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ACOUSTIC PROPERTIES OF BINARY LIQUID MIXTURES CONTAINING N-METHYL FORMAMIDE WITH ANILINES AT DIFFERENT TEMPERATURES

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ABSTRACT

Densities (ρ), viscosity (η) and speed of sound (U) values for the liquid mixture systems of N-Methylformamide with Aniline, N-methylaniline and N,N-Dimethylanilinealong with those of pure liquids were measured over the entire mole fraction range at T=303.15 K, 308.15 K and 313.15 K. From these experimentally determined values, various acoustic parameters such as excess isentropic compressibility (K_s^E), excess molar volume (V^E) and excess free length (L_f^E), excess Gibb's free energy (ΔG^{*E}) and excess enthalpy (H^E) have been calculated. The excess functions have been fitted to the Redlich–Kister type polynomial equation. The presenceofintermolecular interactions in these liquid mixtures was confirmed by studying the deviations observed in the excess parameters.

Keywords: Speed of sound, Viscosity, Redlich-Kister Polynomial, Molar Volume

INTRODUCTION

The density, viscosity and speed of sound studies of pure liquids and their liquid mixtures are important apart from being simple and easy to measure. They find applications in different fields and industries.[1,2] Previously many researchers have worked in this field by measuring the density, viscosity, and speed of sound for a wide range of liquids and their binary as well as ternary mixtures.[3-9] The compounds used here are of great importance for their relevant role in chemistry, biology in liquid mixtures. The study of thermodynamic properties of liquid mixtures containing many components and having data for analysis in terms of various models are of great significance for industrial and pharmaceutical applications.[10] The excess thermodynamic functions are sensitively dependent not only on the differences in intermolecular forces but also on the differences in the size of the molecules.[11] The strength of interactions can be understood by the signs and magnitudes of these excess values. So, we wanted to continue our previous work, by considering the experimentally determined values of speed of sound, density and viscosity and thus by various thermo-acoustic parameters like excess isentropic compressibility (K_s^E), excess free length (L_f^E), excess Gibbs free energy (ΔG^{*E}), excess molar volume (V^E) and excess enthalpy (H^E) have been calculated.[3] With the help of these excess values the intermolecular interactions were predicted.

EXPERIMENTAL

Experimental work was carried on to find out the values of density, viscosity and speed of sound for the mixtures of N-Methylformamide (NMF) with Anilines at 303.15, 308.15, and 313.15 K over the entire composition range. In the present study, we have calculated the excess values of isentropic compressibility, molar volume, free length values, Gibb's free energy and enthalpy to check the applicability of thermo-dynamical ideality (the ideal mixing rules) to the components under study. The excess values of isentropic compressibility, K_s^E were calculated as follows,

$$K_s^{\mathrm{E}} = K_s - K_s^{\mathrm{id}} \tag{1}$$

Where K_s represents the calculated value of isentropic compressibility for the mixture

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$$K_s = \frac{1}{\rho U^2} \tag{2}$$

$K_s^E$is its excess value, $K_s^{id}$is the ideal isentropic compressibility value, ρ is the density and U represents the speed of sound. K_s^{id} for an ideal mixture was calculated from the relation recommended by *Benson and KiyoharaandDouheret et al.*[12-14]

$$K_s^{id} = \sum \phi_i \left\{ K_{s,i}^o + \frac{T V_i^o (\alpha_i^o)^2}{C_{p,i}^o} \right\} - T\left(\sum x_i V_i^o\right)\left(\frac{\sum \phi_i \alpha_i^{o2}}{\sum x_i C_{p,i}^o}\right) \tag{3}$$

in which, $K_{s,i}^o$, V_i°, 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 component i in the mixture. The density values have been used to calculate the excess volumes, V^E, using the equation,

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right) \tag{4}$$

Where,ρ is the density of the mixture and x_1, M_1, and ρ_1 and x_2, M_2, and ρ_2 are the mole fraction, molar mass, and density of pure components 1 and 2, respectively. The excess values of free length (L_f^E), Gibbs free energy (ΔG^{*E}) and enthalpy (H^E) were calculated by using the expressions given in the literature as follows,[15]

$$L_f^E = L_f - K_T (K_s^{id})^{1/2} \tag{5}$$

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)×10^{-8}.
Excess Gibbs free energy of activation of viscous flow ΔG^{*E} was calculated as follows,

$$\Delta G^{*E} = RT\left[\ln\left(\frac{\eta V}{\eta_2 V_2}\right) - x_1 \ln\left(\frac{\eta_1 V_1}{\eta_2 V_2}\right)\right] \tag{6}$$

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 is the molar volume of mixture and V_1, V_2 are the molar volumes of the pure compounds, Excess enthalpy H^E was calculated from usual relation.

$$H^E = H - (x_1 H_1 + x_2 H_2) \tag{7}$$

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

RESULTS AND DISCUSSION

From the experimentally determined values of density, the speed of sound and viscosity, the values of excess isentropic compressibility (K_s^E), excess molar volume (V^E), excess free length (L_f^E), excess Gibbs free energy (ΔG^{*E}) and excess enthalpy (H^E) were calculated.[1] These excess values were plotted against mole fractions separately at three different temperatures as shown in Figures-1 to 5. The deviations observed in the excess parameters indicate the strength of interactions present between these mixtures under study.[16] The variations in these excess parameter values reflect the interactions between the mixing species, depending upon the composition, molecular sizes, and shapes of the components and temperature.

The excess isentropic compressibility (K_s^E) for the liquid mixtures under study is as shown in figure 1. It can be observed that the K_s^E values are positive over the entire mole fraction range indicating the presence of weak interactions in these mixtures and also that the molecules are loosely packed in the mixtures due to their shape and size. The liquids having different molecular sizes and shape mix well thereby reducing the volume which causes the values of K_s^E to be negative and if the liquids are of the almost same size then they do not mix well and there is a lot of free space in between as suggested by *Fort and Moore*.[17]

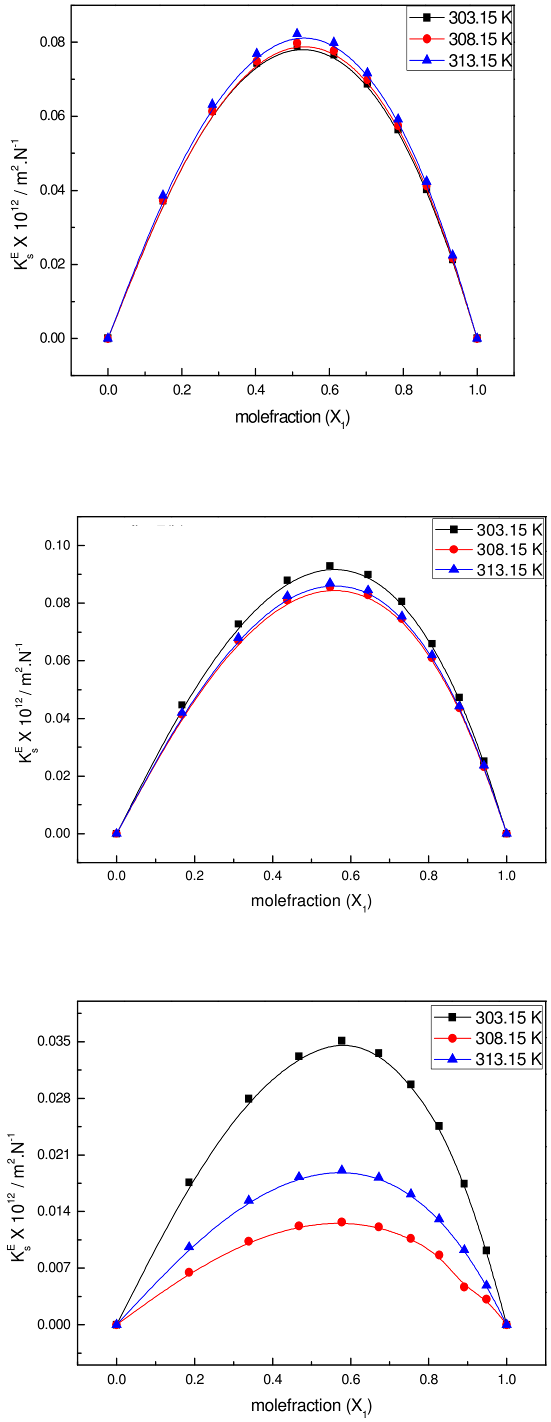

Fig.-1: Variation of Excess Isentropic compressibility with respect to mole fraction at various temperatures for (a) N-Methyl formamide + Aniline ; (b) N-Methyl formamide+N-Methyl aniline (c) N-Methyl formamide + NN Dimethylaniline

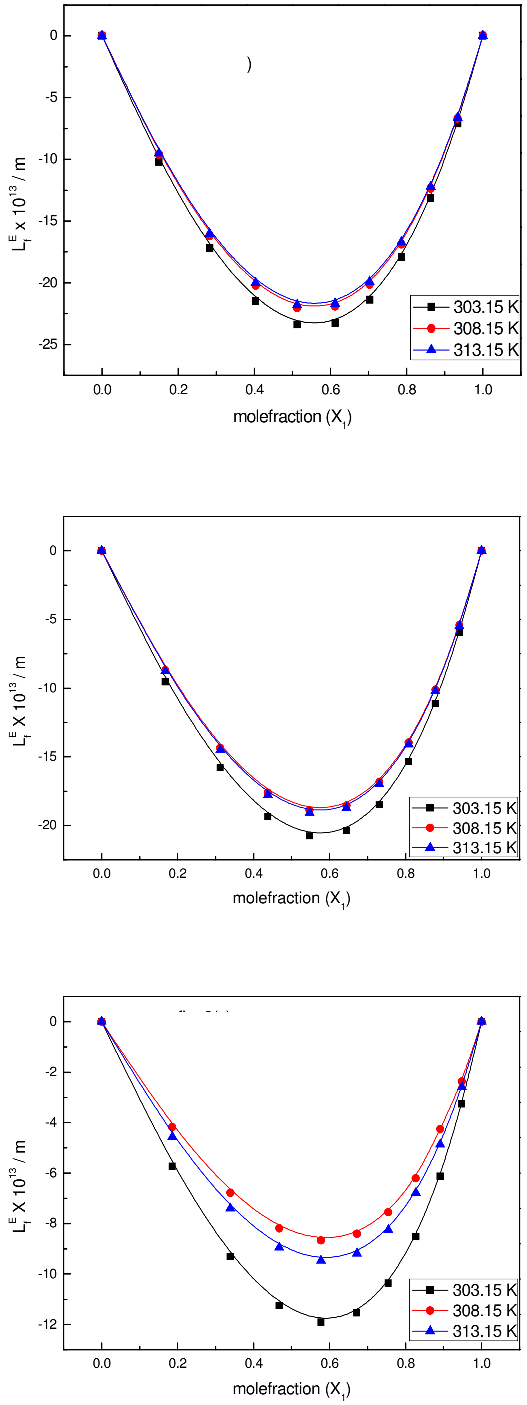

Fig.-2: Variation of excess free length with respect to mole fraction at various temperatures for (a) N-Methyl formamide + Aniline ; (b) N-Methyl formamide+N-Methyl aniline (c) N-Methyl formamide + NN Dimethylaniline.

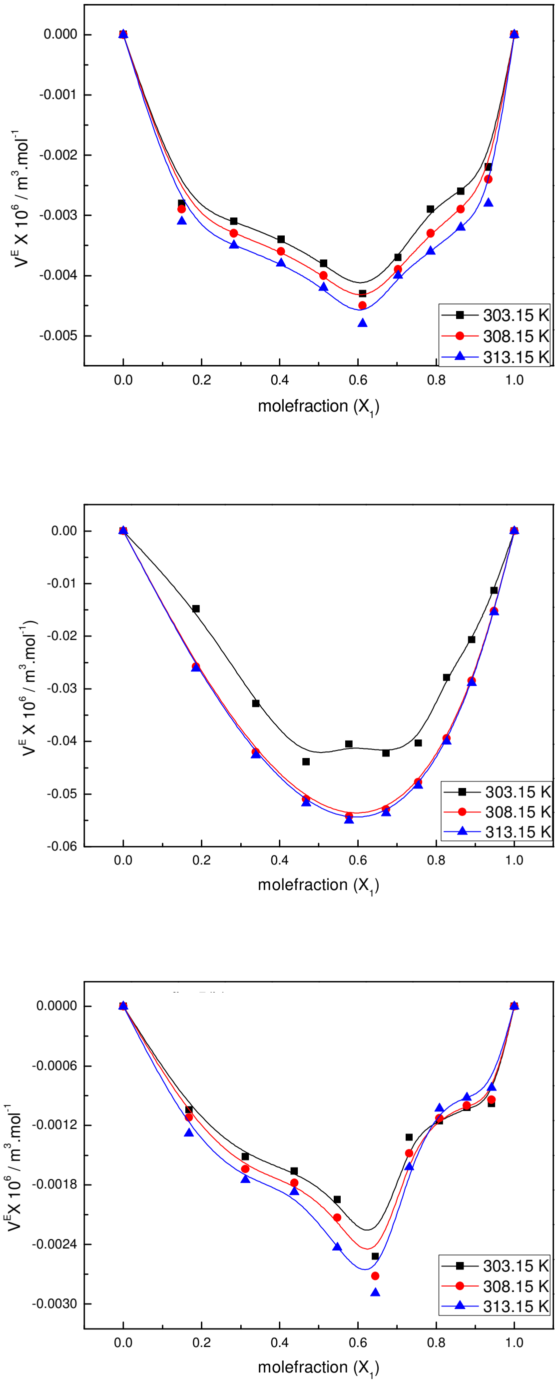

Fig.-3: Variation of Excess Volumes with respect to mole fraction at various temperatures for (a) N-Methyl formamide + Aniline ; (b) N-Methyl formamide+N-Methyl aniline (c) N-Methyl formamide + NN Dimethylaniline

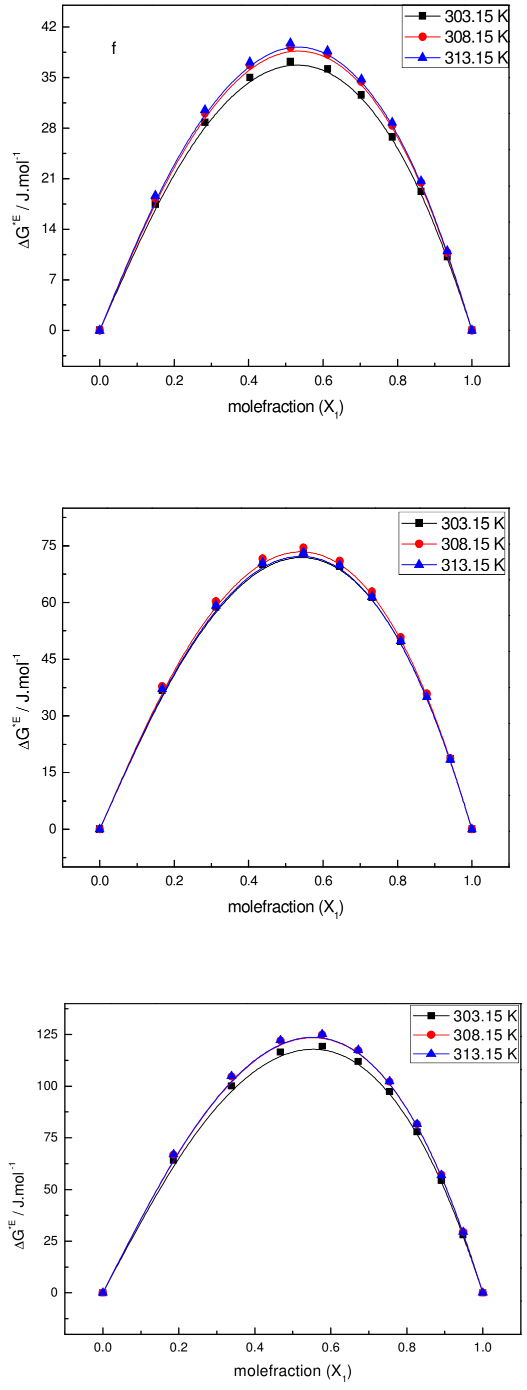

Fig.-4: Variation of excess Gibb's free energy with respect to mole fraction at various temperatures for (a) N-Methyl formamide + Aniline ; (b) N-Methyl formamide+N-Methyl aniline (c) N-Methyl formamide + NN Dimethylaniline

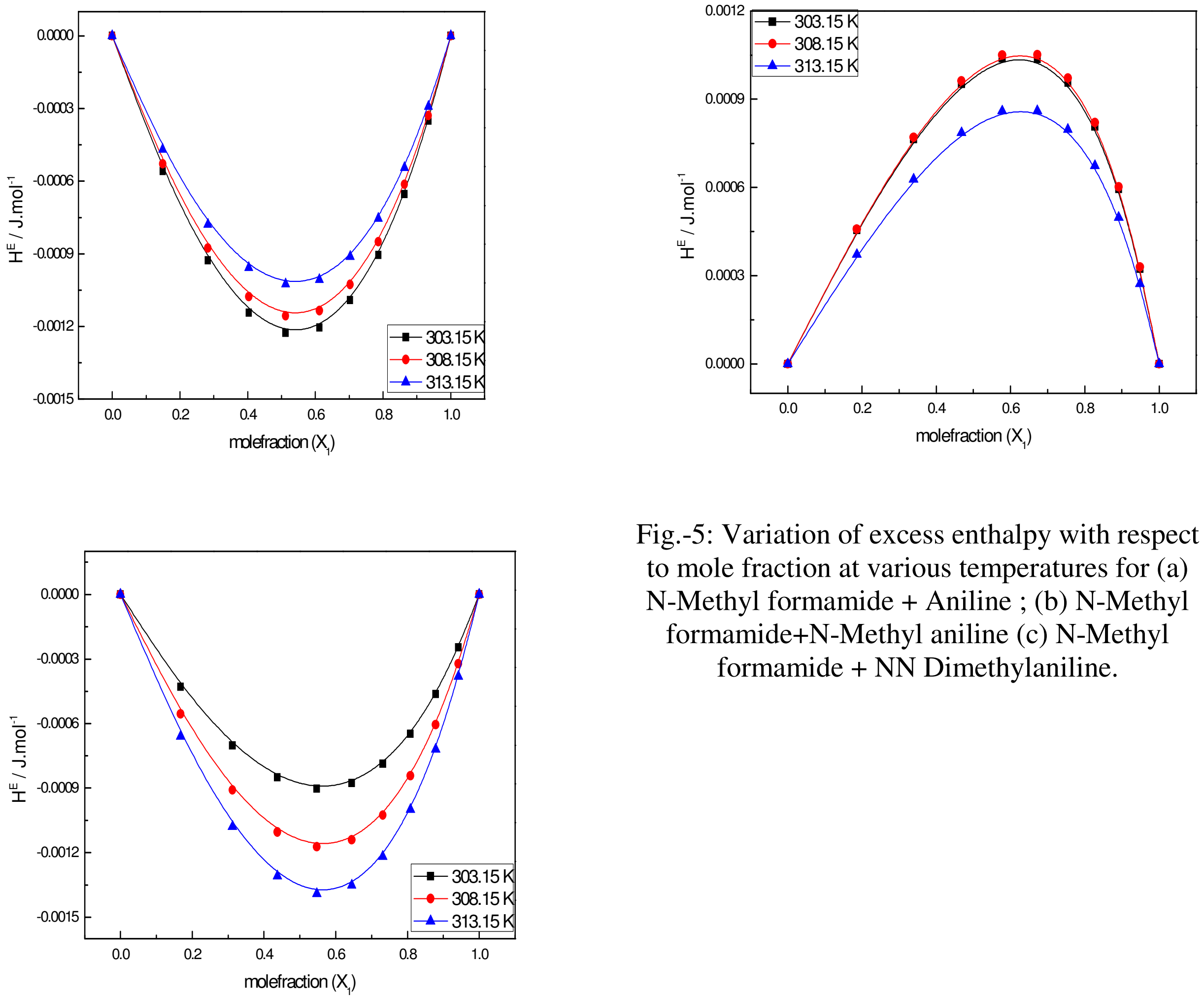

Fig.-5: Variation of excess enthalpy with respect to mole fraction at various temperatures for (a) N-Methyl formamide + Aniline ; (b) N-Methyl formamide+N-Methyl aniline (c) N-Methyl formamide + NN Dimethylaniline.

So, it can be said that the molecular interactions are weak in these liquid mixtures and that the medium is loosely packed.

The nature of the intermolecular interactions in liquid mixtures can be explained by the variation of excess molar volume (V^E), with respect to mole fraction, x_1, as shown in Fig.-3. The expansion in molar volume can be attributed to the presence of weak forces of attraction between the molecules.[18] Similar results were reported by *Garcia et al*.[19] The negative values of V^E indicate that there is more compact packing of molecules which implies that the molecular interactions are strong whereas the positive values indicate a loose packing of molecules in the mixture compared to those in the pure component. Similar results were observed by earlier workers.[20]

It can be observed from Fig.-2 that the L_f^E values are negative which suggest that specific interactions are present between unlike molecules in these systems.[21] From figure-4 the excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) can be observed, where the values are positive over the entire range of mole fraction.

The strength of bond formation in NMF + N, N-Dimethylaniline system is less compared to that of another system, this is indicated by the maximum deviation observed in ΔG^{*E}. Similar results were observed by earlier workers.[21,22]

The excess values of Enthalpy (H^E) move towards positive from negative as shown in figure 5 with respect to the mole fraction, x_1. The positive values of H^E also increase, this is a clear indication that there are dispersion forces between molecules in these liquid mixtures.[23-25] It also suggests the existence of weak dipole-dipole interactions in these systems. Also, the excess values correlate with one another and also supports the inferences drawn for these liquid mixtures.

CONCLUSION

From the measured values of density, the speed of sound and viscosity, values of K_S^E, V^E, L_f^E, ΔG^{*E} and H^E were calculated. Interactions between these mixtures were identified by studying these excess values. Positive values were observed in the case of excess isentropic compressibility, Gibbs free energy of activation while negative values were obtained in excess free length and excess molar volume. The presence of weak bonding between the component molecules can be confirmed with these values. Apart from the above-said values/reasons, the difference in molar masses of the liquid molecules is also responsible for the non-existence of specific interactions.

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