

Excess Properties and Partial Molar Volume of Binary Mixtures of Amides with O-Chloroaniline

T.Kalimulla¹, Shaik. Babu^{1,*}

¹Department of Physics, K L University, Vaddeswaram, Guntur, Andhra Pradesh, India.

Corresponding author

Abstract

Excess molar volume (V^E), excess isentropic compressibility (K_s^E), excess enthalpy (H^E), excess frelength (L_f^E) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) for binary mixtures of O-chloroaniline (O-CA) with Formamide (F), N-Methylformamide (NMF) and N,N-Dimethylformamide (N,N-DMF) at selected compositions were determined from the measured values of densities, speeds of sound, and viscosities of pure components and their mixtures at 303.15- 318.15 K at ambient atmospheric pressure. The excess molar volumes, excess isentropic compressibility, excess enthalpy, excess free length and excess Gibbs energy of activation of viscous flow have been analyzed in terms of interactions arising due to structural effect, charge-transfer complexes and dipole-dipole interaction between unlike molecules. The excess parameters 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. The partial and excess partial molar volumes for each component at infinite dilution have been appraised and reported.

Keywords: Speed of sound, viscosity, density, excess parameters, polynomial equation, partial and excess partial molar volumes.

1. INTRODUCTION

The density (ρ) dynamic viscosity (η) and speed of sound (U) of binary or ternary liquids are indispensable in most fluid mechanics, solution theory, molecular thermodynamics, and various methodical uses.¹⁻³ These values carry a significant role to elucidate the behavior of liquids and their mixtures.⁴⁻¹⁰ The analysis of excess functions and deviations from ideality is essential to interpret the interactions in the mixing process. Therefore, the assessment and forecast of these mixtures as functions of temperature and composition are of noticeable importance. Researchers are highly devoted to discovering the real causes of possible interaction of organic molecules in binary mixtures using physical property data.¹¹ We display ρ and η values in the pure state and for their binary systems of O-chloroaniline (O-CA) with amides, formamide (F), N-methylformamide (NMF), and N,N-dimethylformamide (N,N-DMF) at $T = (303.15 \text{ to } 318.15) \text{ K}$ and atmospheric pressure over the entire range of composition. The experimental ρ , η and U data are used to calculate the excess molar volume (V^E), excess isentropic compressibility (K_s^E), excess enthalpy (H^E),

excess frelength (L_f^E) and excess Gibb's free energy of activation of viscous flow (ΔG^{*E}). The Redlich-Kister equation¹² is used to fit the excess values in order to obtain the binary coefficients and standard deviation. All liquids are used for laboratory and industrial purposes. Here, the O-chloroaniline liquid (O-CA) has been considered as component 1, while the other amides liquids F, NMF, and N,N-DMF have been considered as component 2. Beckett et al.¹³ This work is part of our program to give information/data for the characterization of molecular interactions between solvents in binary systems.¹⁴ The liquids were chosen for the present study on the basis of their medical and Industrial importance. O-Chloroaniline is Intermediate for rubber chemicals, pigments, pesticides and dyes. On the other hand, Formamide is an amide derived from formic acid. it is used as a feedstock in the manufacture of formate esters, as an ionizing solvent, as an RNA stabilizer in gel electrophoresis, and in tissue preservation. More intriguingly, it may be a key compound in the origin of life on Earth. N-Methylformamide (NMF) is closely related to other formamides, not ably formamide and dimethylformamide (DMF). However, industrial use and production of NMF are far less than for either of these other formamides. DMF is favored over NMF as a solvent due to its greater stability. NMF is mainly used as a reagent in various organic syntheses with limited applications as a highly polar solvent. N,N-Dimethylformamide (DMF) Dimethylformamide is odorless whereas technical grade or degraded samples often have a fishy smell due to impurity of dimethylamine. Dimethylamine degradation impurities can be removed by sparging degraded samples with an inert gas such as argon or by sonicating the samples under reduced pressure. As its name indicates, it is a derivative of formamide, the amide of formic acid. DMF is a polar (hydrophilic) aprotic solvent with a high boiling point. It facilitates reactions that follow polar mechanisms, such as S_N2 reactions. In the present study, our focus is on the study of liquid mixtures of substituted amides with O-Chloroaniline because there have been a few studies on these mixtures.^{15,16} It is expected that there will be a significant degree of H-bonding in these binary mixtures we report the densities, speeds of sound and viscosities for three binary systems (O-Chloroaniline with Formamide, N-Methylformamide and N,N-Dimethylformamide) at $T = (303.15\text{--}318.15) \text{ K}$ ambient atmospheric pressure. The experimental data has been used to compute the excess parameters, partial molar volumes and FTIR studies. The results are used to qualitatively discuss specific interactions between unlike molecules.

2. MATERIALS AND METHODS

Chemicals used in the present study are O-Chloroaniline (Sigma–Aldrich), Formamide, N-Methylformamide and N,N-Dimethylformamide (Sigma–Aldrich). These chemicals were purchased from Hi Media Laboratories Pvt. Ltd. Mumbai. These chemicals were further purified by standard methods^{17, 18} like distillation and fractional distillation under reduced pressure, and only the middle fractions were collected. Before use, the chemicals were stored over 0.4 nm molecular sieves for about 72 h to remove water and gas. The purity of the liquid samples was checked by gas chromatography. The water contents were determined by the Karl–Fischer method. The details of the chemicals and purification methods are presented in Table 1. 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 to 318.15 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 distilled 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 ρ , η and U for the liquid mixtures of O-Chloroaniline with Formamide, N-Methylformamide and N,N-Dimethylformamide at 303.15-318.15 K over the entire composition range are given in Table 2.¹⁹⁻²³ The experimentally determined values of ρ , η and U , 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,²³ and Douheret et al.²⁴

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

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

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

$$V^E = \frac{X_1 M_1 + X_2 M_2}{\rho} - \left(\frac{X_1 M_1}{\rho_1} + \frac{X_2 M_2}{\rho_2} \right) \quad (3)$$

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.

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

$$L_f^E = L_f - K_T (K_s^{id})^{1/2} \quad (4)$$

Where L_f represents the calculated value for the mixture and K_T represent a temperature dependent constant whose value is $K_T = (91.368 + 0.3565T) \times 10^{-8}$.

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

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

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 .

Excess enthalpy H^E was calculated from usual relation,

$$H^E = H - (X_1 H_1 + X_2 H_2) \quad (6)$$

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 conventional smooth curve fitting strategy for excess properties of binary mixture involves Redlich-Kister¹⁶ polynomial non-linear regression,

$$Y^E = X_1(1-X_1) \sum_{i=1}^n A_i (2x_1 - 1) \quad (7)$$

Where $Y^E = K_s^E, V^E, \Delta G^{*E}, H^E$. The values of coefficient A_i were determined by a regression analysis based on the least-squares method.

The standard deviation (σ) was calculated using the relation,

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

Where n represents the number of experimental points and m is the number of adjustable parameters.

4. RESULTS AND DISCUSSIONS

Figures 1–5 show the dependence of K_s^E , V^E , L_r^E , ΔG^{*E} and H^E on composition. The values of K_s^E , V^E and L_r^E are negative for all the systems over the entire mole fraction range

and their magnitude decreases with rise in temperature from 303.15-318.15 K. The deviations observed in the excess parameters indicate the strength of interactions present between the component molecules of the binary mixtures under study.²⁵

Table 01: Purity analysis

Chemical Name	Source	Initial mole fraction	Purification method	Final mole fraction	Analysis method
O-Chloroaniline	Hi Media Labs Pvt. Ltd. Mumbai, India.	0.99	Distillation	0.997	Gas liquid chromatography
Formamide		0.99	Distillation	0.998	
NMF		0.99	Distillation	0.998	
DMF		0.99	Distillation	0.998	

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

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	α K K ⁻¹
		expt	Lit	expt	Lit	expt	Lit		
O-Chloroaniline	303.15	1.2026	1.2026 ^a	3.8257	3.8256 ^a	1469.5	1469.6 ^a	131.6 ^a	---
	308.15	1.9801	1.1980 ^a	3.4123	3.4122 ^a	1453.4	1453.3 ^a	133.8 ^a	---
	313.15	1.1930	1.1930 ^a	3.0606	3.0602 ^a	1435.3	1435.2 ^a	136.0 ^a	---
	318.15	1.1884	1.1884 ^a	2.7622	2.7621 ^a	1418.8	1418.9 ^a	138.2 ^a	---
Formamide	303.15	1.1238	1.1237 ^b	2.8018	2.8018 ^b	1585.4	1585.4 ^c	107.11 ^e	0.9967 ^f
	308.15	1.1195	1.1194 ^b	2.4980	2.4980 ^b	1580.5	1580.6 ^c	105.20 ^e	0.9961 ^f
	313.15	1.1155	1.1154 ^b	2.2435	2.2435 ^b	1572.0	1572.0 ^c	108.56 ^e	0.9998 ^f
	318.15	1.1116	1.1115 ^b	2.0324	2.0324 ^b	1561.8	---	---	---
NMF	303.15	0.9947	0.9946 ^b	1.5860	1.5859 ^b	1408.6	1408.5 ^c	124.95 ^e	0.9967 ^f
	308.15	0.9904	0.9903 ^b	1.4628	1.4627 ^b	1398.3	1400.6 ^c	126.05 ^e	0.9961 ^f
	313.15	0.9862	0.9861 ^b	1.3521	1.3520 ^b	1382.6	1382.5 ^c	129.47 ^e	0.9998 ^f
	318.15	0.9821	0.9820 ^b	1.2557	1.2557 ^b	1363.2	---	---	---
DMF	303.15	0.9388	0.9386 ^b	0.7532	0.7485 ^b	1467.2	1469.8 ^d	152.00 ^e	0.9967 ^f
	308.15	0.9346	0.9344 ^b	0.7164	0.7063 ^b	1433.4	1433.2 ^d	153.02 ^e	0.9961 ^f
	313.15	0.9294	0.9296 ^b	0.6833	0.6683 ^b	1418.6	1418.0 ^d	157.14 ^e	0.9998 ^f
	318.15	0.9252	0.9251 ^b	0.6475	0.6461 ^b	1402.4	---	---	---

a D.Ubagaramary et al. [19], b Shamim Akhtar et al. [20], c Puneet kumar pandey et al. [21], d Balaji et al.[22], e Reference[23], f Derive from density data.

Table 03: Parameters (A_i) and Standard Deviation (σ) for O-Chloroaniline with Amides at different temperatures.

Parameter	Temperature (K)	A0	A1	A2	A3	σ
O-CA + Formamide						
$10^{12}K_S^E/(m^2.N^{-1})$	303.15	-0.3133	0.1512	-0.0853	0.0668	0.0002
	308.15	-0.3795	0.1858	-0.1045	0.0763	0.0001
	313.15	-0.4476	0.2200	-0.1248	0.0916	0.0002
	318.15	-0.5020	0.2456	-0.1415	0.1096	0.0003
$10^6 V^E/(m^3.mol^{-1})$	303.15	-3.7157	3.4921	-4.6068	6.9701	0.0378
	308.15	-3.8061	3.4225	-4.7930	7.4238	0.0444
	313.15	-3.8576	3.3255	-5.0223	7.8749	0.0476
	318.15	-3.8921	3.3244	-5.1989	8.1501	0.0511
$10^{13}L_f^E/(m)$	303.15	-4.0061	1.9049	-1.0517	0.8093	0.0030
	308.15	-4.8418	2.3316	-1.2780	0.9108	0.0021
	313.15	-5.6887	2.7437	-1.5124	1.0795	0.0025
	318.15	-6.2994	3.0194	-1.6866	1.2707	0.0043
$\Delta G^E/(J.mol^{-1})$	303.15	14.2065	-3.3417	2.6200	5.4712	0.0585
	308.15	14.7732	-3.2083	2.7093	4.1389	0.0500
	313.15	15.1509	-2.7335	3.3719	2.5511	0.0500
	318.15	15.5848	-2.6875	4.3836	1.4598	0.0216
$H^E/(J.mol^{-1})$	303.15	-0.0128	0.0094	0.0123	0.0246	0.0002
	308.15	-0.0138	0.0018	-0.0025	0.0009	0.0000
	313.15	-0.0135	0.0018	-0.0025	0.0009	0.0000
	318.15	-0.0132	0.0018	-0.0025	0.0009	0.0000
O-CA + NMF						
$10^{12}K_S^E/(m^2.N^{-1})$	303.15	-1.3029	-0.6720	-0.4157	-0.3273	0.0008
	308.15	-1.2959	-0.6688	-0.4134	-0.3244	0.0009
	313.15	-1.3204	-0.6810	-0.4223	-0.3289	0.0008
	318.15	-1.3917	-0.7149	-0.4433	-0.3561	0.0009
$10^6 V^E/(m^3.mol^{-1})$	303.15	-28.0670	-12.7782	-9.6301	-7.9323	0.0888
	308.15	-29.1815	-12.7131	-7.6458	-12.3528	0.1182
	313.15	-30.0700	-11.1655	-7.1747	-18.5958	0.1234
	318.15	-30.6786	-10.8467	-8.3033	-21.5055	0.1540

$10^{13}L_r^E/(\text{m})$	303.15	-14.7130	-7.2906	-4.2495	-3.1316	0.0078
	308.15	-14.6331	-7.2655	-4.2378	-3.1126	0.0085
	313.15	-14.8546	-7.3705	-4.3195	-3.1477	0.0072
	318.15	-15.4124	-7.6075	-4.4504	-3.3627	0.0078
$\Delta G^E/(\text{J.mol}^{-1})$	303.15	3.5694	0.3146	0.2514	0.2589	0.0198
	308.15	3.4900	0.3199	0.0956	0.2751	0.0195
	313.15	3.4079	0.3259	0.0744	0.1150	0.0197
	318.15	3.3415	0.4020	0.0701	-0.3895	0.0186
$H^E/(\text{J.mol}^{-1})$	303.15	0.0235	0.0142	0.0109	0.0109	0.0000
	308.15	0.0217	0.0131	0.0099	0.0099	0.0000
	313.15	0.0201	0.0121	0.0091	0.0090	0.0000
	318.15	0.0185	0.0113	0.0084	0.0082	0.0000
O-CA + N,N-DMF						
$10^{12}K_S^E/(\text{m}^2.\text{N}^{-1})$	303.15	-1.0332	0.4766	-0.2584	-0.1551	0.0004
	308.15	-1.1841	0.5500	-0.2923	-0.1726	0.0004
	313.15	-1.2039	-0.5708	-0.2816	-0.1110	0.0008
	318.15	-1.2421	-0.5763	-0.3094	-0.1823	0.0004
$10^6 V^E/(\text{m}^3.\text{mol}^{-1})$	303.15	-8.7746	-6.5887	-3.8719	4.6855	0.0420
	308.15	-9.2175	-6.5312	-3.8492	3.4361	0.0459
	313.15	-9.6347	-6.7112	-3.4137	2.7014	0.0275
	318.15	-10.1505	-6.4014	-3.2470	0.3000	0.0406
$10^{13}L_r^E/(\text{m})$	303.15	-11.6676	-5.1256	-2.6209	-1.4821	0.0036
	308.15	-13.1673	-5.8010	-2.8810	-1.5898	0.0039
	313.15	-13.3412	-6.0115	-2.7468	-0.8872	0.0100
	318.15	-13.5812	-5.9774	-3.0062	-1.6534	0.0041
$\Delta G^E/(\text{J.mol}^{-1})$	303.15	-1.4197	-1.4882	-0.9023	-0.5182	0.0012
	308.15	-1.2181	-1.4460	-0.8584	-0.4837	0.0011
	313.15	-1.3185	-1.4782	-0.9302	-0.6555	0.0040
	318.15	-1.2923	-1.4543	-0.8741	-0.4867	0.0012
$H^E/(\text{J.mol}^{-1})$	303.15	0.0424	0.0234	0.0200	0.0211	0.0001
	308.15	0.0384	0.0215	0.0174	0.0166	0.0000
	313.15	0.0358	0.0200	0.0158	0.0149	0.0000
	318.15	0.0336	0.0188	0.0146	0.0134	0.0000

Figures 1a, b and c show the excess isentropic compressibility K_s^E for the binary liquid mixtures of O-Chloroaniline with Formamide, N-Methylformamide and N,N-Dimethylformamide, respectively, over the entire mole fraction range and at different temperatures $T = (303.15-318.15)$ K. The excess isentropic compressibility (K_s^E) graphically presented in 1a, b and c. The excess isentropic compressibility has positive values for all studied systems over the whole composition range and become more positive with increasing temperature for all three binary mixtures. The observed values of excess isentropic compressibility (K_s^E) can be qualitatively explained by considering the following factors:

- (i) Disruption of associated structure/molecular order in the pure liquids,
- (ii) The formation of weak bonds dipole-induced-dipole interaction between unlike molecules and
- (iii) Free volume changes from mixing of components of different sizes.

It is clear from Fig. 1a, b and c that the K_s^E values are negative over the entire mole fraction range for the systems under study and at investigated temperatures, this indicates the presence of strong interactions in these mixtures. As the temperature increases, it has been observed that the negative K_s^E values are found to increase in the systems, and the changes in K_s^E values with respect to temperature are small in these mixtures. Also with the increase in temperature, the solute solvent interactions get weaker causing the excess values to decrease at higher temperature. The negative values of K_s^E are of the order (2MCH + F, NMF and N,N-DMF). The sign of excess isentropic compressibility plays a relevant 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, 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 hydrogen bond, 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 Fort and Moore.²⁶ The V^E data for all the binary systems of O-Chloroaniline with Formamide, N-Methylformamide and N,N-Dimethylformamide graphically represented in Figs. 2 a, b and c. These figures suggest that excess volume (V^E) data for the mixtures O-Chloroaniline with Formamide, N-Methylformamide and N,N-Dimethylformamide are negative over the entire composition range at all temperatures. The experimental V^E values can be ascribed qualitatively by considering the factors which influence the excess functions, and these functions depend upon several contributions arising from physical, chemical and structural effects.^{27, 28} The

physical contributions comprising of dispersive forces or weak dipole-dipole interactions lead to positive V^E values. Chemical contributions include breaking up of associates present in pure liquids resulting in positive V^E and specific interactions, like formation of strong hydrogen bonds, charge-transfer complexes and other complex forming interactions including strong dipole-dipole interactions between component molecules, resulting in negative V^E values. The structural contributions include the geometrical fitting of molecules of different molecular sizes into each other's²⁹ yielding negative V^E values. It can be observed from Fig. 3a, b and c that the L_f^E values have a negative trend similar to what we have observed in case of the K_s^E at all the temperatures under study. The negative values of L_f^E suggest that specific interactions are present between unlike molecules in these binary systems.³⁰

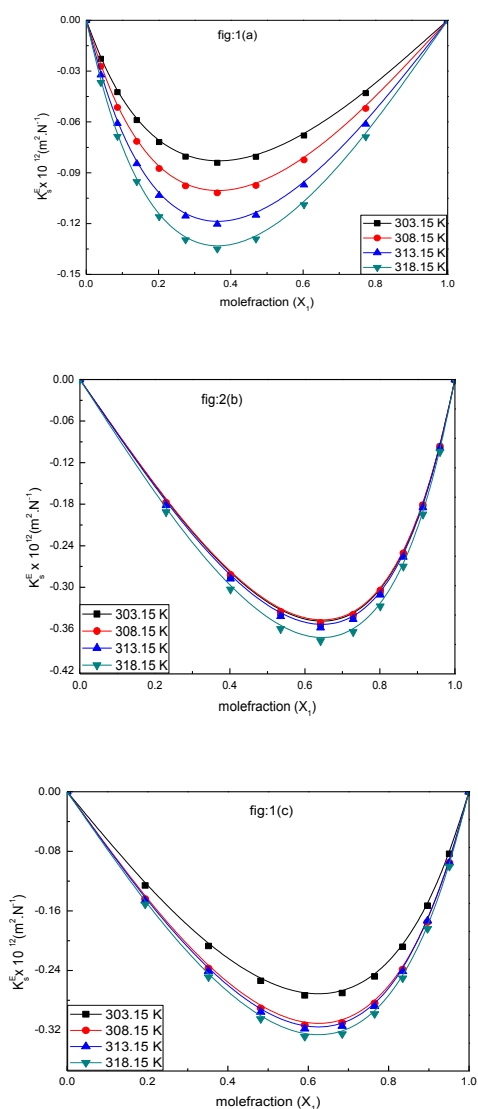


Figure 1: Variation of excess isentropic compressibility (K_s^E) with mole fraction (x_1) in the binary liquid mixtures of O-Chloroaniline with formamide(1.a), N-methylformamide (1.b) and N,N-Dimethylformamide(1.c) at different temperatures.

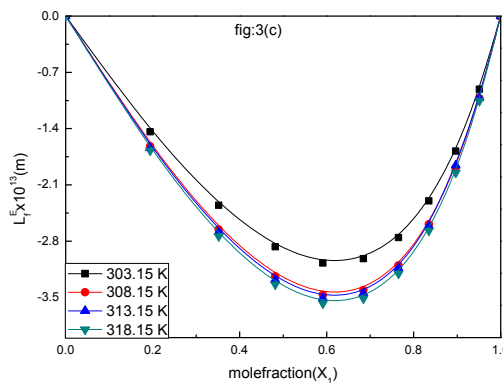
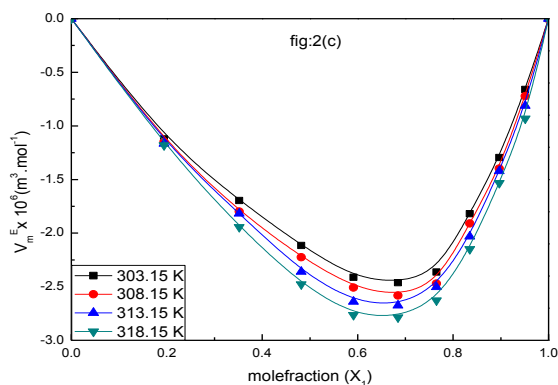
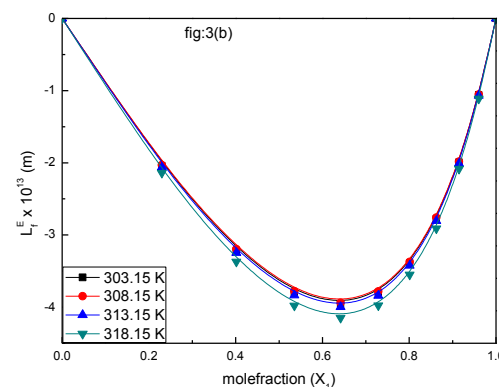
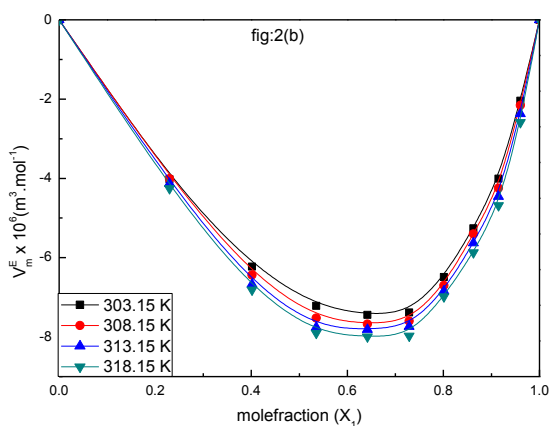
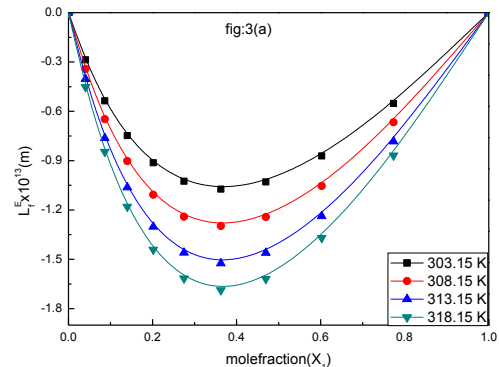
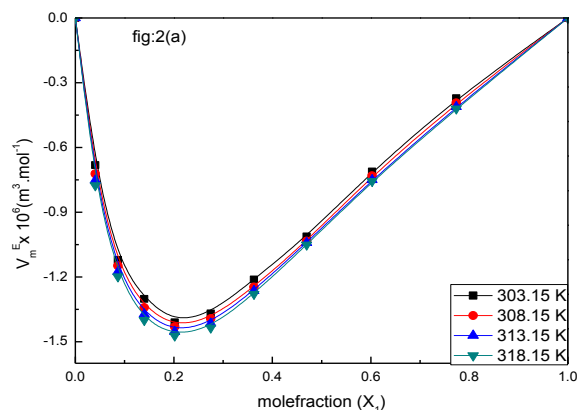


Figure 2: Variation of excess molar volume (V_m^E) with mole fraction (x_1) in the binary liquid mixtures of O-Chloroaniline with formamide(2.a),N-methylformamide(2.b) and N,N-Dimethylformamide(2.c) at different temperatures.

Figure 3: Variation of excess Free length (L_f^E) with mole fraction (x_1) in the binary liquid mixtures of O-Chloroaniline with formamide(3.a),NMF(3.b) and N,N-DMF(3.c) at different temperatures.

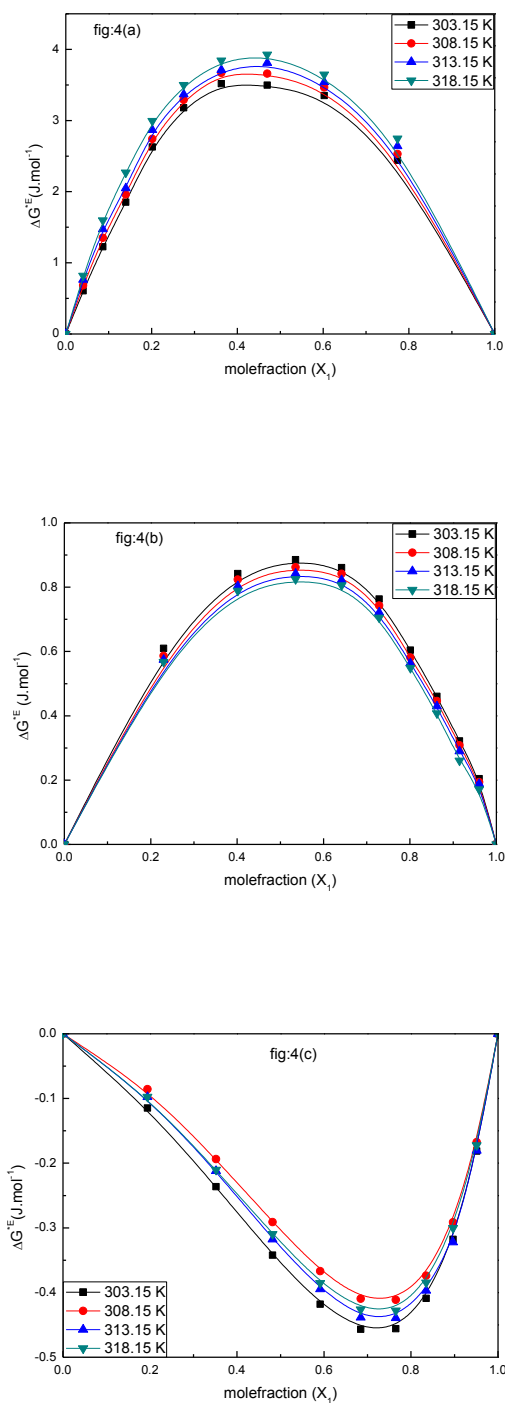


Figure 4: Variation of excess Gibbs's function (ΔG^{*E}) with mole fraction (x_1) in the binary liquid mixtures of O-Chloroaniline with formamide(4.a),N-methylformamide(4.b) and N,N-Dimethylformamide(4.c) at different temperatures.

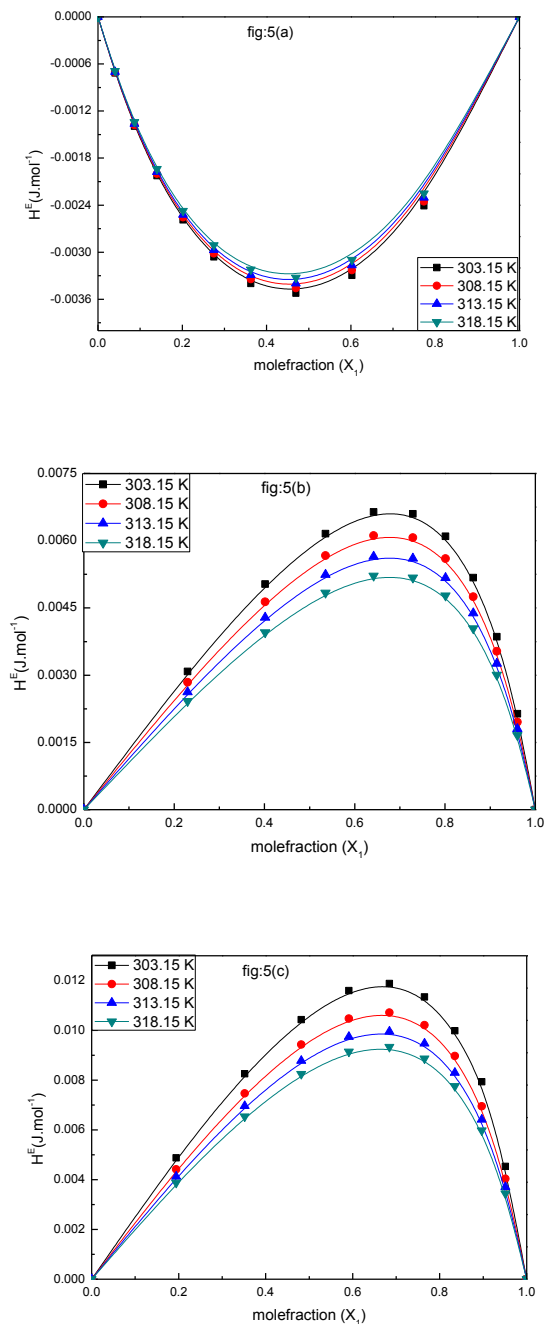


Figure 5: Variation of excess Enthalpy (H^E) with mole fraction (x_1) in the binary liquid mixtures of O-Chloroaniline with formamide(5.a),N-methylformamide(5.b) and N,N-Dimethylformamide(5.c) at different temperatures.

Figure 4a, b and c represent the excess Gibbs's free energy of activation (ΔG^{*E}) with respect to mole fraction x_1 , over the entire composition range and at $T = (303.15-318.15)$ K. It can be seen from Fig. 4a and b that the ΔG^{*E} values are positive and Fig. 4c negative at all temperatures and over the entire range of mole fraction. These positive values indicate the existence of strong intermolecular interaction through hydrogen bonding between the component molecules of the

liquid mixtures under study and negative values indicate weak inter molecular interaction. The maximum deviation is observed in the system indicating the strength of bond formation. Similar results were observed by earlier workers.³¹

From Fig. 5a the excess values of enthalpy (H^E) are negative and from Fig. 4b and c positive with respect to the mole fraction x_1 , over the entire composition range and at $T = (303.15-318.15)$ K. The negative values of H^E tend to decrease with increase in temperature, this insist the fact that there are strong specific interactions between unlike molecules and positive values indicate weak intermolecular interaction in these liquid mixtures. The positive H^E values suggest that Non-existence of inter molecular hydrogen bond. The variations in these above excess parameters with mole fraction x_1 and temperature predict the presence of hydrogen bonding between the compounds in both the binary mixtures. The excess parameters calculated in the present study correlate with one another and at the same time each parameter supports the formation of hydrogen bonding in these binary liquid mixtures. The existing molecular interactions in the systems are well reflected in the properties of partial molar volumes. The partial molar volumes $\bar{V}_{m,1}$ of component 1 and $\bar{V}_{m,2}$ of component 2 in the mixtures over the entire composition range have been calculated by using the following relations:

$$\bar{V}_{m,1} = V_m^E + V_1^* + x_2 \left(\frac{\partial V_m^E}{\partial x} \right)_{T,P} \quad (9)$$

$$\bar{V}_{m,2} = V_m^E + V_2^* + x_1 \left(\frac{\partial V_m^E}{\partial x} \right)_{T,P}$$

where V_1^* and V_2^* are the molar volumes of the pure components of (O-Chloroaniline with Formamide, N-Methylformamide and N, N-Dimethylformamide) respectively. The derivates in the above equations are obtained by differentiating Redlich-Kister equation (7) which leads to the following equations for $\bar{V}_{m,1}$ and $\bar{V}_{m,2}$:

$$\bar{V}_{m,1} = V_1^* + X_2^2 \sum_{i=0}^j A_i (x_2 - x_1)^i - 2 x_1 X_2^2 \sum_{i=1}^j A_i (x_2 - x_1)^{i-1} \quad (10)$$

$$\bar{V}_{m,2} = V_2^* + X_1^2 \sum_{i=0}^j A_i (x_2 - x_1)^i - 2 x_2 X_1^2 \sum_{i=1}^j A_i (x_2 - x_1)^{i-1} \quad (11)$$

using the above equations $\bar{V}_{m,1}^E$, $\bar{V}_{m,2}^E$ have been calculated.

$$\bar{V}_{m,1}^E = \bar{V}_{m,1} - V_1^* \quad (12)$$

$$\bar{V}_{m,2}^E = \bar{V}_{m,2} - V_2^*$$

The pertinent values of $\bar{V}_{m,1}$ and $\bar{V}_{m,2}$ for both the components in the mixtures are less than their respective molar volumes in the pure state; that is, an expansion of volume takes place on mixing 2methylcyclohexanone with amides. These results also support the observed negative values of V_m^E in all the binary systems. Examination data reveals that attractive forces exist between the unlike molecules. These results support the conclusions drawn from V_m^E . The partial molar volumes and excess partial molar volumes of 2MCH and amines in all the binary liquid

mixtures at infinite dilution, $\bar{V}_{m,1}^\infty$, $\bar{V}_{m,2}^\infty$, $\bar{V}_{m,1}^{E,\infty}$, and $\bar{V}_{m,2}^{E,\infty}$, respectively, were obtained by putting $x = 0$ in (10) and $x = 1$ in (11). Consider,

$$\bar{V}_{m,1}^{E,\infty} = A_0 + A_1 + A_2 + A_3 + \dots = \bar{V}_{m,1}^\infty - V_1^* \quad (13)$$

$$\bar{V}_{m,2}^{E,\infty} = A_0 - A_1 + A_2 - A_3 + \dots = \bar{V}_{m,2}^\infty - V_2^*$$

The pertinent values of $\bar{V}_{m,1}^\infty$, $\bar{V}_{m,2}^\infty$, $\bar{V}_{m,1}^{E,\infty}$, and $\bar{V}_{m,2}^{E,\infty}$ are reported in Table 4. From this table it is seen that these values are positive and negative, from which we conclude that strong interactions exist among the unlike molecules of the liquid mixtures.³²

Table 04: Values of partial molar volume of the components at infinite dilution ($V_{m,1}^\infty$, $V_{m,2}^\infty$) and excess partial molar volume at infinite dilution ($V_{m,1}^{E,\infty}$ and $V_{m,2}^{E,\infty}$) for all the systems at three different temperatures.

System	Temperature	$V_{m,1}^\infty \times 10^{-5}$	$V_{m,2}^\infty \times 10^{-5}$	$V_{m,1}^{E,\infty} \times 10^{-5}$	$V_{m,2}^{E,\infty} \times 10^{-5}$
O-Chloroaniline +Formamide	303.15 K	9.9751	4.8994	-0.5903	-5.6660
	308.15 K	1.0012	4.9213	-0.5940	-5.6847
	313.15 K	1.0049	4.9456	-0.6015	-5.7049
	318.15 K	1.0049	4.9456	-0.6426	-5.7460
O-Chloroaniline +NMF	303.15 K	1.1281	6.4248	0.7155	-4.1406
	308.15 K	1.1328	6.4777	0.7219	-4.1283
	313.15 K	1.1377	6.4884	0.7265	-4.1620
	318.15 K	1.0049	4.9456	-0.6426	-5.7460
O-Chloroaniline +N,N-DMF	303.15 K	1.1956	7.9480	1.3905	-2.6174
	308.15 K	1.2056	8.0231	1.4499	-2.5829
	313.15 K	6.6319	2.2809	-4.0185	12.1585
	318.15 K	1.0049	4.9456	-0.6426	-5.7460

5. CONCLUSION

Ultrasonic speeds(U), viscosities (η) and densities(ρ) of formamide (F), N-methylformamide (NMF) and N,Ndimethylformamide (DMF) at different temperatures over the entire composition range have been measured. Examination of Table 2 shows that the speed of sound(U), density (ρ) and viscosity (η) of the pure amides follow the order at 303.15 K, F ($\rho = 1.1237 \text{ g} \cdot \text{cm}^{-3}$) > NMF ($\rho = 0.9946 \text{ g} \cdot \text{cm}^{-3}$) > DMF ($\rho = 0.9386 \text{ g} \cdot \text{cm}^{-3}$) and η of the pure amides follow the order at 303.15 K, F ($\eta = 2.8018 \text{ mp.s}$) > NMF ($\eta = 1.5859 \text{ mp.s}$) > DMF ($\eta = 0.7485 \text{ mp.s}$). The physical data suggest that F is extensively associated through H-bonding. NMF is also associated through H-bonding, but much less extensively, as can be understood by the existence of only one aminic hydrogen capable of H-bond formation and by the steric effect. Unlike these two amides, DMF is associated through weak physical forces, such as, dipole- dipole and dipole-induced dipole interactions. The deviation/excess properties have been fitted

to Redlich-Kister type polynomial and the corresponding standard deviations have been calculated. The calculated values of partial molar volumes have also been examined. The observed low partial molar volumes in the liquid mixture when compared to the respective molar volumes of pure components indicate strong interactions present in the systems.

REFERENCES

- [1] Rolwinson, F.; Swinton, J. *Butterworth Sci. London*. **1982**
- [2] Reichardt, C. *Solvents Solvent Eff. Org. Chem.* **2003**, 3, 329–388
- [3] Pistoia, A.; Elsevier, G. Ed. *New Mater. Perspectives*. **1994**, 137–165
- [4] Habibulla, H.; Das, M.; Rahman, K.N.; Uddin, I.M.; Saifuddin, M.A.; Iwakabe, K.; Hasegawa, K. *J. Chem. Eng. Data*. **2010**, 55, 5370–5374
- [5] Sharma, M.; Thakkar, S.; Patel, K.; Makavana, P. *Adv. Phys. Chem.* **2013**, 1–12
- [6] Aktar, M.S.; Rahaman, S.; Hossain, M. A.; Hossain, M. K.; Akhtar, S. *Eur. Sci. J.* **2015**, 11, 213–225
- [7] Al-Jimaz, A.-H.M.; Al-Kandary, A. S.; Abdul-Latif, J. A. *Fluid Phase Equilib.* **2004**, 218, 247–260
- [8] Kabir-ud-Din, P.; Koya, A. *J. Chem. Eng. Data*. **2010**, 55, 1921–1929
- [9] Kabir-ud-Din, P.; Ajmal Koya. *Langmuir*. **2010**, 26, 7905–7914
- [10] Sarkar, P.; Lam, B.; Alexandridis, S.; *Langmuir*. **2010**, 26, 10532–10540
- [11] Hossain, M.S.; Akhtar, S.; Verpoort, F. *J. Chem. Eng. Data*. **2018**, 63, 1885–1895
- [12] Redlich, O.; Kister, A.T. *Ind. Eng. Chem.* **1948**
- [13] Beckett, R.; Pitzer, C. W.; Spitzer, K. S. **1947**, 69, 2488–2495
- [14] Gowrisankar, K.; Venkatesulu, M.; Srinivasa Krishna, A.; Ravindhranath, T. *J. Chem. Thermodyn.* **2017**, 107, 104–1
- [15] Yadav Dimple, V.K.; Singh, J.S.; Sharma, K.C. *J. Chem. Eng. Data*. **2009**, 54–2
- [16] Saini, V.K.; Yadav, N.; Sunil, J.S.; Sharma, K.J.; Sharma, D. *J. Chem. Thermodyn.* **2011**, 43, 782–79
- [17] Vogel, A.L. *Text Book of Practical Organic Chemistry*. **1989**
- [18] Riddick, T.K.; Bunger, J.A.; Sakano, W.B.; *Organic Solvents*. **1986**
- [19] Ubagaramary, D.; Enoch, I.V.M.V.; Gowrisankar, M.; Mullainathan, S. *Russ. J. Phys. Chem. A*. **2018**, 92, 2665–2678
- [20] Akhtar, S.; Faruk, A.N.M.O.; Saleh, M.A. *Phys. Chem. Liq.* **2001**, 39, 383–399
- [21] Pandey, P.K.; Awasthi, A. *J. Mol. Liq.* **2013**, 187, 343–349
- [22] Balaji, R.; Gowri Sankar, M.; Chandra Shekar, M. *J. Mol. Liq.* **2016**, 216, 330–341
- [23] Kiyohara, O.; Benson, G. *J. Chem. Thermodyn.* **1979**
- [24] Douhéret, G.; Pal, A.; Davis, M.I. *J. Chem. Thermodyn.* **1990**
- [25] Kinart, A.C. C.M.; Klimczak, M. *J. Mol. Liq.* **2010**, 155, 127–133
- [26] M.W.; Fort, R.J. *Trans Faraday Soc.* **1965**, 61, 2102–10
- [27] García, B.; Aparicio, S.; Navarro, A.M.; Alcalde, R.; Leal J.M. *J. Phys. Chem. B*. **2004**
- [28] Iloukhani, H.; Zoorasna, N.; Soleimani, R. *Phys. Chem. Liq.* **2005**
- [29] Awasthi, A.; Rastogi, M.; Shukla, J.P. *Fluid Phase Equilib.* **2004**, 215, 119–127
- [30] Sastry, S.S.; Babu, S.; Vishwam, T.; Tiong, H.S. *J. Therm. Anal. Calorim.* **2014**, 116, 923–935
- [31] Sastry, S.V.K.; Babu, S.; Sietiong, H.; Sastry, S.S. *J. Chem. Pharm. Res.* **2012**, 4, 2122–2125
- [32] Nayeem, S.; Kondaiah, M.; Sreekanth, K. Rao, D.K. *J. Appl. Chem.* **2014**.