Z \times 10^{-3}/\text{kgm}^{-2}\text{s}^{-1}$
0.0000	1.29924	0.0000	1266.0	0.000	0.000	0.000	0.000
0.0709	1.27668	0.0386	1290.3	4.043	-5.806	-1.814	11.49
0.1256	1.25920	0.0699	1308.8	6.994	-9.680	-3.025	19.30
0.1719	1.24438	0.0950	1324.3	9.328	-12.55	-3.921	25.17
0.2619	1.21552	0.1388	1353.8	13.16	-16.92	-5.286	34.32
0.3347	1.19218	0.1641	1376.8	15.45	-19.31	-6.033	39.53
0.4018	1.17067	0.1790	1397.3	16.79	-20.58	-6.431	42.47
0.4825	1.14481	0.1847	1420.8	17.29	-20.93	-6.540	43.59
0.5321	1.12892	0.1815	1434.6	16.95	-20.51	-6.408	42.96
0.6255	1.09900	0.1611	1459.5	15.23	-18.60	-5.812	39.38
0.6917	1.07777	0.1372	1476.4	13.27	-16.45	-5.141	35.10
0.7559	1.05713	0.1095	1492.2	10.74	-13.73	-4.290	29.53

x_1	$\rho/\text{gm.cm}^{-3}$	$V^E/\text{cm}^3.\text{mol}^{-1}$	$u/\text{m.sec}^{-1}$	$\Delta u/\text{m.sec}^{-1}$	$\Delta\kappa_s/\text{TPa}^{-1}$	$\Delta L_f \times 10^{-9}/\text{m}$	$\Delta Z \times 10^{-3}/\text{kgm}^{-2}\text{s}^{-1}$
0.8325	1.03242	0.0719	1510.6	7.287	-9.862	-3.082	21.46
0.9021	1.00984	0.0386	1527.2	4.052	-5.920	-1.850	13.04
1.0000	0.97781	0.0000	1551.0	0.000	0.000	0.000	0.000

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

308.15 K

x_1	$\rho/\text{gm.cm}^{-3}$	$V^E/\text{cm}^3.\text{mol}^{-1}$	$u/\text{m.sec}^{-1}$	$\Delta u/\text{m.sec}^{-1}$	$\Delta\kappa_s/\text{TPa}^{-1}$	$\Delta L_f \times 10^{-9}/\text{m}$	$\Delta Z \times 10^{-3}/\text{kgm}^{-2}\text{s}^{-1}$
0.0000	1.28927	0.0000	1251	0.000	0.000	0.000	0.000
0.0709	1.26733	0.0254	1276.3	5.225	-7.011	-2.214	13.07
0.1256	1.25033	0.0456	1295.3	8.715	-11.47	-3.620	21.62
0.1719	1.23577	0.0741	1311.0	11.35	-14.62	-4.617	27.73
0.2619	1.20751	0.1148	1340.4	15.25	-19.17	-6.052	36.89
0.3347	1.18461	0.1406	1363.1	17.42	-21.52	-6.794	41.86
0.4018	1.16352	0.1537	1383.3	18.59	-22.70	-7.167	44.57
0.4825	1.13812	0.1605	1406.4	18.85	-22.86	-7.219	45.36
0.5321	1.12251	0.1575	1420.1	18.52	-22.40	-7.073	44.70
0.6255	1.09312	0.1360	1444.8	16.78	-20.38	-6.434	41.11
0.6917	1.07219	0.1180	1461.6	14.85	-18.12	-5.721	36.79
0.7559	1.05194	0.0849	1477.4	12.48	-15.39	-4.858	31.47
0.8325	1.02758	0.0521	1495.6	9.002	-11.32	-3.573	23.33
0.9021	1.00532	0.0220	1511.7	5.446	-7.012	-2.214	14.57
1.0000	0.97362	0.0000	1534.0	0.000	0.000	0.000	0.000

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

303.15 K

x_1	$\rho/\text{gm.cm}^{-3}$	$V^E/\text{cm}^3.\text{mol}^{-1}$	$u/\text{m.sec}^{-1}$	$\Delta u/\text{m.sec}^{-1}$	$\Delta\kappa_s/\text{TPa}^{-1}$	$\Delta L_f \times 10^{-9}/\text{m}$	$\Delta Z \times 10^{-3}/\text{kgm}^{-2}\text{s}^{-1}$
0.0000	1.27715	0.0000	1240.0	0.000	0.000	0.000	0.000
0.0699	1.25653	0.0576	1266.5	4.751	-7.190	-2.247	12.41
0.1196	1.24187	0.0918	1284.8	7.584	-11.34	-3.545	19.89
0.1956	1.21938	0.1397	1311.9	11.07	-16.28	-5.089	29.16
0.2517	1.20275	0.1690	1331.3	13.02	-18.95	-5.923	34.44
0.3219	1.18195	0.1935	1354.9	14.74	-21.25	-6.639	39.29
0.3951	1.16021	0.2103	1378.7	15.82	-22.56	-7.050	42.42
0.4706	1.13776	0.2148	1402.5	16.14	-22.82	-7.132	43.61
0.5418	1.11651	0.2117	1424.4	15.90	-22.22	-6.945	43.04
0.6105	1.09594	0.2010	1444.9	15.01	-20.82	-6.506	40.79
0.6825	1.07436	0.1761	1465.8	13.54	-18.62	-5.819	36.91
0.7692	1.04824	0.1373	1490.3	11.08	-15.01	-4.691	30.13
0.8406	1.02666	0.0930	1509.8	8.373	-11.23	-3.511	22.77
0.9065	1.00653	0.0588	1527.3	5.379	-7.077	-2.212	14.42
1.0000	0.97781	0.0000	1551.0	0.000	0.000	0.000	0.000

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

308.15 K

x_1	$\rho/\text{gm.cm}^{-3}$	$V^E/\text{cm}^3.\text{mol}^{-1}$	$u/\text{m.sec}^{-1}$	$\Delta u/\text{m.sec}^{-1}$	$\Delta\kappa_s/\text{TPa}^{-1}$	$\Delta L_f \times 10^{-9}/\text{m}$	$\Delta Z \times 10^{-3}/\text{kgm}^{-2}\text{s}^{-1}$
0.0000	1.27219	0.0000	1229.0	0.000	0.000	0.000	0.000
0.0699	1.25179	0.0418	1256.4	6.120	-8.501	-2.684	14.17

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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	$\Delta Z \times 10^{-3}$ /kgm ⁻² s ⁻¹
0.1196	1.23722	0.0708	1274.9	9.432	-13.10	-4.136	22.19
0.1956	1.21490	0.1075	1301.7	13.04	-18.21	-5.751	31.60
0.2517	1.19831	0.1364	1320.6	14.81	-20.76	-6.555	36.56
0.3219	1.17752	0.1645	1343.3	16.12	-22.75	-7.185	40.77
0.3951	1.15582	0.1822	1366.2	16.66	-23.69	-7.481	43.18
0.4706	1.13345	0.1839	1389.2	16.67	-23.75	-7.499	44.00
0.5418	1.11223	0.1828	1410.4	16.19	-22.98	-7.255	43.13
0.6105	1.09173	0.1700	1430.7	15.48	-21.66	-6.839	41.12
0.6825	1.07016	0.1494	1451.6	14.45	-19.67	-6.210	37.70
0.7692	1.04409	0.1121	1476.2	12.59	-16.33	-5.158	31.60
0.8406	1.02254	0.0705	1495.1	9.717	-12.35	-3.901	24.11
0.9065	1.00240	0.0432	1512.5	6.988	-8.224	-2.597	16.02
1.0000	0.97362	0.0000	1534.0	0.000	0.000	0.000	0.000

N-methyl 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	$\Delta Z \times 10^{-3}$ /kgm ⁻² s ⁻¹
0.0000	1.44215	0.0000	1257.0	0.000	0.000	0.000	0.000
0.0765	1.41013	0.0681	1286.2	6.689	-9.119	-2.850	23.56
0.1419	1.38236	0.1187	1309.4	10.72	-15.01	-4.690	39.37
0.2126	1.35192	0.1647	1333.1	13.60	-19.71	-6.161	52.43
0.2818	1.32169	0.2006	1354.8	14.95	-22.77	-7.117	61.31
0.3526	1.29032	0.2258	1375.9	15.24	-24.63	-7.698	67.01
0.4105	1.26431	0.2385	1392.6	14.91	-25.38	-7.930	69.49
0.4899	1.22811	0.2433	1414.6	13.57	-25.22	-7.882	69.61
0.5569	1.19704	0.2381	1432.6	11.85	-24.16	-7.549	67.03
0.6219	1.16644	0.2229	1449.9	10.06	-22.51	-7.033	62.65
0.6936	1.13212	0.1965	1468.9	7.982	-19.96	-6.237	55.63
0.7772	1.09130	0.1546	1491.0	5.493	-15.99	-4.997	44.54
0.8465	1.05677	0.1115	1509.4	3.529	-11.89	-3.716	33.04
0.9056	1.02678	0.0715	1525.4	2.154	-7.868	-2.459	21.71
1.0000	0.97781	0.0000	1551.0	0.000	0.000	0.00	0.000

N-methyl 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	$\Delta Z \times 10^{-3}$ /kgm ⁻² s ⁻¹
0.0000	1.43655	0.0000	1248	0.000	0.000	0.000	0.000
0.0765	1.40494	0.0395	1278.3	8.421	-10.55	-3.332	26.02
0.1419	1.37737	0.0788	1301.7	13.12	-16.98	-5.361	42.58
0.2126	1.34705	0.1212	1324.8	16.04	-21.77	-6.872	55.44
0.2818	1.31688	0.1590	1345.8	17.21	-24.72	-7.806	63.78
0.3526	1.28553	0.1903	1365.94	17.10	-26.33	-8.313	68.67
0.4105	1.25955	0.2070	1381.8	16.35	-26.81	-8.464	70.42
0.4899	1.22341	0.2158	1402.8	14.69	-26.44	-8.349	70.00
0.5569	1.19242	0.2115	1420.4	13.17	-25.47	-8.041	67.62
0.6219	1.16192	0.1952	1437.5	11.59	-23.91	-7.550	63.51

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	$\Delta Z \times 10^{-3}$ /kgm ⁻² .s ⁻¹
0.6936	1.12772	0.1668	1456.2	9.870	-21.53	-6.799	57.00
0.7772	1.08704	0.1230	1478.1	7.841	-17.76	-5.606	46.56
0.8465	1.05260	0.0815	1496.1	6.021	-13.65	-4.311	35.34
0.9056	1.02266	0.0460	1511.1	4.128	-9.245	-2.919	23.59
1.0000	0.97362	0.0000	1534.0	0.000	0.000	0.000	0.000

contributions. The experimental results suggest that the former effect is dominant in the present investigation for binary mixtures of N-methylaniline with chlorobenzene, + bromobenzene and other effects are dominant for remaining binary mixtures.

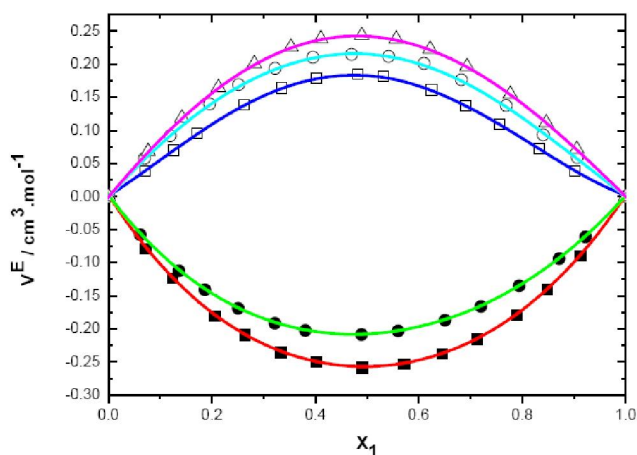
An examination of curves in Figures 1 and 2 suggest that the decrease in negative values of V^E with increase in number of chloro groups in chlorobenzene molecule reveals that dipole-dipole interactions are becoming weaker from 1,2-dichlorobenzene to 1,2,4-trichlorobenzene.

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-methylaniline with chlorobenzenes fall in the order;

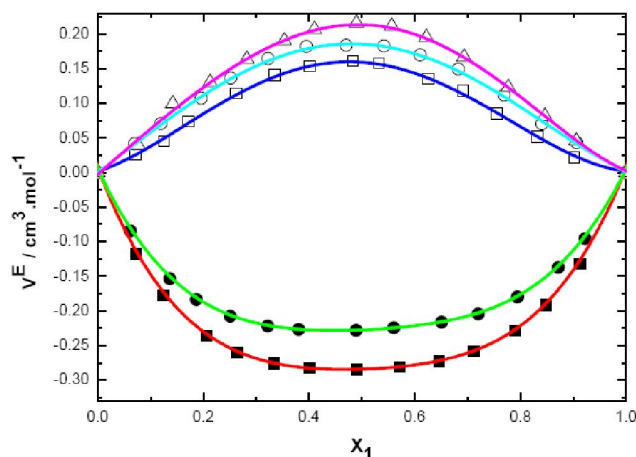
1, 2- dichlorobenzene < 1, 3- dichlorobenzene < 1, 2, 4- trichlorobenzene.

The observed positive V^E values suggest that the volume expansion factors dominating the volume contraction factors. This contention is supported by the posi-



Mole fraction of N-MA (X_1)

Figure 1 : Variation of excess molar volume (V^E) with mole fraction (x_1) of N-methylaniline in the binary liquid mixtures of N-ethylaniline with chlorobenzene, bromobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene at 303.15 K.



Mole fraction of N-MA (X_1)

Figure 2 : Variation of excess molar volume (V^E) with mole fraction (x_1) of N-methylaniline in the binary liquid mixtures of N-ethylaniline with chlorobenzene, bromobenzene, 1, 2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene at 308.15 K.

tive excess volumes data for the mixtures of acetophenone with 1, 2-dichloroethane and 1, 2-dibromoethane with aliphatic ketones^[14,15]. When a halogen atom is introduced into the aromatic ring, it causes to 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 increase the distance of closest approach of the N-methylaniline and dichloro, trichlorobenzene molecule resulting decrease in 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 and trichlorobenzenes is probably because of the difference in their shapes which leading 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].

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The negative excess volume can be attributed to the dipole – dipole interactions between unlike molecules through hydrogen bonding and positive values indicate that it is due to breaking up of self-associated structures of the components of the mixtures indicating the dominance of dipole- dipole interactions over the effect of H-bonding.

Isentropic compressibility (κ_s)

Generally, the excess properties of the mixtures are influenced by three main types of contributions, namely (i) non specific vander Waals type forces, (ii) hydrogen-bonding, charge transfer, dipole-dipole interactions and dipole-induced dipole interactions, and donor – acceptor interaction between unlike molecules, and (iii) fitting of smaller molecules into the voids created by the bigger molecules. The first effect leads to expansion in volume hence leads to negative contribution towards deviation in ultrasonic speed (Δu), and positive contribution towards deviation in isentropic compressibility ($\Delta \kappa_s$). However, the remaining effects lead to negative contribution towards deviation in isentropic compressibility and positive contribution towards deviation in ultrasonic speed.

A perusal of data in TABLE 2 shows that the values of Δu are positive for N-methylaniline + chlorobenzene, + 1,2-di chlorobenzene, + 1,3- dichlorobenzene, and 1,2,4-trichlorobenzene, whereas for the mixtures of N-methylaniline + bromobenzene is negative over the entire composition ranges at (303.15 and 308.15) K.

TABLE 2 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. The negative values of $\Delta \kappa_s$ suggest that the mixtures are less compressible than the corresponding ideal mixture. According to Fort and Moore^[16], the liquids of different molecular size usually mix with decrease in volume yielding negative $\Delta \kappa_s$ values. The strength of the interactions between component molecules increases when excess values tend to become increasingly negative. As the temperature increases, the $\Delta \kappa_s$ values also increase in the present system, suggesting that the donor – acceptor interactions, towards complex formation between unlike molecules.

From experimental results suggest that the negative $\Delta \kappa_s$ values may be ascribed to the closer approach of

the dissimilar molecules due to electrostatic interactions and possibly π - electron donor – acceptor complex formation occurs between the components of the mixture.

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

bromobenzene < Chlorobenzene < 1,2-dichlorobenzene \approx 1,3-dichlorobenzene < 1,2,4-trichlorobenzene

An examination of curves in Figures 2 and 3 reveals that deviation in isentropic compressibility ($\Delta \kappa_s$) is negative for all the binary mixtures over the entire the composition range at (303.15 and 308.15) K. The large negative $\Delta \kappa_s$ values for the binary mixture N-methylaniline + 1, 2, 4- trichlorobenzene are attributed to the presence of strong specific interaction between N-methylaniline and 1, 2, 4- trichlorobenzene. The specific interaction could be of donor - acceptor type in which the nitrogen atom of amino group of N-methylaniline with its unshared pair of electrons acts as electron – donor towards electron acceptor chlorine atoms of 1, 2, 4- trichlorobenzene. Further, presence of one more chlorine atom in 1, 2, 4- trichlorobenzene increase its electron – accepting capacity and therefore, it interacts more strongly towards N-methylaniline molecule as compared to 1,2-dichlorobenzene and 1,3-dichlorobenzene, causing deviation in isentropic compressibility more negative for N-methylaniline + 1, 2,

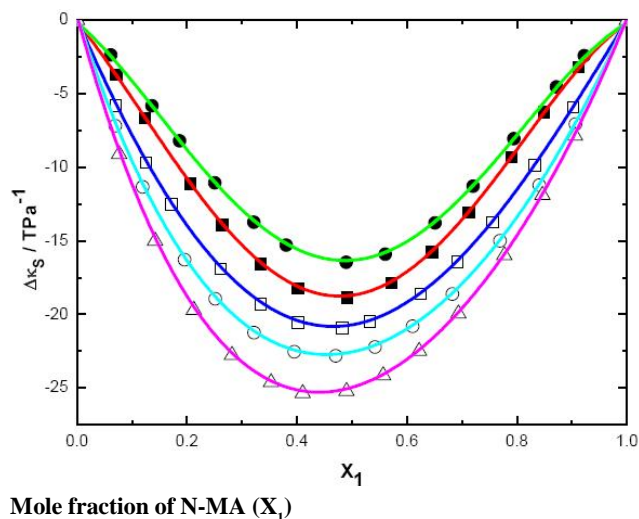
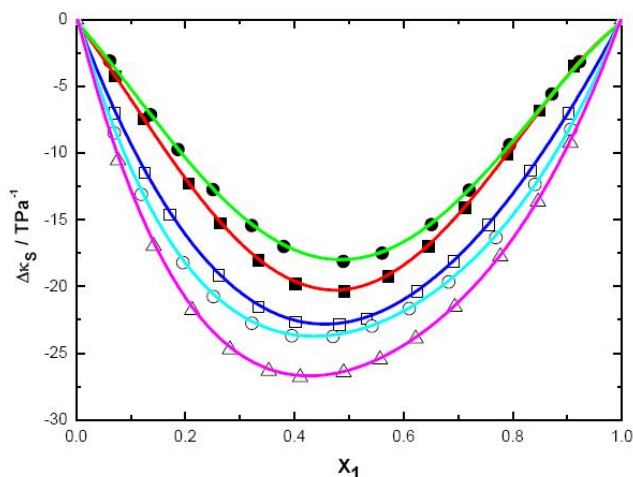


Figure 3 : Deviation in isentropic compressibility ($\Delta \kappa_s$) with mole fraction (x_1) of N-methylaniline in the binary liquid mixtures of N-methylaniline with chlorobenzene, bromobenzene, 1, 2-dichlorobenzene (\square), 1,3-dichlorobenzene and 1,2,4-trichlorobenzene at 303.15 K



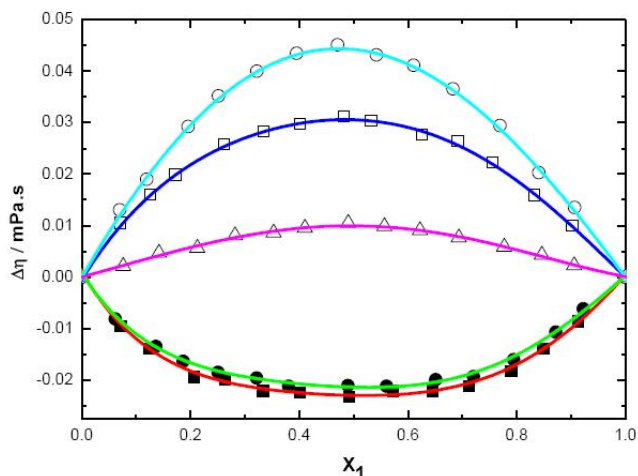
Mole fraction of N-MA (x_1)

Figure 4 : Deviation in isentropic compressibility ($\Delta\kappa_s$) with mole fraction (x_1) of N-methylaniline in the binary liquid mixtures of N-ethylaniline with chlorobenzene, bromobenzene, 1, 2-dichlorobenze, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene at 308.15 K.

4- trichlorobenzene than for N-methylaniline + 1,2-dichlorobenzene and 1,3-dichlorobenzene.

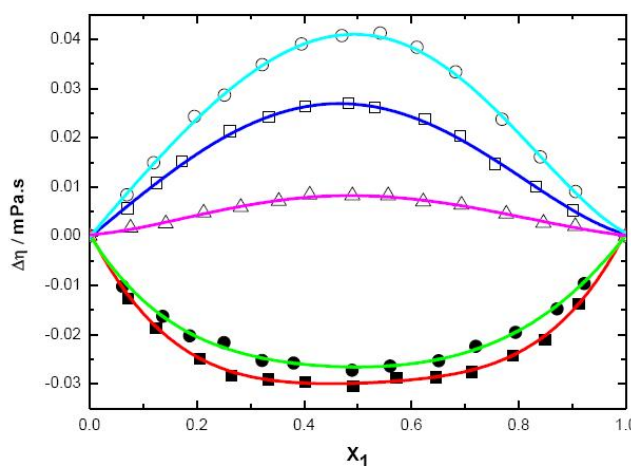
An examination data in TABLE 2 indicates that the values of ΔL_f are negative for all binary systems over the entire composition range at (303.15 and 308.15) K may be due to the thermal energy activates the molecules towards complex formation between unlike molecules.

A perusal of data in TABLE 2 shows that the values of ΔZ are positive for all binary systems over the



Mole fraction of N-MA (x_1)

Figure 5 : Deviation of viscosity $\Delta\eta$ with mole fraction (x_1) of N-methylaniline in the binary liquid mixtures of N-ethylaniline with chlorobenzene, bromobenzene, 1,2-dichlorobenze, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene at 303.15 K



Mole fraction of N-MA (x_1)

Figure 6 : Deviation of viscosity $\Delta\eta$ with mole fraction (x_1) of N-methylaniline in the binary liquid mixtures of N-ethylaniline with chlorobenzene, bromobenzene, 1, 2-dichlorobenze, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene at 308.15 K

entire composition range at (303.15 and 308.15) K may be ascribed to the dipole-dipole interactions between dissimilar molecules and π - electron donor – acceptor complex formation between the components of the mixture.

Deviation in viscosity

According to Fort & Moore^[17] 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^[18] 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 increase in viscosity in mixtures than in pure components. The former effect produces negative deviation in viscosity and latter effect produces positive deviation in excess viscosity.

An examination of curves in Figures 5 and 6 shows that deviation in viscosity is positive for mixtures of N-methylaniline with 1,2-dichlorobenzene, + 1,3-dichlorobenzene, + 1,2,4-trichlorobenzene and is negative for the systems containing bromobenzene and chloroben-

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TABLE 3 : Mole fraction of *N*-methylaniline (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 303.15K and 308.15 K

N-methyl 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			
0.0719	0.777	-0.009	0.231	0.143	0.139	1.153
0.1242	0.826	-0.014	0.386	0.146	0.143	1.160
0.2059	0.904	-0.019	0.571	0.144	0.140	1.165
0.2641	0.963	-0.02	0.693	0.147	0.143	1.173
0.3338	1.032	-0.022	0.769	0.142	0.139	1.174
0.4016	1.101	-0.022	0.816	0.140	0.136	1.177
0.4914	1.192	-0.023	0.811	0.134	0.130	1.178
0.5725	1.276	-0.022	0.768	0.129	0.126	1.179
0.6459	1.351	-0.022	0.681	0.123	0.120	1.176
0.7125	1.420	-0.021	0.581	0.117	0.114	1.172
0.7899	1.502	-0.018	0.447	0.112	0.108	1.169
0.8492	1.567	-0.014	0.338	0.109	0.106	1.163
0.9125	1.637	-0.009	0.205	0.107	0.103	1.155
1.0000	1.735	0.000	0.000			
N-methyl 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			
0.0719	0.734	-0.013	0.206	0.151	0.149	0.969
0.1242	0.773	-0.019	0.282	0.126	0.136	0.998
0.2059	0.839	-0.025	0.398	0.123	0.129	1.012
0.2641	0.885	-0.028	0.451	0.114	0.112	1.021
0.3338	0.942	-0.029	0.575	0.106	0.101	1.039
0.4016	1.001	-0.030	0.689	0.107	0.115	1.042
0.4914	1.079	-0.030	0.653	0.105	0.110	1.04
0.5725	1.154	-0.029	0.646	0.109	0.107	1.032
0.6459	1.218	-0.029	0.588	0.104	0.101	1.025
0.7125	1.277	-0.028	0.434	0.100	0.099	1.017
0.7899	1.345	-0.024	0.361	0.090	0.085	1.018
0.8492	1.389	-0.021	0.227	0.044	0.037	1.084
0.9125	1.452	-0.014	0.199	0.029	0.027	1.109
1.0000	1.548	0.000	0.000			
N-methyl aniline (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}
0.000	1.014	0.000	0.000			
0.0614	1.040	-0.008	0.217	0.006	0.009	1.395
0.1364	1.109	-0.013	0.340	0.009	0.011	1.271

x_1	η /mPa.s	$\Delta\eta$ /mPa.s	G^{*E} /J.mol ⁻¹	d_{12}	W_{vis}/RT	H_{12}
0.1865	1.122	-0.016	0.503	0.013	0.016	1.358
0.2505	1.166	-0.018	0.545	0.016	0.019	1.357
0.3215	1.211	-0.020	0.793	0.019	0.022	1.372
0.3806	1.252	-0.021	0.809	0.023	0.026	1.370
0.4898	1.340	-0.021	0.854	0.028	0.031	1.348
0.5606	1.397	-0.021	0.819	0.024	0.028	1.331
0.6512	1.472	-0.020	0.789	0.023	0.025	1.305
0.7202	1.519	-0.019	0.489	0.019	0.020	1.309
0.7945	1.583	-0.016	0.420	0.017	0.018	1.273
0.8718	1.641	-0.011	0.320	0.010	0.011	1.268
0.9225	1.675	-0.006	0.204	0.008	0.006	1.310
1.0000	1.735	0.000	0.000			

N-methyl 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			
0.0614	0.98	-0.010	0.166	0.003	0.004	1.253
0.1364	1.037	-0.016	0.240	0.006	0.009	1.143
0.1865	1.043	-0.020	0.390	0.009	0.010	1.224
0.2505	1.079	-0.022	0.427	0.013	0.014	1.227
0.3215	1.112	-0.025	0.544	0.016	0.019	1.237
0.3806	1.146	-0.026	0.567	0.019	0.021	1.238
0.4898	1.217	-0.027	0.627	0.023	0.028	1.216
0.5606	1.265	-0.026	0.546	0.021	0.024	1.202
0.6512	1.327	-0.025	0.532	0.019	0.020	1.177
0.7202	1.367	-0.022	0.419	0.015	0.016	1.184
0.7945	1.42	-0.020	0.351	0.010	0.012	1.149
0.8718	1.467	-0.015	0.249	0.007	0.010	1.138
0.9225	1.495	-0.010	0.179	0.002	0.005	1.170
1.0000	1.548	0.000	0.000			

N-methyl 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}
0.000	1.234	0.000	0.000			
0.0709	1.280	0.010	0.139	0.082	0.084	1.564
0.1256	1.313	0.016	0.215	0.076	0.079	1.558
0.1719	1.340	0.020	0.268	0.073	0.076	1.554
0.2619	1.391	0.026	0.344	0.069	0.072	1.551
0.3347	1.430	0.028	0.378	0.065	0.068	1.548
0.4018	1.465	0.030	0.394	0.063	0.066	1.546
0.4825	1.507	0.031	0.402	0.062	0.065	1.547
0.5321	1.531	0.030	0.390	0.060	0.063	1.546
0.6255	1.575	0.028	0.351	0.057	0.060	1.543
0.6917	1.607	0.026	0.322	0.058	0.061	1.547

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x_1	η /mPa.s	$\Delta\eta$ /mPa.s	G^{*E} /J.mol ⁻¹	d_{12}	W_{vis}/RT	H_{12}
0.7559	1.635	0.022	0.269	0.056	0.059	1.545
0.8325	1.667	0.016	0.193	0.053	0.055	1.542
0.9021	1.696	0.010	0.119	0.052	0.054	1.541
1.0000	1.735	0.000	0.000			

N-methyl 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}
0.000	1.148	0.000	0.000			
0.0709	1.182	0.006	0.091	0.053	0.054	1.391
0.1256	1.209	0.011	0.161	0.056	0.058	1.397
0.1719	1.232	0.015	0.219	0.059	0.061	1.402
0.2619	1.274	0.021	0.296	0.058	0.061	1.403
0.3347	1.306	0.024	0.333	0.056	0.059	1.402
0.4018	1.335	0.026	0.355	0.056	0.058	1.403
0.4825	1.368	0.027	0.359	0.054	0.057	1.402
0.5321	1.387	0.026	0.347	0.052	0.055	1.401
0.6255	1.422	0.024	0.312	0.050	0.053	1.399
0.6917	1.445	0.020	0.269	0.047	0.050	1.396
0.7559	1.465	0.015	0.206	0.042	0.044	1.388
0.8325	1.491	0.010	0.144	0.039	0.041	1.384
0.9021	1.514	0.005	0.080	0.035	0.036	1.377
1.0000	1.548	0.000	0.000			

N-methyl 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			
0.0699	1.017	0.013	0.298	0.181	0.184	1.442
0.1196	1.062	0.019	0.446	0.166	0.170	1.432
0.1956	1.132	0.029	0.646	0.161	0.165	1.435
0.2517	1.182	0.035	0.750	0.156	0.160	1.435
0.3219	1.242	0.040	0.830	0.149	0.153	1.434
0.3951	1.303	0.043	0.873	0.143	0.147	1.433
0.4706	1.364	0.045	0.876	0.137	0.141	1.433
0.5418	1.418	0.043	0.831	0.131	0.134	1.429
0.6105	1.470	0.041	0.771	0.126	0.130	1.429
0.6825	1.522	0.037	0.675	0.121	0.125	1.426
0.7692	1.583	0.029	0.53	0.116	0.120	1.425
0.8406	1.630	0.020	0.376	0.109	0.113	1.418
0.9065	1.675	0.013	0.236	0.109	0.112	1.422
1.0000	1.735	0.000	0.000			

N-methyl 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			

x_1	η /mPa.s	$\Delta\eta$ /mPa.s	G^{*E} /J.mol ⁻¹	d_{12}	W_{vis}/RT	H_{12}
0.0699	0.949	0.008	0.228	0.136	0.138	1.286
0.1196	0.988	0.015	0.374	0.137	0.141	1.292
0.1956	1.047	0.024	0.558	0.137	0.140	1.299
0.2517	1.088	0.029	0.646	0.132	0.136	1.298
0.3219	1.140	0.035	0.739	0.131	0.134	1.301
0.3951	1.192	0.039	0.791	0.127	0.131	1.303
0.4706	1.243	0.041	0.797	0.123	0.126	1.303
0.5418	1.29	0.041	0.776	0.120	0.124	1.304
0.6105	1.332	0.038	0.713	0.115	0.119	1.302
0.6825	1.374	0.033	0.619	0.110	0.113	1.298
0.7692	1.421	0.024	0.462	0.100	0.103	1.288
0.8406	1.46	0.016	0.325	0.093	0.096	1.282
0.9065	1.496	0.009	0.193	0.087	0.090	1.275
1.0000	1.548	0.000	0.000			

N-methyl 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			
0.0765	1.783	0.002	0.026	0.008	0.010	1.775
0.1419	1.782	0.005	0.052	0.010	0.013	1.779
0.2126	1.780	0.006	0.066	0.014	0.016	1.777
0.2818	1.779	0.008	0.088	0.016	0.018	1.780
0.3526	1.776	0.009	0.097	0.020	0.020	1.779
0.4105	1.774	0.010	0.106	0.021	0.022	1.780
0.4899	1.771	0.010	0.113	0.022	0.024	1.781
0.5569	1.767	0.010	0.109	0.020	0.022	1.780
0.6219	1.763	0.009	0.102	0.017	0.019	1.779
0.6936	1.758	0.008	0.089	0.014	0.017	1.778
0.7772	1.752	0.006	0.070	0.012	0.016	1.777
0.8465	1.747	0.004	0.052	0.008	0.013	1.777
0.9056	1.742	0.002	0.031	0.007	0.010	1.773
1.0000	1.735	0.000	0.000			

N-methyl 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			
0.0765	1.618	0.002	0.023	0.007	0.013	1.597
0.1419	1.614	0.003	0.038	0.006	0.012	1.595
0.2126	1.611	0.005	0.062	0.008	0.015	1.599
0.2818	1.607	0.006	0.077	0.008	0.015	1.599
0.3526	1.603	0.007	0.092	0.009	0.016	1.601
0.4105	1.600	0.008	0.105	0.010	0.017	1.602
0.4899	1.594	0.008	0.106	0.009	0.017	1.602
0.5569	1.589	0.008	0.105	0.010	0.017	1.602

Full Paper

x_1	η /mPa.s	$\Delta\eta$ /mPa.s	G^{*E} /J.mol ⁻¹	d_{12}	W_{vis}/RT	H_{12}
0.6219	1.583	0.007	0.095	0.009	0.016	1.600
0.6936	1.577	0.006	0.085	0.009	0.016	1.600
0.7772	1.569	0.005	0.064	0.008	0.015	1.598
0.8465	1.562	0.003	0.042	0.006	0.013	1.595
0.9056	1.557	0.002	0.029	0.007	0.013	1.597
1.0000	1.548	0.000	0.000			

zene over the entire composition ranges at (303.15 and 308.15) K. In the present work, the positive values of $\Delta\eta$ may be attributed to specific interactions through of hydrogen bonding (O-H...N) resulting in the formation of complexes between the component molecules^[18,19] 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

$$G^{*E} = RT [\ln \eta V - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \quad (6)$$

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 have their usual meanings.

Grunberg and Nissan^[20] proposed the following equation for the measurement of viscosity of liquid mixtures:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12} \quad (7)$$

where d_{12} is a parameter proportional to interchange energy, which reflects the non-ideality of the system.

Katti and Chaudhri^[21] proposed the following equation:

$$\ln \eta V = x_1 \ln V_1 \eta_1 + x_2 \ln V_2 \eta_2 + x_1 x_2 W_{vis}/RT \quad (8)$$

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

Hind et al.^[22] suggested an equation for the viscosity of binary liquid mixtures as

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 H_{12} \quad (9)$$

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

Attempts^[17,19,20] have been made to explain the behavior of liquid mixtures on the basis of sign and magnitude of excess Gibbs free energy of activation of viscous flow (G^{*E}), and Nissan's parameter (d_{12}). Nigam and Mahl^[23] concluded from the study on bi-

nary mixtures that (i) if $\Delta\eta > 0$, $d_{12} > 0$ and magnitude of both are large then strong specific interaction would be present; (ii) if $\Delta\eta < 0$, $d_{12} > 0$ then weak specific interaction would be present; (iii) if $\Delta\eta < 0$, $d_{12} < 0$ magnitude of both are large then the dispersion force would be dominant.

The positive values of G^{*E} and d_{12} indicate strong specific interactions such as hydrogen bonding, dipole-dipole interactions, other complexes and charge transfer whereas their negative values show weaker interaction.

From TABLE 3 shows that G^{*E} and d_{12} values are positive for all binary systems over the entire composition range at (303.15 and 308.15 K), further supporting the complex formation between the components of the mixtures.

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.

The variation of V^E , Δu , $\Delta\kappa_s$ and $\Delta\eta$ with mole fraction was fitted to the Redlich-Kister polynomial equation^[24] of the type

$$Y^E = x_1 x_2 [a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \quad (10)$$

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:

$$\sigma(Y^E) = [\sum(Y^E_{obs} - Y^E_{cal})^2 / (n-m)]^{1/2} \quad (11)$$

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 is determined by a multiple-regression analysis on the least square method and summarized along with the standard deviations

TABLE 4 : Coefficients of Redlich – Kister equation and standard deviation (σ) of the system

Binary mixtures	T/K		a_0	a_1	a_2	σ
N-MA + bromobenzene	303.15	$V^E/\text{cm}^3.\text{mol}^{-1}$	-0.834	0.076	-0.119	0.001
		$\Delta u/\text{m}.\text{sec}^{-1}$	-15.98	-5.23	-0.227	0.039
		$\Delta\kappa_s/\text{TPa}^{-1}$	-65.81	5.363	38.24	0.002
		$\Delta\eta/\text{mPa}.\text{s}$	-0.085	0.013	-0.039	0.001
N-MA + chlorobenzene	303.15	$V^E/\text{cm}^3.\text{mol}^{-1}$	-1.032	0.021	-0.167	0.001
		$\Delta u/\text{m}.\text{sec}^{-1}$	30.015	-3.612	-8.255	0.033
		$\Delta\kappa_s/\text{TPa}^{-1}$	-75.41	10.59	39.15	0.003
		$\Delta\eta/\text{mPa}.\text{s}$	-0.092	0.008	-0.048	0.001
N-MA + 1,2dichlorobenzene	303.15	$V^E/\text{cm}^3.\text{mol}^{-1}$	0.736	-0.113	-0.332	0.001
		$\Delta u/\text{m}.\text{sec}^{-1}$	-85.46	10.59	14.85	0.043
		$\Delta\kappa_s/\text{TPa}^{-1}$	-83.35	13.10	8.834	0.014
		$\Delta\eta/\text{mPa}.\text{s}$	0.122	-0.019	0.015	0.001
N-MA + 1,3dichlorobenzene	303.15	$V^E/\text{cm}^3.\text{mol}^{-1}$	0.864	-0.120	-0.125	0.001
		$\Delta u/\text{m}.\text{sec}^{-1}$	97.16	-8.99	-4.395	0.027
		$\Delta\kappa_s/\text{TPa}^{-1}$	-90.65	15.84	-8.565	0.012
		$\Delta\eta/\text{mPa}.\text{s}$	0.176	-0.023	-0.011	0.001
N-MA + 1,2,4-trichlorobenzene	303.15	$V^E/\text{cm}^3.\text{mol}^{-1}$	0.974	-0.085	-0.112	0.001
		$\Delta u/\text{m}.\text{sec}^{-1}$	101.75	7.844	8.107	0.078
		$\Delta\kappa_s/\text{TPa}^{-1}$	-100.30	22.03	-14.13	0.029
		$\Delta\eta/\text{mPa}.\text{s}$	0.0414	-0.003	0.021	0.001
N-MA + bromobenzene	308.15	$V^E/\text{cm}^3.\text{mol}^{-1}$	-0.911	0.058	-0.661	0.001
		$\Delta u/\text{m}.\text{sec}^{-1}$	-15.16	-6.77	5.492	0.024
		$\Delta\kappa_s/\text{TPa}^{-1}$	-72.37	6.675	31.58	0.003
		$\Delta\eta/\text{mPa}.\text{s}$	-0.103	0.005	-0.065	0.001
N-MA + chlorobenzene	308.15	$V^E/\text{cm}^3.\text{mol}^{-1}$	-1.134	0.048	-0.805	0.001
		$\Delta u/\text{m}.\text{sec}^{-1}$	64.50	41	-25.99	0.041
		$\Delta\kappa_s/\text{TPa}^{-1}$	-81.45	12.84	39.82	0.034
		$\Delta\eta/\text{mPa}.\text{s}$	-0.115	0.007	-0.099	0.001
N-MA + 1,2dichlorobenzene	308.15	$V^E/\text{cm}^3.\text{mol}^{-1}$	0.645	-0.098	-0.485	0.002
		$\Delta u(\text{m}.\text{sec}^{-1})$	129.90	-15.79	14.69	0.041
		$\Delta\kappa_s/\text{TPa}^{-1}$	-91.02	16.23	-2.168	0.019
		$\Delta\eta/\text{mPa}.\text{s}$	0.108	-0.024	-0.047	0.001
N-MA + 1,3dichlorobenzene	308.15	$V^E/\text{cm}^3.\text{mol}^{-1}$	0.746	-0.093	-0.266	0.002
		$\Delta u/\text{m}.\text{sec}^{-1}$	106.26	-7.802	-43.05	0.041
		$\Delta\kappa_s/\text{TPa}^{-1}$	-93.94	19.33	-27.22	0.076
		$\Delta\eta/\text{mPa}.\text{s}$	0.165	-0.016	-0.070	0.001
N-MA + 1,2,4-trichlorobenzene	308.15	$V^E/\text{cm}^3.\text{mol}^{-1}$	0.865	-0.024	-0.459	0.001
		$\Delta u/\text{m}.\text{sec}^{-1}$	90.82	4.380	-28.78	0.044
		$\Delta\kappa_s/\text{TPa}^{-1}$	-105.7	23.66	-32.69	0.098
		$\Delta\eta/\text{mPa}.\text{s}$	0.032	-0.002	-0.012	0.001

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 used for interpolat-

ing the experimental data measured in this work 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-methylaniline 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. Thus supports the contention of Kaulgud that V^E and $\Delta\kappa_s$ are dependent of different factors. According to his theory a more 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.

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