

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.

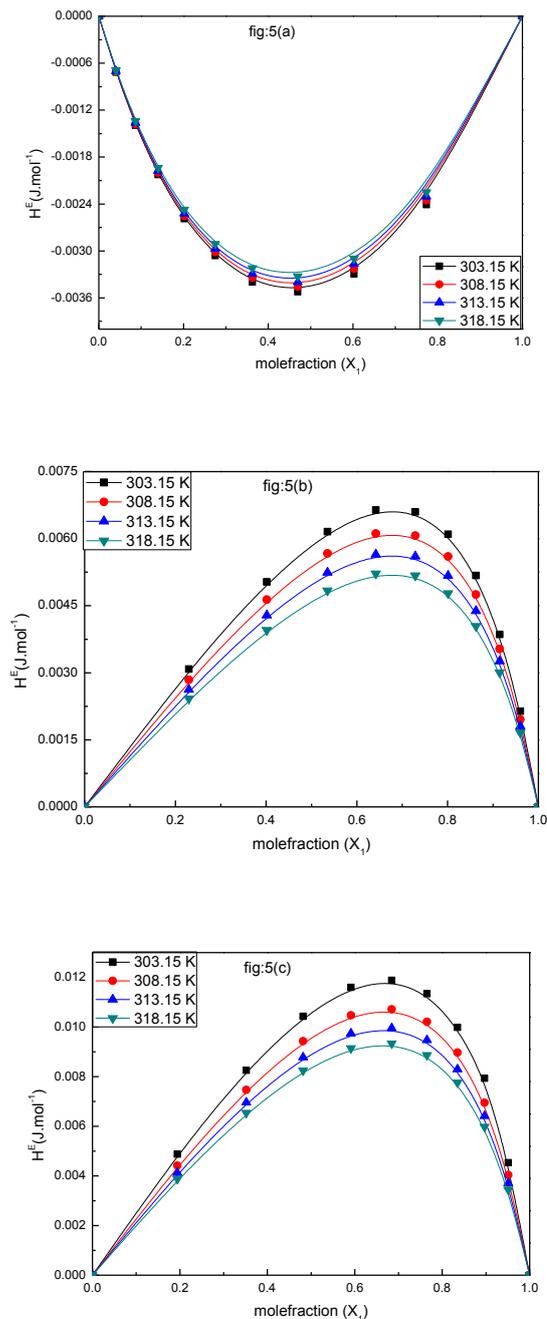


Figure 5: Variation of excess Enthalpy (H^E) with mole fraction (x_1) in the binary liquid mixtures of O-Chloroaniline with formamide(5.a),N-methylformamide(5.b) and N,N-Dimethylformamide(5.c) at different temperatures.

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**.