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Ultrasonic Investigations in Binary Liquid Mixtures of 2-Methylcyclohexanone with Formamide, N-Methylformamide and N,N-Dimethylformamide at Different Temperatures.

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Abstract

Ultrasonic velocity(U), viscosity (η) and density (ρ) of binary liquid mixtures 2-methylcyclohexanone with formamide, N-Methylformamide and N,N-Dimethylformamide have been measured at three temperatures 303.15,308.15 and 313.15 K, over the entire composition range. These experimental data have been used to calculated the excess isentropic compressibility (K_s^E), excess enthalpy (H^E), excess free length (L_f^E), excess Gibb's free energy (ΔG^{*E}) and excess molar volume (V_m^E). The excess values have been fitted to the Redlich-Kister type polynomial equation. The deviations of excess values provide valuable

information that allows us to have a better understanding of the structure of liquids and intermolecular interactions in liquid mixtures. The results of these observations have been interpreted in terms of structural effects of the solvents. Further the experimental and derived results are analyzed in terms of structural molecular interactions between component molecules with FT-IR spectral studies.

Key words: Ultrasonic velocity, density, viscosity, Excess parameters, R-K polynomial equation, FTIR studies.

1. INTRODUCTION

Now-a-days ultrasonic is an area of intense scientific and technological research. In view of its extensive scientific and engineering applications it attracts attention of researchers, non-destructive testing professionals, industrialists, technologists, medical practitioners, instrumentation engineers, software engineers and medical scientists. The study of ultrasonic waves in pure and liquid mixtures is useful to examine the nature of intermolecular interactions occurred in these liquids. The acoustic parameters are useful in understanding molecular structure and molecular interactions in the medium. Recent development in science and technology for non – destructive technique are spectacular and holds significant possibilities for better new applications in molecular structure, molecular interactions, medicines and underwater acoustics. Development of sensors, electronic instrumentation and computer software added sophistication to the experimental and theoretical agreement of different ultrasonic parameters. Thermodynamics studies of binary liquid mixtures have attracted much attention of scientists. The measurement of ultrasonic speed enables us to the accurate measurement of some useful acoustic and thermodynamic parameters and their excess values. These excess acoustic parameters in binary liquid mixture are useful in understanding the solute-solvent interactions. The variation in ultrasonic velocity gives information about the bonding between molecules and formation of complexes at various concentration and temperature through molecular interactions. In order to have clear understanding of intermolecular interaction between component molecules of an attempt has been made to study the ultrasonic behavior of 2-Methylcyclohexanone(2-MCH) with formamide(F), N-Methylformamide(N-MF) and N,N-Dimethylformamide(N,N-DMF) at three temperature. Thermo-acoustic parameters are the essential sources of information for better understanding of non-ideal behavior of complex binary liquid system[1].

So from the experimentally determined values of speed of sound density and viscosity, various excess thermo-acoustic parameters like excess isentropic compressibility (K_s^E), excess Enthalpy (H^E), excess molar volume (V^E), excess Gibb's free energy (ΔG^{*E}) and excess free length (L_f^E) have been calculated[2][3][4][5]. These parameters analyzed with Redlich- Kister polynomial non-linear regression.

2. EXPERIMENTAL

2.1. Materials

The chemicals used were of analytical reagent (AR) grade which were obtained from Merck Co.Inc., Germany, with purities of greater than 0.99. All the chemicals were further purified by standard methods[6] and only middle fractions were collected. The purity analysis of the chemicals used in the present study is given in **Table1** and purity checked by gas chromatographic analysis. The density, viscosity and speed of sound were experimentally determined at different temperatures and compared to literature values[7][8][9][10][11]. Comparison of experimental density (ρ), viscosity (η) and speed of sound (U) of pure liquids with literature values is given in **Table 2.**

The binary liquid mixtures of varying composition were prepared by mass in special air-tight bottles and adequate

precautions have been taken to minimize evaporation losses. 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.

2.2. Methods

All liquid mixtures were prepared by weighing an amount of pure liquids in an electronic balance with a precision of ±0.1 kg m^{-3}. The binary mixtures were prepared just before use. The uncertainty in mole fraction was estimated to be less than ±0.0001.

The speed of sound was measured with an ultrasonic interferometer (Mittal Enterprises, Delhi, India) working at 2 MHz frequency and 303.15, 308.15 and 313.15 K temperature. The uncertainty in the speed of sound was found to be ±0.1 ms^{-1}. An electronically digital operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desire temperature.

The viscosities were measured with Ostwald viscometer. The viscometer was calibrated at each temperature using redistilled water. The uncertainty in viscosity measurement is up to 0.001 mPa s. The flow time has been measured after the attainment of bath temperature by each mixture. The flow measurements were made with an electronic stop watch with precision of 0.01 s. For all pure components and mixtures, 3-4 readings were taken, and the average of these values was used in all the calculations.

The densities of the pure compounds and their mixtures were determined accurately using 10 mL specific gravity bottles in digital electronic balance with an uncertainty of ±0.1 kg m^{-3}. The average uncertainty in the measured density was ±0.001 kg m^{-3}.

3. THEORY

The values of experimentally determined density, viscosity and speed of sound for the liquid mixtures of 2-Methylcyclohexanone(2-MCH) with formamide(F), N-Methylformamide(N-MF) and N,N-Dimethylformamide(N,N-DMF) at 303.15, 308.15 and 313.15 K over the entire composition range are given in **Table 3.**Using the experimentally determined values of speed of sound, density and viscosity, various thermodynamic parameters like excess isentropic compressibility (K_s^E), excess Enthalpy (H^E), excess molar volume (V^E), excess Gibb's free energy (ΔG^{*E}) and excess free length (L_f^E) were calculated.

The excess values of isentropic compressibility, K_s^E Were calculated as follows;

$$K_s^E = K_s - K_s^{id} \quad (1)$$

Where K_s^E is its excess value, $K_s^{id}$is the ideal isentropic compressibility value and K_s represent the calculated value of isentropic compressibility for the mixture. K_s^{id} for an ideal mixture was calculated from the relation recommended by Kiyohara and Benson[12], Benson and Kiyohara[11] and Douheret et al.[13].

$$K_s^{id} = \sum \phi_i \left\{ K_{s,i}^{\circ} + \frac{TV_i^{\circ}(\alpha_i^{\circ})^2}{C_{p,i}^{\circ}} \right\} - T(\sum x_i V_i^{\circ}) \left[\frac{\sum \phi_i \alpha_i^{\circ 2}}{\sum x_i C_{p,i}^{\circ}} \right] \quad (2)$$

In which$K_{s,i}^{\circ}$, V_0^i, α_i^o, $C_{p,j}^o$ are the isentropic compressibility, molar volume, isobaric thermal expansion coefficient and molar isobaric heat capacity of pure component *i*, *T* represents temperature, $\phi_i$is the volume fraction and x_i represents the mole fraction of *i* in the mixture.

Excess enthalpy H^E was calculated from usual relation,

$$H^E = H - (x_1H_1 + x_2H_2) \quad (3)$$

Where *H* represents the calculated value of enthalpy for the mixture and H_1, H_2 represent enthalpy of pure components 1 and 2, respectively

The density values have been used to calculate the excess volumes, V^E, using the following equation,

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2} \right) \quad (4)$$

Where ρ is the density of the mixture and x_1, M_1, and x_2, M_2, and ρ_1, ρ_2 are the
mole fraction, molar mass, and density of pure components 1 and 2, respectively.

Excess Gibbs free energy of activationΔG^{*E} was calculated as follows,

$$\Delta G^{*E} = RT \left[ln\left(\frac{\eta V}{\eta_2 V_2}\right) - X_1 ln\left(\frac{\eta_1 V_1}{\eta_2 V_2}\right) \right] \quad (5)$$

Where *R* represents gas constant, *T* is absolute temperature, η is the viscosity of the mixture and η_1, η_2 are the viscosities of the pure compounds, V_m is the molar volume of the mixture and V_1,V_2 are the volumes of the *R*.

The excess values of the free length L_f^E were calculated by using the expression,

$$L_f^E = L_f - K_T(K_s^{id})^{1/2} \quad (6)$$

Where L_f represents the calculated value for the mixture and K_T represent a temperature dependent constant whose value is $K_T = (91.368 + 0.3565T)\,X10^{-8}$.

The conventional smooth curve fitting strategy for excess properties of binary mixture involves Redlich-Kister[14] polynomial non-linear regression,

$$Y^E = x_1(1 - x_1)\sum_{i=0}^{3} A_i (2x_1 - 1)^{i-1} \quad (7)$$

Here Y^E means excess parameter of any value (*i.e.*, L_f^E, K_s^E, V^E, ΔG^{*E}, H^E) should be used. The standard deviation was calculated is as follows.

$$\sigma(Y^E) = \left[\sum \frac{((Y^E)_{obs} - (Y^E)_{cal})^2}{n - m} \right]^{\frac{1}{2}} \quad (8)$$

Where *n* represent the number of experimental values and *m* is the adjustable parameter.

Table 01:
Purity analysis

Chemical name	Source	Initial moleI fraction	Purification method	Final mole fraction	Analysis method
2-Methylcyclohexanone	Hi Media Laboratories Pvt. Ltd. Mumbai, India Tokyo Industries.co .Ltd, Japan	0.99	Distillation	0.995	Gas liquid chromatography
Formamide		0.99	Distillation	0.997	
DMF		0.99	Distillation	0.997	
NMF		0.99	Distillation	0.997	

Table 02:
Comparison of experimental densities (ρ), viscosities (η) and speed of sound (U) of pure liquids with literature values.

Liquid	Temp T (K)	Density(ρ) kg m^3		Viscosity(η) mPa.S		Speed of sound (U)m.s-1		CP J K^{-1} mol^{-1}	ὰ K K^{-1}
		expt	Lit	expt	Lit	expt	Lit		
2-Methylcyclo hexanone	303.15	0.9193	0.9195[a]	2.2239	2.2242[a]	1345.18	1344.6[a]	---	---
	308.15	0.9152	---	2.1740	---	1339.09	---	---	---
	313.15	0.9107	---	2.0235	---	1331.05	---	---	---
Formamide	303.15	1.1245	1.1247[b]	2.9210	2.80[b]	1585.30	1585.4[c]	107.11[h]	0.9967[i]
	308.15	1.1203	1.1205[b]	2.5234	2.500[b]	1580.58	1580.6[c]	105.20[h]	0.9961[i]
	313.15	1.1162	1.1164[b]	2.3012	2.29	1571.92	1572.0[c]	108.56[h]	0.9998[i]
NMF	303.15	0.9943	0.9946[b]	1.5857	1.5859[b]	1408.39	1408.5[c]	107.11[h]	0.9967[i]
	308.15	0.9902	0.9903[b]	1.4624	1.4627[b]	1400.64	1400.6[c]	105.20[h]	0.9961[i]
	313.15	0.9859	0.9861[b]	1.3528	1.3520[b]	1383.24	1382.5[c]	108.56[h]	0.9998[i]
DMF	303.15	0.9382	0.9394[b]	0.7530	0.7520[b]	1468.14	1469.8[d]	107.11[h]	0.9967[i]
	308.15	0.9353	0.9357[b]	0.7210	0.7210[b]	1432.96	1433.2[d]	105.20[h]	0.9961[i]
	313.15	0.9304	0.9302[b]	0.6923	0.6900[b]	1418.12	1418.0[d]	108.56[h]	0.9998[i]

a Gowrisankar et al. [7], b Hosseinali Zarei et al. [8], c Puneet kumar Pandey et al. [9]. d Balaji et al. [10], h Reference[37], i Derive from density data

Table 03: Experimental values of Density (ρ), Viscosity (η) and Speed of sound (U) for 2-Methylcyclohexanone(2MCH) with Formamide/NMF/DMF.

X1	Density(ρ) Kg. m^3	Speed of Sound(U) $m.s^{-1}$	Viscosity(η) mPa.s	X1	Density(ρ) Kg. m^3	Speed of Sound(U) $m.s^{-1}$	Viscosity(η) mPa.s
2MCH+ Formamide							
303.15 K							
0.0000	0.9193	1345.18	2.2239	0.3758	1.0424	1489.25	2.6421
0.0427	0.9398	1369.19	2.2936	0.4837	1.0629	1513.26	2.7118
0.0912	0.9603	1393.20	2.3633	0.6162	1.0834	1537.27	2.7815
0.1468	0.9808	1417.21	2.4330	0.7832	1.1039	1561.28	2.8512
0.2111	1.0013	1441.22	2.5027	1.0000	1.1245	1585.30	2.9210
0.2864	1.0219	1465.24	2.5724				
308.15 K							
0.0000	0.9152	1339.09	2.1740	0.3758	1.0177	1483.98	2.3836
0.0427	0.9357	1363.23	2.2089	0.4837	1.0382	1508.13	2.4185
0.0912	0.9562	1387.38	2.2438	0.6162	1.0587	1532.28	2.4535
0.1468	0.9767	1411.53	2.2788	0.7832	1.0792	1556.43	2.4884
0.2111	0.9972	1435.68	2.3137	1.0000	1.0997	1580.58	2.5234
0.2864	1.0177	1459.83	2.3487				
313.15 K							
0.0000	0.9107	1331.05	2.0235	0.3758	1.0340	1475.57	2.1901
0.0427	0.9312	1355.13	2.0512	0.4837	1.0545	1499.65	2.2178
0.0912	0.9518	1379.22	2.0790	0.6162	1.0751	1523.74	2.2456
0.1468	0.9723	1403.31	2.1068	0.7832	1.0956	1547.83	2.2734
0.2111	0.9929	1427.39	2.1345	1.0000	1.1162	1571.92	2.3012
0.2864	1.0134	1451.48	2.1623				

X1	Density(ρ) Kg. m^3	Speed of Sound(U) $m.s^{-1}$	Viscosity(η) mPa.s	X1	Density(ρ) Kg. m^3	Speed of Sound(U) $m.s^{-1}$	Viscosity(η) mPa.s
2MCH + NMF							
303.15 K							
0.0000	0.9194	1343.98	2.2239	0.4413	0.9643	1382.62	1.8409
0.0553	0.9268	1350.42	2.1600	0.5513	0.9718	1389.06	1.7771
0.1163	0.9343	1356.86	2.0962	0.6781	0.9793	1395.50	1.7133
0.1841	0.9418	1363.30	2.0324	0.8258	0.9868	1401.94	1.6495
0.2598	0.9493	1369.74	1.9686	1.0000	0.9943	1408.39	1.5857
0.3450	0.9568	1376.18	1.9048				
308.15 K							
0.0000	0.9119	1418.8	0.7110	0.4413	1.0490	1458.6	4.4242
0.0553	0.9197	1337.89	2.1738	0.5513	0.9588	1375.54	1.7469
0.1163	0.9275	1344.16	2.1026	0.6781	0.9667	1381.81	1.6758
0.1841	0.9353	1350.44	2.0315	0.8258	0.9745	1388.09	1.6046
0.2598	0.9432	1356.71	1.9603	1.0000	0.9823	1394.36	1.5335
0.3450	0.9510	1362.99	1.8892				
313.15 K							
0.0000	0.9104	1329.76	2.0232	0.4413	0.9557	1361.84	1.6209
0.0553	0.9179	1335.10	1.9561	0.5513	0.9632	1367.19	1.5539
0.1163	0.9255	1340.45	1.8891	0.6781	0.9708	1372.54	1.4868
0.1841	0.9330	1345.80	1.8220	0.8258	0.9783	1377.89	1.4198
0.2598	0.9406	1351.15	1.7550	1.0000	0.9859	1383.24	1.3528
0.3450	0.9481	1356.50	1.6880				
2MCH + N,N-DMF							
303.15 K							
0.0000	0.9196	1344.56	2.2243	0.4942	0.9307	1418.08	1.3415
0.0675	0.9214	1356.91	2.0771	0.6032	0.9326	1431.06	1.1943
0.1400	0.9233	1369.27	1.9300	0.7227	0.9344	1443.42	1.0472
0.2182	0.9251	1381.63	1.7829	0.8543	0.9363	1455.78	0.9001
0.3028	0.9270	1393.99	1.6357	1.0000	0.9382	1468.14	0.753
0.3945	0.9289	1406.35	1.4886				
308.15 K							
0.0000	0.9145	1338.18	2.1747	0.4942	0.9269	1395.04	1.3024
0.0675	0.9165	1347.65	2.0293	0.6032	0.929	1404.52	1.1571
0.1400	0.9186	1357.13	1.8839	0.7227	0.9311	1414.00	1.0117
0.2182	0.9207	1366.61	1.7385	0.8543	0.9332	1423.48	0.8663
0.3028	0.9228	1376.09	1.5932	1.0000	0.9352	1432.96	0.721
0.3945	0.9249	1385.57	1.4478				
313.15 K							
0.0000	0.911	1330.36	2.0238	0.4942	0.9226	1383.01	1.2249
0.0675	0.9129	1339.13	1.8906	0.6032	0.9245	1391.79	1.0917
0.1400	0.9148	1347.91	1.7575	0.7227	0.9265	1400.56	0.9586
0.2182	0.9168	1356.68	1.6243	0.8543	0.9284	1409.34	0.8254
0.3028	0.9187	1365.46	1.4912	1.0000	0.9304	1418.12	0.6923
0.3945	0.9207	1374.24	1.3580				

RESULTS AND DISCUSSIONS

The experimental values of speed of sound, density and viscosity in case of the binary liquid mixtures under study over the entire range of composition and at three temperatures, T = 303.15, 308.15 and 313.15 K are given in table. From this available data of speed of sound, density and viscosity, values of excess isentropic compressibility (K_s^E), excess enthalpy (H^E), excess free length (L_f^E), excess Gibb's free energy (ΔG^{*E}) and excess molar volume (V^E) were calculated. These excess parameters were plotted against mole fraction of amides over the entire mole fraction range and at different temperatures. The plots are shown in Fig. 1,2,3, 4 and 5. The excess parameters of isentropic compressibility (K_s^E), enthalpy (H^E), free length (L_f^E),Gibb's free energy (ΔG^{*E}) and excess molar volume (V^E) are analyzed with Redlich-Kister polynomial non-linear regression, and the values of A_i are determined and reported along with standard deviation between experimental values and calibrated values has been illustrated in **Table 4** .

Table 04 Coefficients of Redlich-Kister equation and Standard Deviations (σ) for 2-Methylcyclohexanone(2MCH) with formamide , NMF and DMF at T=303.15 K, 308.15K and 313.15K

Parameter	Temperature (K)	A0	A1	A2	A3	σ
2MCH + **Formamide**						
$10^{12}K_S{}^E/(m^2.N^{-1})$	303.15	-2.7744	1.4863	-0.9708	0.7711	0.0024
	308.15	-2.8315	1.5180	-0.9961	0.7954	0.0024
	313.15	-2.8930	1.5517	-1.0190	0.8137	0.0024
10^6 $V^E/(m^3.mol^{-1})$	303.15	-29.064	14.303	-8.2481	5.7898	0.0174
	308.15	-29.0649	14.3030	-8.24818	5.78984	0.0174 2
	313.15	-29.287	14.402	-8.359	5.9325	0.0167
$10^{13}L_f^E/$ (m)	303.15	-29.221	14.551	-8.542	6.116	0.0180
	308.15	-29.928	14.910	-8.793	6.337	0.0181
	313.15	-30.630	15.260	-9.004	6.487	0.0179
$\Delta G^E/(J.mol^{-1})$	303.15	9.2087	3.4178	0.7608	0.4632	0.0005
	308.15	9.2321	3.4034	0.7562	0.4799	0.0001
	313.15	9.2080	3.4099	0.7537	0.4799	0.0007
$H^E/(J.mol^{-1})$	303.15	-0.0051	-0.0013	-0.0004	-0.0003	0.0000
	308.15	-0.0084	0.0006	-0.0016	0.0004	0.0000
	313.15	-0.0088	0.0009	-0.0017	0.0005	0.0000
2MCH + **NMF**						
$10^{12}K_S{}^E/(m^2.N^{-1})$	303.15	-0.6876	0.2471	-0.925	0.0324	0.0000
	308.15	-0.7091	0.2545	-0.0945	0.0417	0.0001
	313.15	-0.6525	0.2323	-0.0865	0.0362	0.0001
10^6 $V^E/(m^3.mol^{-1})$	303.15	-9.1779	3.1587	-1.1036	0.3185	0.0010
	308.15	-9.7384	3.3513	-1.1766	0.4852	0.0026
	313.15	-9.4346	3.2488	-1.1633	0.4524	0.0028
$10^{13}L_f^E/$ (m)	303.15	-6.9130	2.3623	-0.8332	0.2662	0.0004
	308.15	-7.1384	2.4345	-0.8481	0.3623	0.0015
	313.15	-6.5923	2.2399	-0.7886	0.3168	0.0017
$\Delta G^E/(J.mol^{-1})$	303.15	4.5600	1.2456	0.2039	0.0566	0.0003
	308.15	4.4733	1.2717	0.2007	0.0959	0.0007
	313.15	4.4127	1.2935	0.1852	0.0929	0.0007
$H^E/(J.mol^{-1})$	303.15	-0.0082	0.0016	-0.0007	0.0002	0.0000
	308.15	-0.0089	0.0019	-0.0008	0.0003	0.0000
	313.15	-0.0086	0.0018	-0.0008	0.0002	0.0000
2MCH + **N,N-DMF**						
$10^{12}K_S{}^E/(m^2.N^{-1})$	303.15	-0.5836	0.1653	-0.0630	0.0014	0.0015
	308.15	-0.4735	0.1261	-0.0342	-0.0041	0.0001
	313.15	-0.4448	0.1166	-0.0274	0.0039	0.0001
10^6 $V^E/(m^3.mol^{-1})$	303.15	-1.7093	0.3993	-0.0218	-0.0496	0.0031
	308.15	-1.9466	0.4758	-0.1001	-0.2232	0.0022
	313.15	-1.8169	0.4301	-0.0323	-0.0713	0.0031
$10^{13}L_f^E/$ (m)	303.15	-5.7066	1.5015	-0.5685	-0.0235	0.0164
	308.15	-4.6670	1.1629	-0.2969	-0.0662	0.0011
	313.15	-4.3985	1.0823	-0.2313	0.0229	0.0018
$\Delta G^E/(J.mol^{-1})$	303.15	3.0891	0.1325	0.1632	0.0026	0.0031
	308.15	2.8765	0.2118	0.0787	-0.0585	0.0005
	313.15	2.8878	0.2225	0.0972	-0.0165	0.0008
$H^E/(J.mol^{-1})$	303.15	-0.0062	0.0017	-0.0003	0.0000	0.0000
	308.15	-0.0048	0.0017	-0.0002	0.0000	0.0000
	313.15	-0.0048	0.0016	-0.0002	0.0001	0.0000

Table : 5 Partial molar volumes for 2-Methylcyclohexanone with formamide/DMF/NMF at different temperatures

Mole fraction	2MCH + Formamide		Mole fraction	2MCH +NMF		Mole fraction	2MCH +DMF	
	$\bar{v}_{m,1}x10^{-5}$	$\bar{v}_{m,2}x10^{-5}$		$\bar{v}_{m,1}x10^{-5}$	$\bar{v}_{m,2}x10^{-5}$		$\bar{v}_{m,1}x10^{-5}$	$\bar{v}_{m,2}x10^{-5}$
303.15 K								
0.0000	9.4956	4.8993	0.0000	11.2389	6.4248	0.0000	12.0393	7.9479
0.0427	9.5877	4.8606	0.0553	11.2240	6.4205	0.0675	11.9360	7.9570
0.0912	9.6873	4.8904	0.1163	11.2337	6.4144	0.1400	11.9594	7.9620
0.1468	9.7643	4.8912	0.1841	11.2465	6.4094	0.2182	11.9558	7.9442
0.2112	9.8212	4.8450	0.2598	11.2559	6.4070	0.3028	11.9490	7.9411
0.2865	9.8725	4.7952	0.3450	11.2635	6.4063	0.3945	11.9565	7.9492
0.3759	9.9163	4.7872	0.4413	11.2705	6.4069	0.4942	11.9572	7.9467
0.4837	9.9397	4.8071	0.5513	11.2753	6.4114	0.6032	11.9529	7.9456
0.6163	9.9689	4.8383	0.6781	11.2786	6.4233	0.7227	11.9642	7.9547
0.7833	9.9442	4.9591	0.8258	11.2824	6.4475	0.8543	11.9425	7.9433
1.0000	9.9751	5.3788	1.0000	11.2810	6.4668	1.0000	11.9560	7.8646
308.15 K								
0.0000	9.5080	4.9213	0.0000	11.2485	6.4777	0.0000	12.0492	7.9922
0.0427	9.6255	4.8986	0.0553	11.2664	6.4745	0.0675	11.9818	7.9966
0.0912	9.7193	4.8655	0.1163	11.2810	6.4879	0.1400	11.9898	7.9972
0.1468	9.7971	4.8405	0.1841	11.2871	6.4733	0.2182	11.9883	7.9890
0.2112	9.8612	4.8282	0.2598	11.2974	6.4522	0.3028	11.9878	7.9895
0.2865	9.9116	4.8226	0.3450	11.3121	6.4515	0.3945	11.9947	7.9938
0.3759	9.9503	4.8182	0.4413	11.3172	6.4623	0.4942	11.9948	7.9902
0.4837	9.9803	4.8243	0.5513	11.3166	6.4623	0.6032	11.9896	7.9887
0.6163	9.9975	4.8625	0.6781	11.3325	6.4734	0.7227	11.9954	7.9968
0.7833	10.0152	4.9772	0.8258	11.3136	6.5039	0.8543	11.9882	7.9947
1.0000	10.0120	5.4252	1.0000	11.3136	6.5039	1.0000	11.9940	7.9370
313.15 K								
0.0000	9.5527	4.9456	0.0000	11.3110	6.4884	0.0000	12.0452	8.0230
0.0427	9.6536	4.9303	0.0553	11.3147	6.4822	0.0675	12.0583	8.0182
0.0912	9.7469	4.8707	0.1163	11.3278	6.4676	0.1400	12.0517	8.0130
0.1468	9.8299	4.8318	0.1841	11.3423	6.4667	0.2182	12.0528	8.0232
0.2112	9.8963	4.8316	0.2598	11.3517	6.4720	0.3028	12.0538	8.0269
0.2865	9.9449	4.8469	0.3450	11.3580	6.4714	0.3945	12.0543	8.0207
0.3759	9.9849	4.8477	0.4413	11.3664	6.4678	0.4942	12.0584	8.0190
0.4837	10.0187	4.8456	0.5513	11.3730	6.4737	0.6032	12.0578	8.0240
0.6163	10.0266	4.8858	0.6781	11.3709	6.4869	0.7227	12.0504	8.0239
0.7833	10.0692	5.0013	0.8258	11.3846	6.5103	0.8543	12.0659	8.0278
1.0000	10.0490	5.4419	1.0000	11.3770	6.5543	1.0000	12.0560	8.0338

The deviations observed in the excess parameters indicate the strength of interactions present between the component molecules of binary mixtures under study[15]. The variations in these excess parameter values reflect the interactions between the mixing species, and shapes of the components and temperature. The effects which influence the values of excess thermodynamic functions may be the result of physical, chemical, and structural contributions such as;

1. Chemical effects, like the breaking of molecular association present in the pure liquid which results in the positive values of K_s^E, H^E, L_f^E, ΔG^{*E} and V^E on the other hand charge transfer forces, formation of hydrogen bonds, and other complex forming interaction result in the negative values of K_s^E, H^E, L_f^E, ΔG^{*E} and V^E [16].
2. Physical contributions are from dispersion forces or weak dipole-dipole interactions causing the positive values of K_s^E, H^E, V^E, ΔG^{*E} and negative L_f^E.
3. The structural contributions arising from the geometrical fitting of one component into the other because of the differences in the size and shape of the component molecules resulting in the negative values of K_s^E, H^E, V^E, ΔG^{*E} and positive L_f^E.

It is clear from Fig. 1 that the K_s^E values are negative over the entire mole fraction range and the changes in K_s^E values with respect to temperature are small in all the mixtures. The sign of excess isentropic compressibility plays a vital role in assessing the compactness due to molecular interaction in liquid mixtures through charge transfer, dipole–dipole interactions, and dipole induced dipole interactions, interstitial accommodation and orientational ordering leading to more compact structure making, which enhances excess isentropic compressibility to have negative values. Fort and Moore[17] suggested that the liquids having different molecular sizes and shapes mix well there by reducing the volume which causes the values of K_s^E to be negative. It also suggests that the liquids are less compressible when compared to their ideal mixtures

signifying the chemical effects including charge transfer forces, formation of H bonds and other complex forming interactions. It can also be said that the molecular interactions are strong in these binary liquid mixtures and that the medium is highly packed. Similar results were obtained by earlier workers[18][19].So, strong hydrogen bonding is expected in liquid systems which are reflected from the negative values of K_s^E in these mixtures.

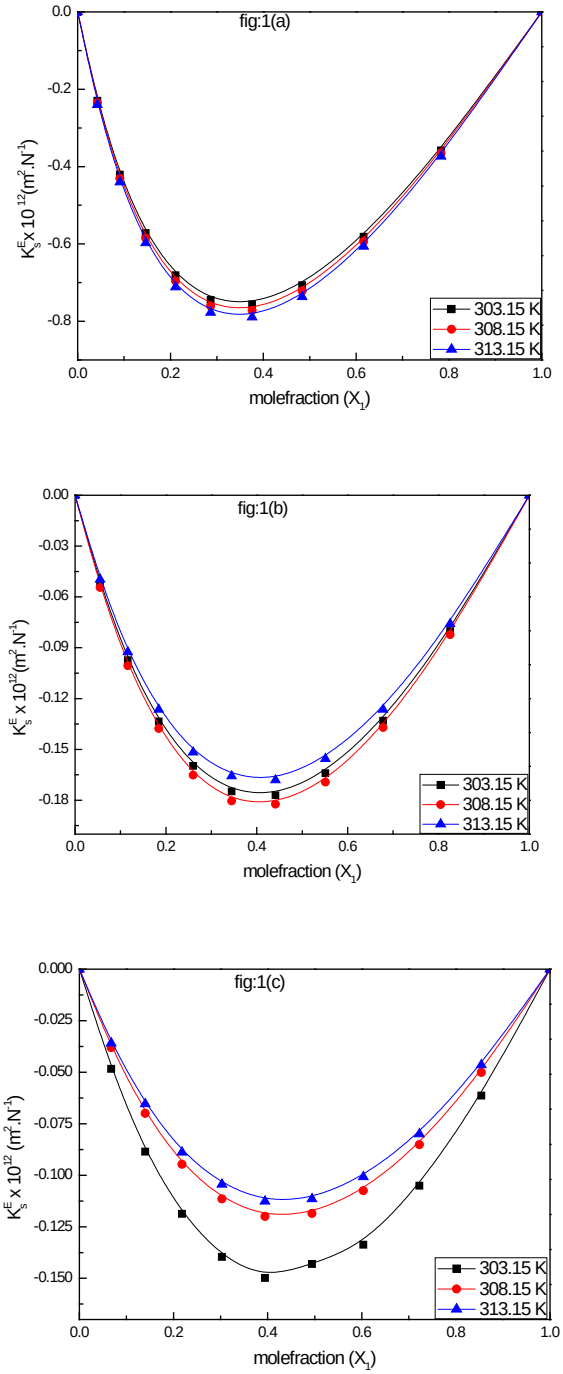


Figure 1: Variation of excess isentropic compressability (K_s^E) with mole fraction (x_1) in the binary liquid mixtures of 2-methylcyclohexanone with formamide(1.a),N-methylformamide(1.b) and N,N-Dimethylformamide(1.c) at 303.15 K (■), 308.15 K(●) and 313.15 K (▲).

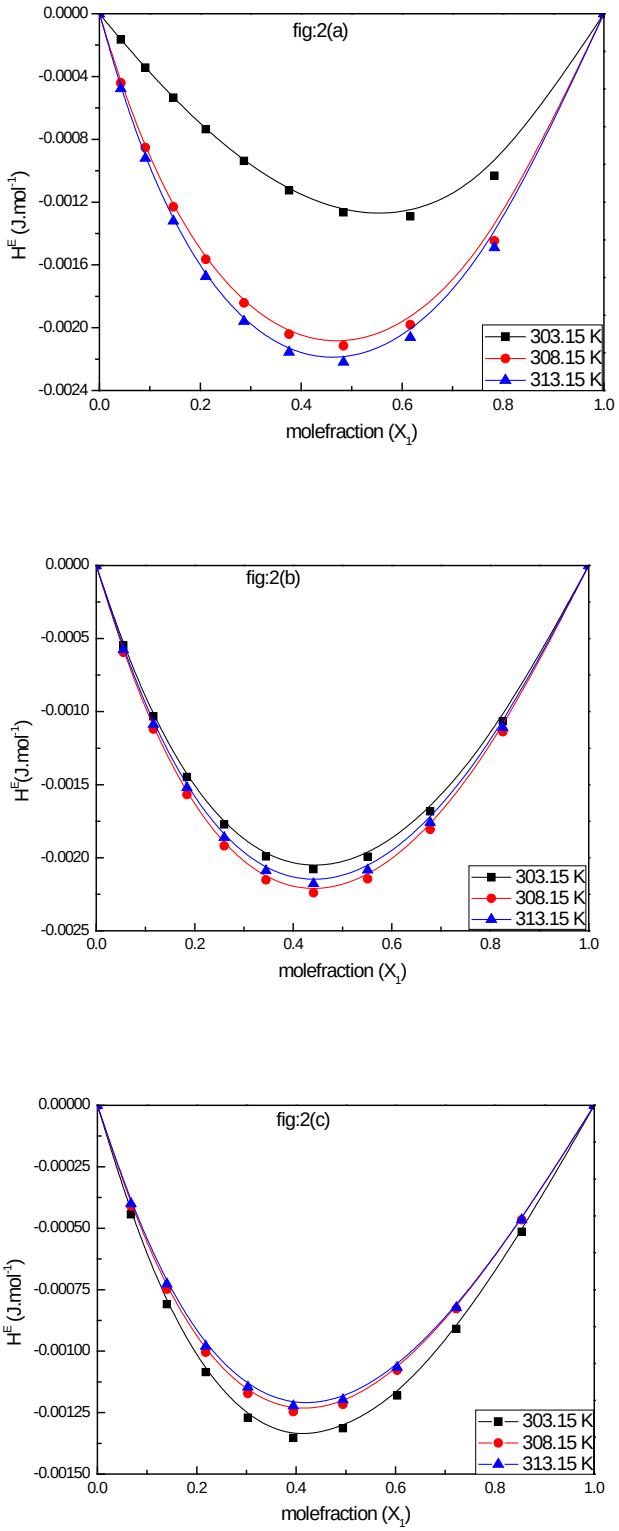
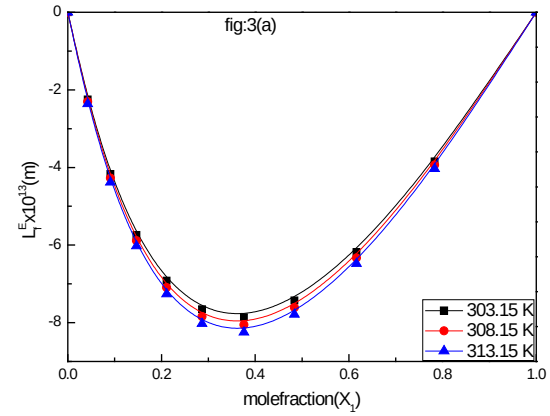
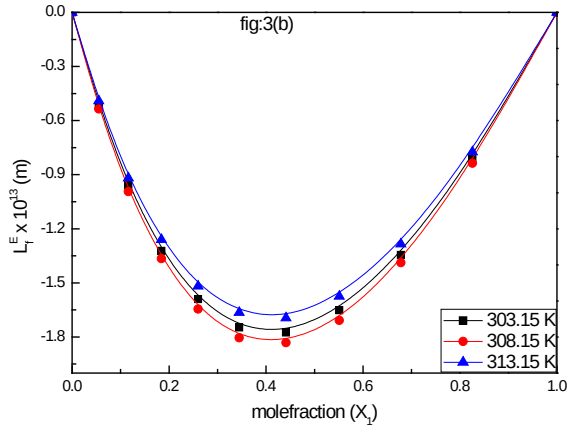


Figure 2: Variation of excess Enthalpy (H^E) with mole fraction (x_1) in the binary liquid mixtures of 2-methylcyclohexa:none with formamide(2.a),N-methylformamide(2.b) and N,N-Dimethylformamide(2.c) at 303.15 K (■), 308.15 K(●) and 313.15 K (▲).





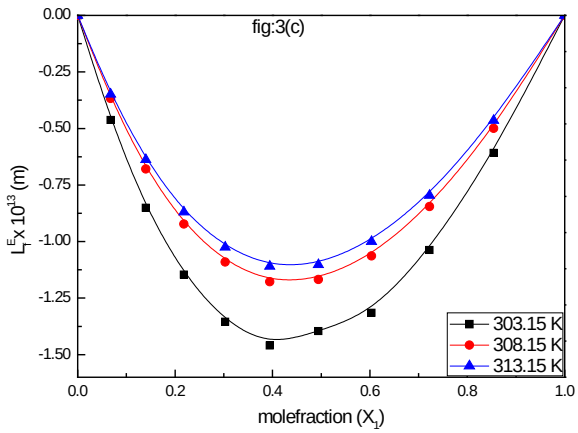
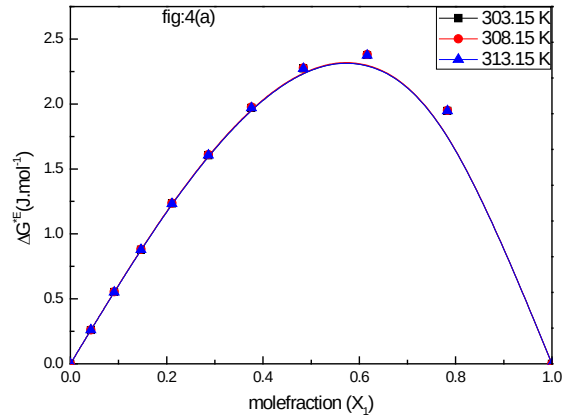
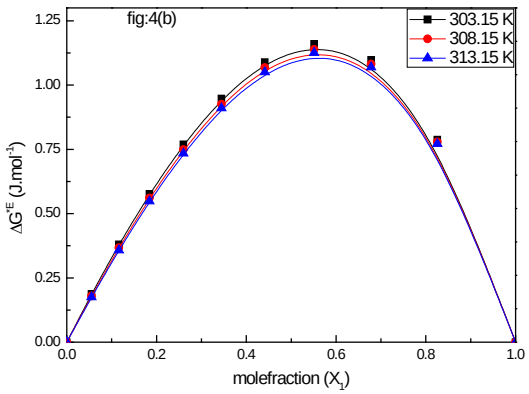


Figure 3: Variation of excess Free length (L_f^E) with mole fraction (x_1) in the binary liquid mixtures of 2-methylcyclohexanone with formamide(3.a),N-methylformamide(3.b) and N,N-Dimethylformamide(3.c) at 303.15 K (■), 308.15 K(●) and 313.15 K (▲).





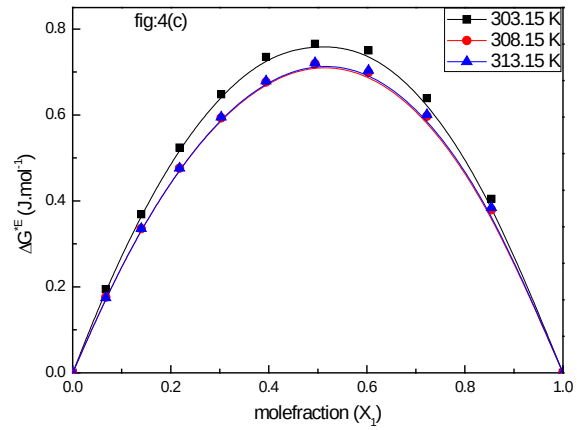


Figure 4: Variation of excess Gibb's function (ΔG^E) with mole fraction (x_1) in the binary liquid mixtures of 2-methylcyclohexanone with formamide(4.a),N-methylformamide(4.b) and N,N-Dimethylformamide(4.c) at 303.15 K (■), 308.15 K(●) and 313.15 K (▲).

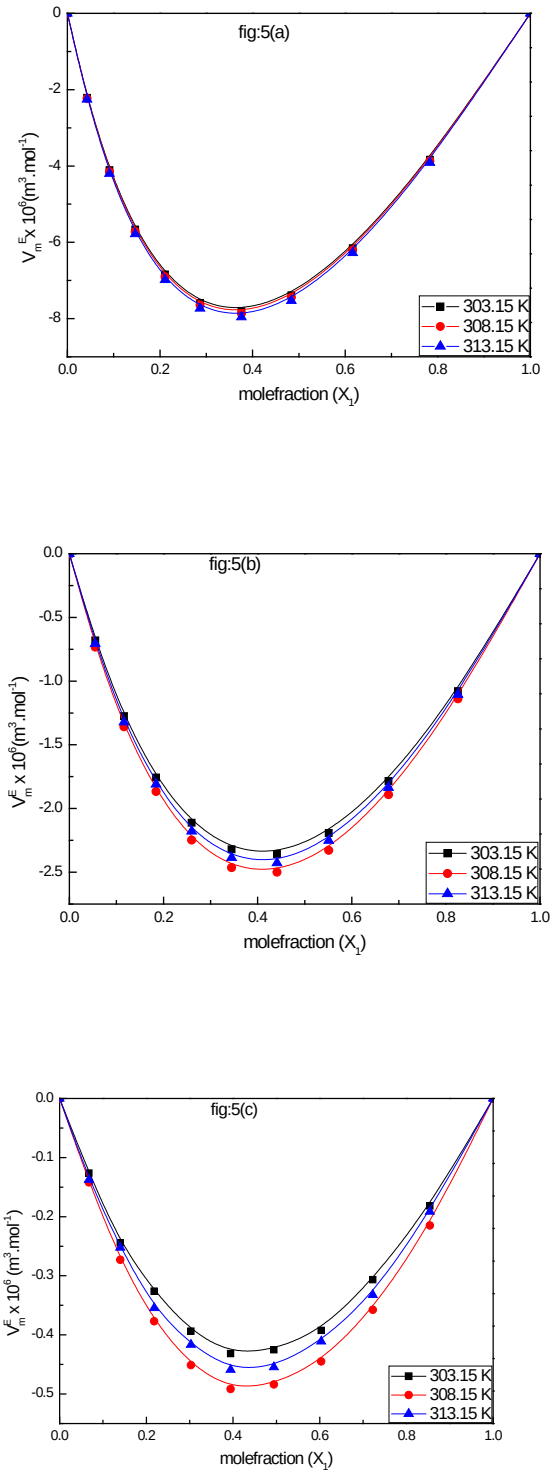


Figure 5: Variation of excess Molar volume (V_m^E) with mole fraction (x_1) in the binary liquid mixtures of 2-methylcyclohexanone with formamide(5.a),N-methylformamide(5.b) and N,N-Dimethylformamide(5.c) at 303.15 K (■), 308.15 K(●) and 313.15 K (▲).

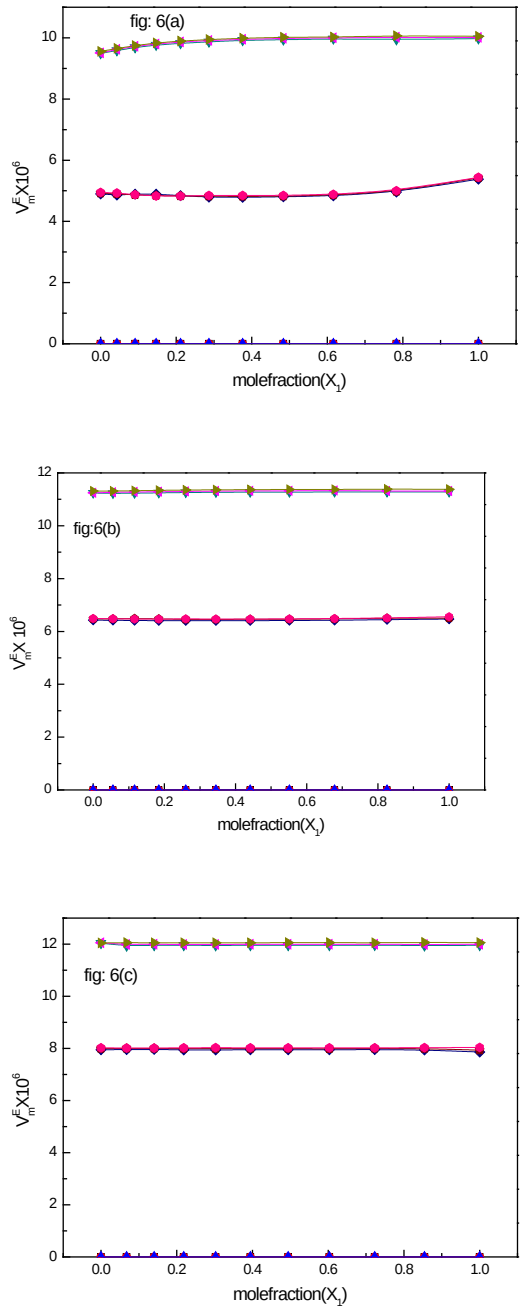


Figure 6: Variation of total molar volume(V_m), partial molar volume,($V_{m,1}$) and partial molar volume ($V_{m,2}$) with mole fraction (x_1) in the binary liquid mixtures of 2-methylcyclohexanone with formamide,N-Methylformamide and N,N-Dimethylformamide at 303.15 K (■), 308.15 K(●) and 313.15 K (▲).

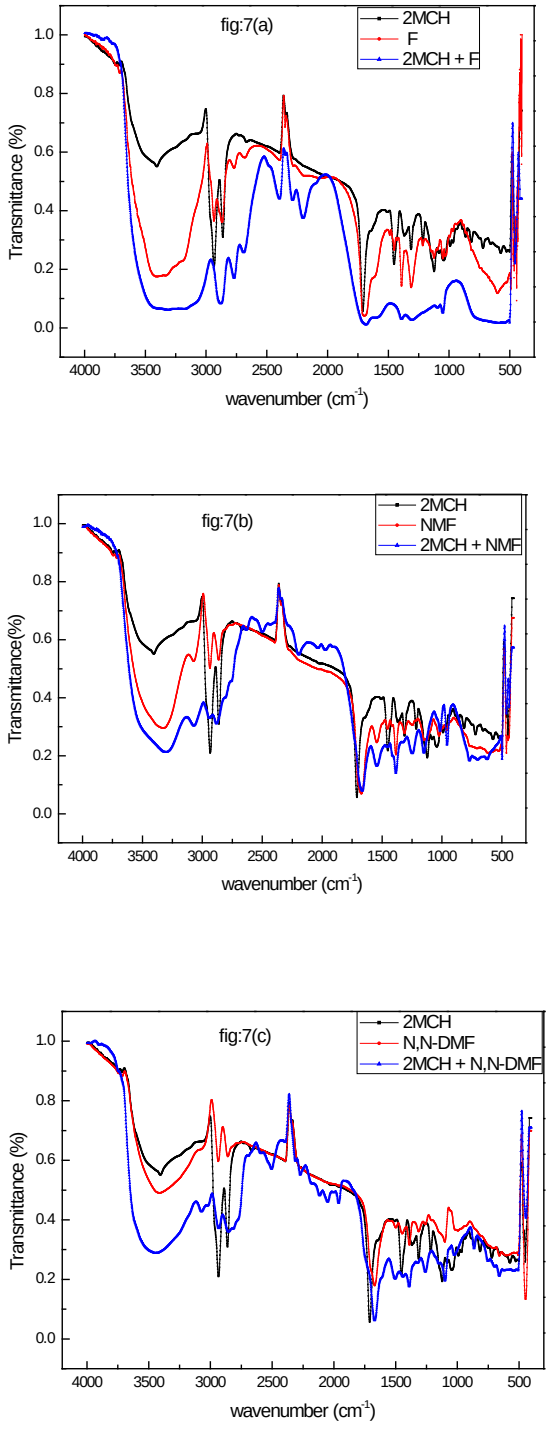


Figure 7: Fourier transform infrared spectra of pure 2-methylcyclohexanone with formamide(7.a),N-methylformamide(7.b) and N,N-Dimethylformamide(7.c).

From Fig. 2 it is clear that the excess values of enthalpy(H^E) are negative with respect to the mole fraction, x_1, over the entire composition range and at T= 303.15, 308.15, 313.15 K. The negative values of H^E insists on the fact that there are strong specific interactions between unlike molecules in these liquid mixtures[20]. The negative H^E values also suggest the existence of inter molecular hydrogen bond and the breaking of associated structures in case of aniline with formamide.

It can be observed from Fig. 3 that the L_f^E values have a negative it suggest that specific interactions are present between unlike molecules in these binary systems[21].

Fig.4 represents the excess Gibb's free energy of activation (ΔG^{*E}) with respect to mole fraction x_1, over the entire composition range and at T= 303.15, 308.15, 313.15 K. It can be seen from the above figure, that the negative values of ΔG^{*E} indicates there is more compact packing of the molecules which implies that the molecular interactions are strong whereas the positive values indicate a loose packing of molecules in the binary mixture compared to those in the pure component. Similar results were observed by earlier workers[22].

The variation of excess molar volume (V^E), with respect to mole fraction x_1, is given in Fig.5 over the entire composition range and at T= 303.15, 308.15, 313.15 K. The strength of the intermolecular interactions in binary liquid mixtures can be explained using the sign and magnitude of the V^E values. The negative values of V^E are due to strong specific interactions like the formation of hydrogen bonds, association through weaker physical forces and accommodation of one component molecules into the voids in the network of the other component molecules. so in the present study we observed that the behavior of V^E can be ascribed to the formation of hydrogen bond and the structural characteristics like geometrical fitting of one component into the other as a result of the increase in difference of size and shape of the component molecules. The negative values of V^E indicate that there is more compact packing of the molecules which implies that the molecular interactions are strong in these mixtures. Similar results were observed by earlier workers[23][24].

FT-IR spectra of pure 2MCH, amides, and binary mixtures of 2MCH with amides at equal concentrations are depicted in Figures 7(a, b and c).According to Karunakar and Srinivas[25], the intensity of an absorption in the IR spectrum is related to the change in dipole moment that occurs during the vibration. Consequently, vibrations that produce a large change in dipole moment result in a more intense absorption than those that result in a relatively modest change in dipole. Vibrations that do not result in a change in dipole moment will show little or no absorption for this vibration. In the present FT-IR spectra liquid mixture shows very large variations in the intensity of the respective bonds, that is, dipole moment, and hence it supports that strong interactions take place between the components of liquid molecules[26].

4. Conclusions

The values of excess isentropic compressibility (K_s^E), excess enthalpy (H^E),excess free length (L_f^E), excess molar volume (V^E)are found to be negative, excess Gibb's free energy (ΔG^{*E}) values changed from negative to positive for all the binary systems over the entire range of composition and at all temperatures considered in the present study. This is a clear indication for the presence of

hydrogen bonding between the component molecules. The strength of specific interactions between unlike molecules is decreasing with increase in the binary mixture (2-Methylcyclohexanone(2-MCH) with formamide(F), N-Methylformamide(N-MF) and N,N-Dimethylformamide(N,N-DMF).

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