

# Volumetric, Speed Of Sound Data and Viscosity for the Binary Mixtures of 2-Methylaniline with Aliphatic Ketones and Cyclic Ketones at Different Temperatures

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**ABSTRACT:** Density ( $\rho$ ), viscosity ( $\eta$ ), and speed of sound ( $u$ ) were measured for the binary systems of methylaniline (2-MA) with acetone (AC), methylethylketone (MEK), methylpropylketone (MPK), diethylketone (DEK), methylisobutylketone (MIBK), acetophenone (AP), cyclopentanone (CP), and cyclohexanone (CH) and their pure liquids at 298.15 K and 308.15 K over the entire composition range. By using this data, the excess molar volumes ( $V^E$ ), deviation in isentropic compressibility ( $\Delta\kappa_s$ ), deviation in viscosity ( $\Delta\eta$ ) were calculated. These results were fitted to the Redlich-Kister polynomial equation. The variations of these properties with composition of the mixtures suggest that the dipole-dipole interactions, hydrogen-bond and charge-transfer complex formation between 2-methylaniline and ketones. The magnitude of these properties was found to depend on the chain length and ring size of the ketone molecules.

**KEYWORDS:** Speed of sound, viscosity, density, excess thermodynamic parameters.

## I. INTRODUCTION

The present investigation is continuation of the research [1-4] on thermodynamic properties of binary liquid mixtures. Volumetric and ultrasonic investigation of liquid mixtures is of considerable importance in understanding the molecular interaction occurring among component molecules and find their applications in several industrial and technological processes. 2-methylaniline is used in the manufacture of dyes, rubber vulcanization accelerators, hypnotic and anesthetic pharmaceuticals, and pesticides. Ketones are important intermediates in the synthesis of many organic compounds such as alkoxides, hydroxyalkynes, phosphine oxides and cyanohydrins. Among the various ketones, acetophenone is used to create fragrances that resemble jasmine and is also used in chewing gum. Carbonyl group can interact with basis group like amino group to form hydrogen bond and influence the properties of such compounds. The aim of the present work is to know the effect of position of the carbonyl group in the ketonic molecule which can affect both the sign and magnitude of various thermodynamic functions when mixed with 2-methylaniline. For this, measurements of density, speed of sound and viscosity of the binary mixtures (2-methylaniline + ketones) were performed over the entire range of composition in the temperature range 298.15 K and 308.15 K at intervals of 10K. In recent years, several studies have been developed to study thermodynamic and transport properties of binary liquid mixtures containing ketones [5-9]. A perusal of the literature reveals that the thermo physical property studies on the binary mixtures containing 2-methylaniline are not yet reported. This paper presents the data on density, viscosity and speed of sound measurements in the system of 2-methylaniline with eight ketones at 298.15 K and 308.15 K. Using this experimental data, excess molar volume ( $V^E$ ), deviation in isentropic compressibility ( $\Delta\kappa_s$ ) and deviation in viscosity ( $\Delta\eta$ ) were calculated. The measured data have been used to explain the nature of intermolecular interactions between component molecules.

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## II. EXPERIMENTAL

### A. Materials

The mass fraction purity of all the liquids from the S.D. Fine Chemicals, Ltd., India was as follows: 2-methylaniline(0.995), acetone(0.995),methylethylketone(0.995),methylpropylketone (0.994), diethylketone (0.993), methylisobutylketone (0.994), acetophenone(0.992), cyclopentanone(0.991) and cyclohexanone (0.993). Prior to experimental measurements, all the liquids were purified using double distillation and then partially degassed with a vacuum pump under an inert atmosphere. The purity of all these solvents was compared with the measured density, speed of sound and viscosity of the pure liquids with the literature values [11-18] are given in Table 1 at 298.15 K.

Table 1: Comparison of Experimental and Literature values of density  $\rho$ , ultrasonic velocity  $u$  and viscosity ( $\eta$ ) for pure Components at 298.15 K

Pure components	Density		velocity		Viscosity	
	Experimental	Literature	Experimental	Literature	Experimental	Literature
2-methylaniline	0.99434	0.99430 <sup>a</sup>	1601.8	1603.0 <sup>a</sup>	3.738	3.725 <sup>h</sup>
Acetone	0.78428	0.78430 <sup>b</sup>	1165.3	1158.2 <sup>d</sup>	0.3031	0.3025 <sup>b</sup>
methyl ethyl ketone	0.79919	0.79960 <sup>c</sup>	1196.2	1191.6 <sup>d</sup>	0.3835	0.378 <sup>c</sup>
methyl propyl ketone	0.80175	0.80176 <sup>d</sup>	1215.0	1197.0* <sup>d</sup>	0.461	0.438* <sup>d</sup>
diethyl ketone	0.80933	0.80932 <sup>d</sup>	1212.0	1200.0* <sup>d</sup>	0.446	0.442 <sup>d</sup>
Methyl isobutyl ketone	0.79608	0.79609 <sup>e</sup>	1187.0	1170.0* <sup>e</sup>	0.543	0.541 <sup>e</sup>
Acetophenone	1.02361	1.02360 <sup>e</sup>	1479.2	1476.2 <sup>e</sup>	1.658	1.652 <sup>f</sup>
Cyclopentanone	0.94318	0.94320 <sup>e</sup>	1397.0	1394 <sup>g</sup>	1.082	1.084 <sup>e</sup>
Cyclohexanone	0.94111	0.94110 <sup>e</sup>	1413.0	1417 <sup>g</sup>	2.019	2.011 <sup>e</sup>

\*303.15k

a Reference [11], b Reference [12],c Reference [13],d Reference [14],e Reference [15],f Reference [16],g Reference [17], h Reference[18].

### B.Method

The water content of solvents used in this work was measured by an Analab (Micro Aqua Cal 100) Karl Fischer Titrator and Karl Fisher reagent. It can detect water content from less than  $10 \times 10^{-6}$  to 100 % by conductometric titration with dual platinum electrodes. 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  $\pm 0.1$ 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 using 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 the temperature accuracy of 308.15 K  $\pm 0.03$  K. The uncertainty in density measurement liquid mixtures is  $\pm 5 \times 10^{-5}$  gm cm<sup>-3</sup>.

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 298.15 K and 308.15 K by using a digital constant temperature water bath. The uncertainty in the measurement of speed of sound is  $\pm 0.2\%$ . The temperature stability is maintained within  $\pm 0.02$  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  $\lambda$  is the wave length. The frequency ( $\nu$ ) of

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the crystal being accurately known (2.0 MHz), the speed of sound,  $u$  in  $\text{m}\cdot\text{sec}^{-1}$  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 [10]. The viscosities of pure liquids and their mixtures were determined at atmospheric pressure and at temperature 298.15 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 0.5mm internal diameter.

The viscometer thoroughly cleaned and perfectly dried, is filled with the sample liquid by fitting the viscometer to about  $30^\circ$  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  $\pm 0.01$  K for about 20 minutes to obtain thermal equilibrium. An electronic digital stopwatch with an uncertainty  $\pm 0.01$ 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,  $\rho$  is the density and  $t$  represents the flow time. The uncertainty of viscosity thus estimated was found to be  $\pm 0.005$  mPa.s.

### III. THEORY AND CALCULATIONS

The experimental densities have been used to calculate the excess molar volumes ( $V^E$ ) using the following equation:

$$V^E / \text{cm}^3 \cdot \text{mol}^{-1} = [x_1 M_1 + x_2 M_2] / \rho - [x_1 M_1 / \rho_1 + x_2 M_2 / \rho_2] \quad (2)$$

where  $x_1$  and  $x_2$  are the mole fractions of 2-methylaniline and ketones respectively.  $M_1$ ,  $M_2$  and  $\rho_1$  and  $\rho_2$  are the molecular weights and density of components 2-methylaniline and ketones respectively and  $\rho$  is the density of the mixture.

The observed excess volumes ( $V^E$ ) have a negative value for all binary systems over the whole composition range at the studied temperatures. The excess volumes for the above mentioned systems are the resultant contribution from several opposing effects, namely chemical, physical and structural. The chemical or specific interactions result in volume contractions, leading to negative excess volume and these include charge-transfer complexes, dipole-dipole, dipole-induced dipole interactions and H-bonding between component molecules. The physical interactions or non-specific interactions are weak and hence contribute a positive  $V^E$  while the structural contributions are mostly negative and arise from several effects such as interstitial accommodation and geometrical fitting of one component into another due to the differences in the molar volume and free volume between components.

The observed negative  $V^E$  values can be explained by the nitrogen atom of 2-methylaniline with a lone pair of electrons which can act as an electron donor to the carbon atoms of polarized carbonyl group which are electrophilic in nature, leading to complex formation. In other words, there is clear spectroscopic evidence for N-H...O hydrogen bonded complex formation of 2-methylaniline with ketones [19, 20]. Accordingly, the negative values obtained in this study can be mainly attributed to the complex formation between components of the investigated mixtures. Also, dipole-dipole van der Waals forces contribute to the negative  $V^E$  due to the values of the dipole moments of the components [21].

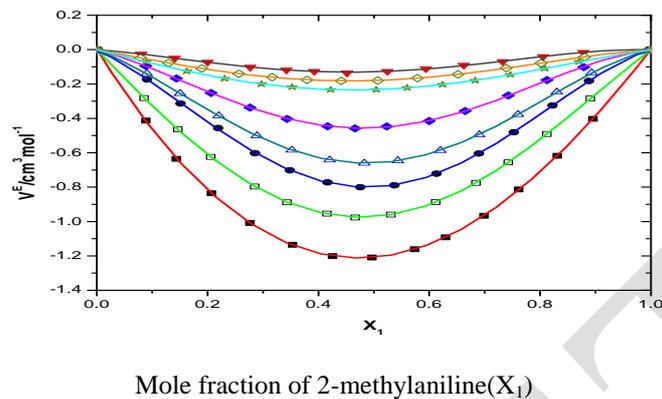


Fig.1 : Excess molar volume ( $V^E$ ) with mole fraction( $X_1$ ) of 2-methylaniline in the binary liquid mixtures of 2-methylaniline with acetone (■), methyl ethyl ketone (□),methyl propyl ketone (● ), diethyl ketone (Δ ), Methyl isobutyl ketone (◆ ),Acetophenone(▼), cyclopentanone (◇ ), cyclohexanone (★) at 298.15 K.

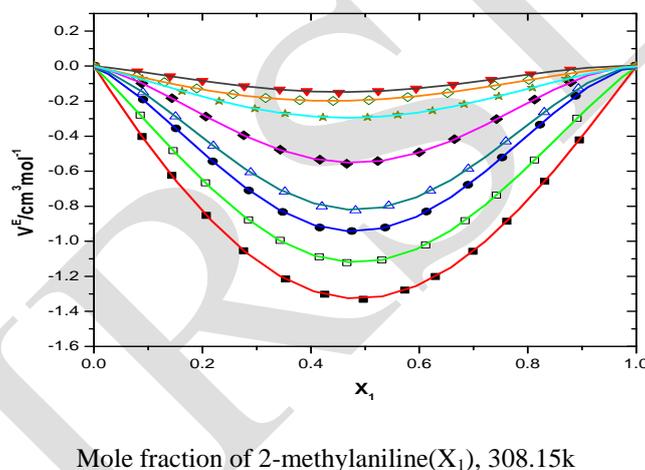


Fig.2 : Excess molar volume ( $V^E$ ) with mole fraction( $X_1$ ) of 2-methylaniline in the binary liquid mixtures of 2-methylaniline with acetone (■), methyl ethyl ketone (□),methyl propyl ketone (● ), diethyl ketone (Δ ), Methyl isobutyl ketone (◆ ),Acetophenone(▼), cyclopentanone (◇ ), cyclohexanone (★) at 308.15 K.

From Fig 1 and Fig 2, the  $V^E$  values of 2-methylaniline with aliphatic ketones are in the following order:

$$AC < MEK < MPK < DEK < MIBK < CP < CH < AP$$

For the binary mixtures investigated, a decrease in  $V^E$  over the whole composition range is noticeable with increasing temperature from (298.15 K and 308.15 K). The increase of temperature leads to increase in kinetic energy of the self-associated species of 2-methylaniline, i.e., it promotes their dissociation. Since the self-association is more exothermic than N-H...O complex formation between components in the mixture, the increase of temperature has greater effect on 2-methylaniline self-association. As a result, the equilibrium is shifted towards the complex and  $V^E$  become more negative at higher temperatures [21].

Viscosity ( $\eta$ ) for the mixtures of 2-methylaniline with ketones and excess Gibbs energy of activation of viscous flow ( $G^{*E}$ ) were calculated by the following relations:

$$\Delta\eta / \text{mPa.s} = \eta - [x_1\eta_1 + x_2\eta_2] \tag{3}$$

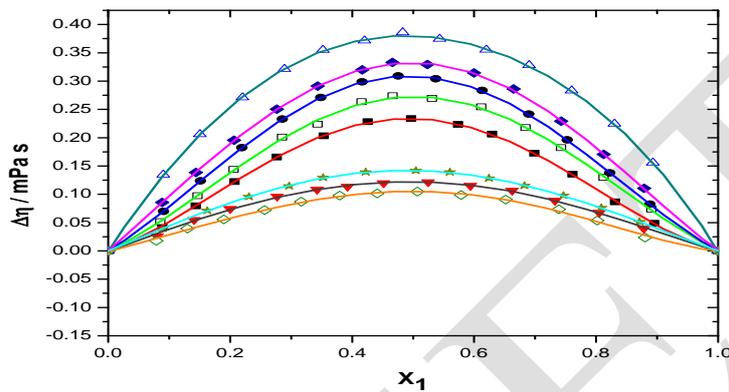
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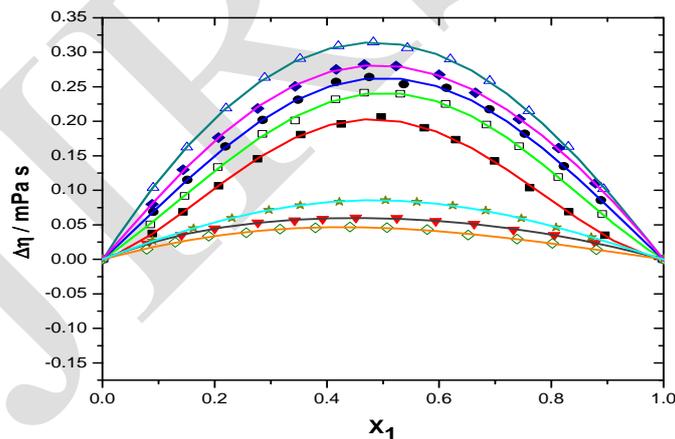
$$G^{*E}/J.mol^{-1}=RT [\ln\eta V-(x_1\ln\eta_1 V_1+x_2\ln\eta_2 V_2)] \tag{4}$$

where,  $\eta_1, \eta_2, \eta, V_1, V_2$  and  $V$  are the viscosity of components 2-methylaniline, ketones and mixture and molar volumes of component 2-methylaniline, ketones and mixture respectively. The viscosity data of all the liquid mixtures are graphically given in Fig 3 and Fig 4.



Mole fraction of 2-methylaniline( $X_1$ ),

Fig.3: Deviation in viscosity ( $\Delta\eta$ )with mole fraction( $x_1$ ) of 2-methylaniline in the binary liquid mixtures of 2-methylaniline with acetone (■), methyl ethyl ketone (□), methyl propyl ketone (●), diethyl ketone (Δ), Methyl isobutyl ketone(◆),Acetophenone(▼), cyclopentanone (◇), cyclohexanone (★) 298.15 K.



Mole fraction of 2-methylaniline( $X_1$ ), 308.15k

Fig. 4 :Deviation in viscosity ( $\Delta\eta$ )with mole fraction( $x_1$ ) of 2-methylaniline in the binary liquid mixtures of 2-methylaniline with acetone (■), methyl ethyl ketone (□), methyl propyl ketone (●), diethyl ketone (Δ), Methyl isobutyl ketone(◆),Acetophenone(▼), cyclopentanone (◇), cyclohexanone (★) at 308.15 K.

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Viscosity deviation data in the present investigation depends on the following factors:

- 1) The geometrical difference in size and shape of component molecules and loss of dipolar association in pure component may contribute to decrease in viscosity.
- 2) Specific interactions between unlike components like hydrogen bond formation and charge transfer complexes may cause for increase in viscosity in mixtures than in pure components. The first factor produces negative viscosity deviation, while the second factor leads to contribute positive viscosity deviation. An examination of viscosity deviation data reveal that the later factor which is responsible for viscosity deviation is dominant in all the binary mixtures of 2-methylaniline with ketones.

According to the view of Fort and Moore [22], positive  $\Delta\eta$  values indicate specific interactions, while negative values indicate the dominance of dispersion forces. According to investigation, positive viscosity deviation values indicate the presence of charge-transfer interactions leading to the formation of complex species between unlike molecules [22]. These conclusions are in excellent agreement with the drawn  $V^E$  values. The magnitude of positive viscosity deviation values increase with increase in temperature for all binary systems. The positive trend in  $\Delta\eta$  for all the mixtures of 2-methylaniline with ketones indicate that the disrupt hetero and homo association of the molecules resulting in an increase in fluidity of the liquids giving higher viscosity deviation at higher temperatures. Similar results have been reported earlier [23]. According to Reed and Taylor and Meyer et al., positive  $G^{*E}$  values indicate specific interactions, while negative values indicate the dominance of dispersion forces [24, 25]. A perusal of Table 3 shows that the values of  $G^{*E}$ , and  $d_{12}$  are positive for all binary systems over the entire composition range at 298.15 K and 308.15 K. The sign of the values of excess Gibbs free energy of activation of viscous flow can be considered as a reliable criterion for understanding the nature of interaction between unlike molecules [25]. In the present case, the positive values of  $G^{*E}$  and  $d_{12}$  may be attributed to the complex formation between component molecules [22].

The deviation in isentropic compressibility ( $\Delta\kappa_s$ ) were obtained from the relations

$$\kappa_s = u^{-2} \rho^{-1} \tag{5}$$

$$\Delta\kappa_s = \kappa_s - [x_1 \kappa_{s1} + x_2 \kappa_{s2}] \tag{6}$$

where  $\kappa_s$ ,  $\rho$ ,  $u$ ,  $\kappa_{s1}$ ,  $\rho_1$ ,  $x_1$ ,  $\kappa_{s2}$ ,  $\rho_2$  and  $x_2$  are density, speed of sound, isentropic compressibility and mole fraction of the components 1, components 2, and mixtures respectively.

Deviation in isentropic compressibility ( $\Delta\kappa_s$ ) data for all the mixtures were graphically depicted in Fig 5 and Fig 6.

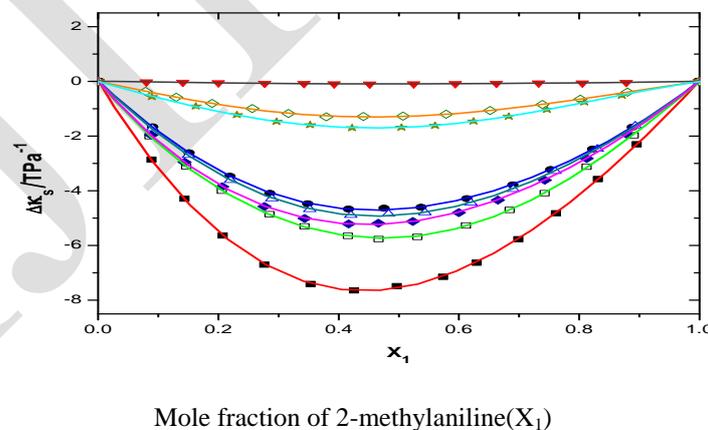


Fig.5: Deviation in Isentropic Compressibility ( $\Delta\kappa_s$ ) with mole fraction( $X_1$ ) of 2-methylaniline in the binary liquid mixtures of 2-methylaniline with acetone (■), methyl ethyl ketone (□), methyl propyl ketone (●), diethyl ketone (Δ), Methyl isobutyl ketone (◆), Acetophenone(▼), cyclopentanone (◇), cyclohexanone (★) at 298.15 K

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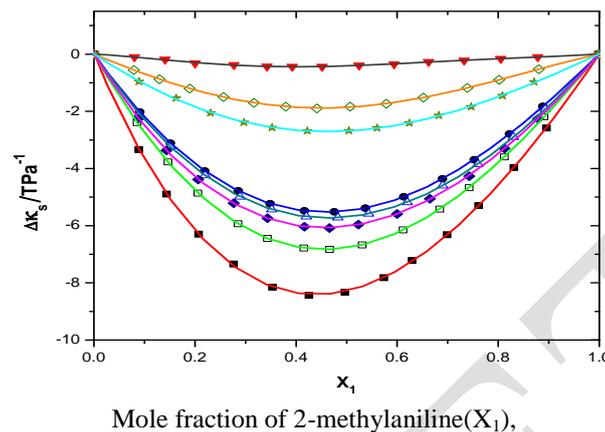


Fig. 6 : Deviation in Isentropic Compressibility ( $\Delta\kappa_s$ ) with mole fraction( $x_1$ ) of 2-methylaniline in the binary liquid mixtures of 2-methylaniline with acetone (■), methyl ethyl ketone (□), methyl propyl ketone (●), diethyl ketone (Δ), Methyl isobutyl ketone (◆), Acetophenone (▼), cyclopentanone (◇), cyclohexanone (★) 308.15 K.

It is evident from Fig5 and Fig 6 that the  $\Delta\kappa_s$  values are negative for all binary mixtures and can be explained in terms of electron-transfer complex formation between the molecules of mixing components. Nitrogen atom is the donor [26] possessing lone pairs of electrons and hence, 2-methylaniline is a good electron pair donor to ketones leading to the formation of donor-acceptor interactions between them. This type of similar trend was observed for high polar solvent of N,N-dimethyl formamide with ketones [27].

The values  $\Delta\kappa_s$  for all binary systems fall in the order:

$$AC < MEK < MIBK < DEK < MPK < CH < CP < AP$$

The sign and magnitude of the deviation in speed of sound( $\Delta u$ ) and deviation in acoustic impedance( $\Delta Z$ ) on mixing were found to depend upon several contributions, which are of physical or / and chemical nature. The physical contributions comprise the dispersion forces and non-specific physical weak interactions that lead to negative values in  $\Delta u$  and  $\Delta Z$ . Chemical contributions involve breaking up of H-bonded structure, if any, resulting in negative  $\Delta u$  and  $\Delta Z$  values and specific interactions such as formation of H-bonds, charge-transfer complex, and strong dipole-dipole interactions between component molecules result in positive  $\Delta u$  and  $\Delta Z$  values, making the system more ordered due to increased intermolecular interaction.

The  $\Delta u$  values for 2-methylaniline with cyclopentanone, cyclohexanone and acetophenone are positive and for mixtures of 2-methylaniline with acetone, methylethylketone, diethyl ketone, methylisopropylketone, methylisobutylketone are negative over the entire composition range at 298.15 K and 308.15 K. Positive deviations indicate the increasing strength of interaction between component molecules of binary liquid mixtures [28]. If strong interactions arise among the components of a mixture leading to the formation of molecular aggregates and more compact structures, then sound will travel faster through the mixture by means of longitudinal waves and hence the speed of sound deviations with respect to linear behavior will be positive. While if the structure-breaking factor in the mixture predominates resulting expansion, then the speed of sound through the mixture will be slower resulting into negative deviation in speed of sound [29].

The  $\Delta Z$  values are positive for binary systems of 2-methylaniline with acetophenone, cyclopentanone and cyclohexanone over the entire composition range at 298.15 K and 308.15 K and are negative for the remaining binary mixtures.

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The variation of  $V^E$ ,  $\Delta\kappa_s$  and  $\Delta\eta$  with mole fraction were fitted to the Redlich - Kister polynomial equation [30] of the type,

$$Y^E = x_1x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \quad (7)$$

where  $Y^E$  is  $V^E$  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,  $\sigma$  obtained by the method of least – squares with equal weights assigned to each point were calculated. The standard deviation ( $\sigma$ ) is defined as:

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

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 determined by the least square method and summarized along with the standard deviations between the experimental and fitted values of  $V^E$ ,  $\Delta\kappa_s$  and  $\Delta\eta$  in Table 2.

Table 2: Coefficients of Redlich – Kister equation and standard deviation values at 298.15 K and 308.15 K.

Binary mixtures	temperature	Functions	$a_0$	$a_1$	$a_2$	$\sigma$
2-methylaniline + acetone	298.15k	$V^E / \text{cm}^3 \cdot \text{mol}^{-1}$	-4.838	0.534	0.197	0.003
		$\Delta\kappa_s / \text{TPa}^{-1}$	-30.264	6.886	0.506	0.038
		$\Delta\eta / \text{mPa} \cdot \text{s}$	0.935	-0.041	-0.629	0.001
	308.15k	$V^E / \text{cm}^3 \cdot \text{mol}^{-1}$	-5.301	0.323	0.887	0.002
		$\Delta\kappa_s / \text{TPa}^{-1}$	-33.083	8.263	-1.627	0.034
		$\Delta\eta / \text{mPa} \cdot \text{s}$	0.809	-0.084	-0.610	0.002
2-methylaniline + methyl ethyl ketone	298.15k	$V^E / \text{cm}^3 \cdot \text{mol}^{-1}$	-3.889	0.457	0.982	0.001
		$\Delta\kappa_s / \text{TPa}^{-1}$	-22.787	3.116	0.572	0.043
		$\Delta\eta / \text{mPa} \cdot \text{s}$	1.089	0.019	0.019	0.003
	308.15k	$V^E / \text{cm}^3 \cdot \text{mol}^{-1}$	-4.474	0.400	1.792	0.002
		$\Delta\kappa_s / \text{TPa}^{-1}$	-27.117	5.044	1.000	0.004
		$\Delta\eta / \text{mPa} \cdot \text{s}$	0.966	-0.003	-0.466	0.002
2-methylaniline + methyl propyl ketone	298.15k	$V^E / \text{cm}^3 \cdot \text{mol}^{-1}$	-3.196	0.242	1.939	0.003
		$\Delta\kappa_s / \text{TPa}^{-1}$	-18.775	2.464	0.378	0.041
		$\Delta\eta / \text{mPa} \cdot \text{s}$	1.236	-0.043	-0.629	0.001
	308.15k	$V^E / \text{cm}^3 \cdot \text{mol}^{-1}$	-3.765	0.503	2.765	0.002
		$\Delta\kappa_s / \text{TPa}^{-1}$	-21.966	3.842	0.890	0.005
		$\Delta\eta / \text{mPa} \cdot \text{s}$	1.054	0.005	-0.320	0.003
2-methylaniline + diethyl ketone	298.15k	$V^E / \text{cm}^3 \cdot \text{mol}^{-1}$	-2.641	0.233	1.674	0.001
		$\Delta\kappa_s / \text{TPa}^{-1}$	-19.641	2.709	0.852	0.035
		$\Delta\eta / \text{mPa} \cdot \text{s}$	1.520	-0.011	0.176	0.003
	308.15k	$V^E / \text{cm}^3 \cdot \text{mol}^{-1}$	-3.272	0.381	2.633	0.003
		$\Delta\kappa_s / \text{TPa}^{-1}$	-22.815	3.366	-0.031	0.004
		$\Delta\eta / \text{mPa} \cdot \text{s}$	1.258	-0.105	-0.128	0.002
2-methylaniline + methyl isobutyl ketone	298.15k	$V^E / \text{cm}^3 \cdot \text{mol}^{-1}$	-1.823	0.243	1.246	0.002
		$\Delta\kappa_s / \text{TPa}^{-1}$	-20.768	4.061	-0.615	0.024
		$\Delta\eta / \text{mPa} \cdot \text{s}$	1.329	-0.041	-0.455	0.002
	308.15k	$V^E / \text{cm}^3 \cdot \text{mol}^{-1}$	-2.198	0.348	1.873	0.002
		$\Delta\kappa_s / \text{TPa}^{-1}$	-24.110	4.196	-0.513	0.010

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2-methylaniline+acetophenone	298.15k	$\Delta\eta/\text{mPa}\cdot\text{s}$	1.126	0.007	-0.174	0.002
		$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.517	0.165	0.434	0.002
		$\Delta\kappa_s/\text{TPa}^{-1}$	-0.368	-0.019	0.098	0.005
	308.15k	$\Delta\eta/\text{mPa}\cdot\text{s}$	0.495	-0.021	-0.171	0.003
		$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.584	0.182	0.469	0.001
		$\Delta\kappa_s/\text{TPa}^{-1}$	-1.687	0.581	0.917	0.028
2-methylaniline+cyclopentanone	298.15k	$\Delta\eta/\text{mPa}\cdot\text{s}$	0.237	-0.046	0.040	0.001
		$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.719	0.183	0.309	0.001
		$\Delta\kappa_s/\text{TPa}^{-1}$	-5.159	0.976	1.273	0.019
	308.15k	$\Delta\eta/\text{mPa}\cdot\text{s}$	0.427	-0.034	-0.257	0.003
		$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.779	0.282	0.306	0.001
		$\Delta\kappa_s/\text{TPa}^{-1}$	-7.440	1.828	1.882	0.009
2-methylaniline + cyclohexanone	298.15k	$\Delta\eta/\text{mPa}\cdot\text{s}$	0.184	-0.054	-0.022	0.001
		$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-1.181	0.228	0.665	0.002
		$\Delta\kappa_s/\text{TPa}^{-1}$	-10.773	1.879	0.992	0.020
	308.15k	$\Delta\eta/\text{mPa}\cdot\text{s}$	0.341	-0.029	-0.058	0.001
		$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.934	0.182	0.304	0.001
		$\Delta\kappa_s/\text{TPa}^{-1}$	-6.716	1.566	1.854	0.016
		$\Delta\eta/\text{mPa}\cdot\text{s}$	0.569	-0.032	-0.158	0.001

Gruenberg-Nissan proposed the following empirical equation [31]

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12} \quad (9)$$

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

Katti and Chaudhri equation takes the form [32]

$$\ln \eta V = x_1 \ln V_1 \eta_1 + x_2 \ln V_2 \eta_2 + x_1 x_2 W_{\text{vis}}/RT \quad (10)$$

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

Hind et al suggested the following equation [33]

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 H_{12} \quad (11)$$

where  $H_{12}$  is Hind interaction parameter.

Fort and Moore [22] reported that for any binary liquid mixture, a positive value of  $d_{12}$  indicates the presence of specific interactions and a negative value of  $d_{12}$  indicates the presence of weak interactions between the unlike molecules. It is observed that the interaction parameter  $d_{12}$  values are positive for all binary systems over the entire range of the composition and temperature, indicating the specific interactions through complex formation between the unlike molecules.

Interaction parameter  $W_{\text{vis}}/RT$  shows almost the same trend as that of  $d_{12}$ . In fact, one could say that the parameters  $d_{12}$  and  $W_{\text{vis}}/RT$  exhibit almost similar behavior. After a thorough study of the behavior of excess properties and interaction parameters of selected binary mixtures, it is observed that specific interaction is present in the all binary systems at studied temperatures.

## IV. CONCLUSIONS

The experimental values of density, viscosity and speed of sound for the binary mixtures of 2-methylaniline with acetone, methylethylketone, methylpropylketone, diethyl ketone, methyl isobutyl ketone, acetophenone, cyclopentanone and cyclohexanone at different compositions were measured at the temperatures of 298.15 K and 308.15 K. From this data, thermodynamic excess functions have been calculated and correlated using the Redlich –

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Kister type polynomial equation. The sign and magnitude of these thermodynamic excess functions have been discussed in terms of electron-transfer complexes, Hydrogen-bond, and dipole-dipole interactions between the component molecules.

## REFERENCES

- [1] M. Gowrisankar, P. Venkateswarlu, K. Siva kumar, S. Sivarambabu, "Thermodynamics of amine + ketone mixtures 3. Volumetric, speed of sound data and viscosity at (303.15 K and 308.15K) for the binary mixtures of N,N-dimethylaniline + propiophenone, + p-methylacetophenone, + p-chloroacetophenone", J. Mol. Liq., vol.173,pp.172-179,2013.
- [2] Gowri sankar M, Sivarambabu S, Venkateswarlu P, Siva kumar K, "Volumetric, speed of sound data and viscosity at (303.15 and 308.15) K for the binary mixtures of N,N-dimethylaniline + aliphatic ketones (C<sub>3</sub>-C<sub>5</sub>), +4-methyl-2-pentanone, +acetophenone, + cycloketones", J. Ind. Eng. Chem. DOI: 10.1016/j.jiec.2013.04.035,2013.
- [3] M. Gowri sankar, P. Venkateswarlu, K. Siva kumar, S. Sivarambabu, "Ultrasonic studies on molecular interactions in binary mixtures of N-methyl aniline with methyl isobutylketone, + 3-pentanone, + cycloalkanones at 303.15 K", J. Soln. Chem., vol.42,pp. 916-935,2013.
- [4] G. S. Manukonda, P. Venkateswarlu, S. K. Kasibhatta, S.R.B. Sakamuri, "Density, ultrasonic velocity, viscosity and their excess parameters of the binary mixtures of N,N-dimethylaniline with 1-Alkanols (C<sub>3</sub>-C<sub>5</sub>), +2-Alkanols (C<sub>3</sub>-C<sub>4</sub>), + 2-methyl-1-propanol, + 2-methyl-2-propanol at 303.15 K", Korean J. Chem. Eng., vol. 30,pp. 1131-1141,2013
- [5] M Sreenivasulu and PR Naidu, "Excess Volumes and Isentropic Compressibilities of Binary Mixtures of Butylamine and Cyclic Ketones", Aust. J. Chem., vol. 32(8), pp 1649 – 1652,1979.
- [6] García, B., Alcalde, R., Aparicio, S., Leal, J.M., "The N-methylpyrrolidone-(C<sub>1</sub>-C<sub>10</sub>) alkan-1-ols solvent systems", Physical Chemistry Chemical Physics, 4 (7), pp. 1170-1177,2002.
- [7] P.M. Krishna, R.B. Kumar, B. Sathyanarayana, K.S. Kumar, N. Sathyanarayana, "Densities and speeds of sound for binary liquid mixtures of thiolane-1,1-dioxide with butanone, pentan-2-one, pentan-3-one and 4-methyl-pentan-2-one at (303.15 or 308.15 or 313.15) K", J. Chem. Eng., Vol.54, pp. 1947–1950,2009.
- [8] P. G. Kumari, P. Venkatesu, M. V. Prabhakara Rao, M. J. Lee and M. H. Lin, "Excess molar volumes and ultrasonic studies of N methyl- 2-pyrrolidone with ketones at T =303.15 K", Journal of Chemical Thermodynamics, vol. 41, pp. 586–590, 2009.
- [9] R.K. Bachu, M.K. Patwari, S. Boodida, S. Nallani "Volumetric and transport properties of binary liquid mixtures of Aliphatic ketones with phenylacetone at T = 308.15 K", J. Chem. Eng., vol. 53, pp. 2403–2407,2008.
- [10] R. Palepu, J. Diver, D. Campell, "Thermodynamic and Transport properties of o-chlorophenol with Aniline and N-alkyl anilines", J. Chem. Eng., vol.30, pp.355-360,1985.
- [11] Neeti Saini, J.S. Yadav, Sunil K. Jangra, Dimple Sharma, V.K. Sharma, "Thermodynamic studies of molecular interactions in mixtures of o-toulidine with pyridine and picolines", J. Chem. Thermodynamics, vol.43, pp.782–795,2011.
- [12] Lorenzo De Lorenzi, Maurizio Fergaglia, Giovanni Torriano, "Densities and Viscosities of 1, 1, 1-Trichloroethane with 13 Different Solvents at 298.15 K", J. Chem. Eng., vol. 40, pp.1172-1177,1995.
- [13] MahendraNath Roy, BiswajitSinha, and Vikas Kumar Dakua, "Excess Molar Volumes and Viscosity Deviations of Binary Liquid Mixtures of 1,3-Dioxolane and 1,4-Dioxane with Butyl Acetate, Butyric Acid, Butylamine, and 2-Butanone at 298.15 K", J. Chem. Eng., vol. 51, pp590-594,2006.
- [14] ManukondaGowrisankar, PonneriVenkateswarlu, KasibhattaSivakumar, Sakamuri Sivarambabu, "Thermodynamics of amine + ketone mixtures: Volumetric, speed of sound data and viscosity at 303.15 K and 308.15 K for the binary mixtures of N,N-diethylaniline + aliphatic ketones (C<sub>3</sub>-C<sub>5</sub>) + 4-methyl-2-pentanone", Arabian Journal of Chemistry, vol.9,pp.42,2013.
- [15] M. Gowrisankar, S.Sivarambabu, P.Venkateswarlu, K. Siva kumar, "Molecular interactions between amine and cyclic ketones at different temperatures", J. Therm Anal Calorim, vol. 115,pp.1821-1827,2014.
- [16] M. N. Roy\*, B. K. Sarkar and R. Chanda, "Viscosity, Density, and Speed of Sound for the Binary Mixtures of Formamidewith 2-Methoxyethanol, Acetophenone, Acetonitrile, 1, 2-Dimethoxyethane, andDimethylsulfoxide at Different Temperatures", Journal of Chemical and Engineering, vol.52,pp.1630-1637,2007.
- [17] Carolina Bermúdez-Salguero, Jesús Gracia-Fadrique, Encina Calvo, and Alfredo Amigo, "Densities, Refractive Indices, Speeds of Sound, and Surface Tensions for Dilute Aqueous Solutions of 2-Methyl-1-propanol, Cyclopentanone, Cyclohexanone, Cyclohexanol, and Ethyl Acetoacetate at 298.15 K", Journal of Chemical & Engineering, vol. 56 (10), pp.3823-3829,2011.
- [18] Ervin VQrtesi, "Viscosity of Ortho-Substituted Aromatic Amines", J. Chem. Eng., vol 25, pp.387-388,1980.
- [19] Jui-Tang Chen, Wong-Chao Chang, "Densities and viscosities of propylene glycol", J. Chem. Eng., Vol.50, pp.1753-1756, 2005.
- [20] Jaganath, A.P.Dixit, "Ultrasonic velocities in, and adiabatic compressibilities and excess volumes for, binary liquid mixtures of acetone with tetrachloroethylene, trichloroethylene, methylene chloride, 1,2-dichloroethane, and cyclohexane" J. Chem. Eng., vol.29, pp.313,1984.
- [21] K.C. Reddy, S.V. Subramanyam, J. Bhimasenachar, "Ultrasonic behaviour of binary liquid mixtures containing triethylamine", Part 1, Trans Faraday Soc., vol.58,pp. 2352-2359,1962.
- [22] R.J. Fort, W.R. Moore, "Viscosities of binary liquids mixtures", Trans. Faraday Soc. Vol.62, pp.1112-1119,1966.
- [23] T.N. Aminabhavi and B. Gopalkrishna, "Densities, viscosities, refractive-indexes, and speeds of sound of the binary-mixtures of (2-methoxyethyl) ether with nonane, decane, dodecane, tetradecane, and hexadecane at 298.15-k, 308.15-k, and 318.15-k", J. Chem. Eng., vol.39, pp.529,1994.
- [24] R. Meyer, M. Meyer, J. Metzger, and A. Peneloux, "Thermodynamics and physicochemical properties of binary solvent", Chem. Phys., vol. 62, pp.406,1971.
- [25] T.M. Reed, T.E. Taylor, "Viscosities of liquid mixtures", J. Phys. Chem., vol 63,pp 58-67,1959.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 11, November 2014

- [26] A. Krishnaiah, D.N. Rao, P.R. Naidu, "Ultrasonic studies of binary mixtures of chlorobenzene with acetonitrile and propionitrile", Indian J. Chem., vol.21A, pp. 290-292,1982.
- [27] P. Venkatesu, M.V. P. Rao, "Excess volumes of N,N Dimethyl formamide with ketones at 303.15K", J. Chem. Eng., vol. 41, pp.1059 - 1060,1996.
- [28] T. Ramanujappa, J.A. Bhavani, E. Raja Gopal, N. ManoharaMurthi, "Excess sound velocity and excess specific acoustic impedance of (2, 2,2-trifluoroethan-1-ol+benzene), (benzene+dimethyl sulphoxide) and (2,2,2-trifluoroethan-1-ol+dimethyl sulphoxide) at 298.15 K" Indian. J. Pure Appl. Phys., Data 38,301-305(2000).
- [29] Reddy, Y., Naidu, P.S., RavindraPrasad, K., "Ultrasonic study of acetophenone in the binary mixtures containing isopropanols as common component", Indian. J. Pure Appl. Phys., vol.32, pp.958-963,1994.
- [30] O. Redlich, A.T. Kister, "Thermodynamics of non-electrolytic solutions. Algebraic representation of Thermodynamic properties and the classification of solutions", Ind. Eng. Chem., vol. 40, pp. 345-348,1948.
- [31] L. Grunberg, A.H. Nissan, "Mixture law for viscosity", Nature, vol.164, pp.799-800,1949.
- [32] P.K. Katti, M.H. Chaudhri, "Viscosities of binary mixtures benzyl acetate with dioxane, aniline and m-cresol", J Chem Eng., vol. 9, pp. 442 - 443,1964.
- [33] R.K. Hind, E. McLaughlin, A. Ubbelohde, "Structure and viscosity of liquid camphor and pyrene mixtures", Trans Faraday soc., vol.56, pp.328 - 330,1960.