# EXCESS MOLAR VOLUMES, SPEEDS OF SOUND AND VISCOSITIES FOR BINARY MIXTURES OF 2-METHYLANILINE WITH SELECTED DI- AND TRI -CHLOROSUBSTITUTED BENZENE AT VARIOUSTEMPERATURES- COMPARISON WITH PRIGOGINE-FLORYPATTERSON THEORY 

Muvva Raghavendra ${ }^{1}$, A. Venkatesulu ${ }^{2}$, K. Samba Siva Rao ${ }^{3}$ and K. Ravindhranath ${ }^{4}$<br>${ }^{1}$ Department of Physics, Rayalaseema University, Kurnool, Andhra Pradesh, India<br>${ }^{2}$ Department of Physics, Government First Grade College, Hosakote, Bangalore Rural, Karnataka, India<br>${ }^{3}$ Department of Physics, J.K.C.C. Acharya Nagarjuna University, Guntur, Andhra Pradesh, India<br>${ }^{4}$ Department of Chemistry, K L University, Guntur, Andhra Pradesh, India<br>E-Mail: venkatesuluadavala@gmail.com


#### Abstract

The densities $(\rho)$, speeds of sound $(u)$, and viscosities $(\eta)$ are reported for binary mixtures of 2-methylaniline with di- and tri- chloro substituted benzenenamely,1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene over the entire composition range at $\mathrm{T}=(303.15-318.15) \mathrm{K}$ and at atmospheric pressure 0.1 MPa . The excess properties such as excess molar volume, excess isentropic compressibility and deviation in viscosity are calculated from the densities, speeds of sound and viscosities. The excess functionsare correlated by the Redlich - Kister equation. The partial molar volumes, partial molar isentropic compressibilities, excess partial molar volumes and excess partial molar isentropic compressibilities are calculated for all the binary systems throughout the composition range and at infinity dilutions. The $V^{E}$ results are analyzed in the light of Prigogine-Flory-Patterson theory. Analysis of each of the three contributions namely, interactional, free volume and $P^{*}$ contribution to $V^{E}$ has shown that the interactional contribution is positive for all systems and the free volume and $P^{*}$ contributions are negative for all the mixtures. The variations of these parameters with composition and temperature are discussed in terms of intermolecular interactions prevailing in these mixtures.


Keywords: density, speed of sound, viscosity, 2-methylaniline, di- and tri- chloro substituted benzene, charge-transfer complexes, PFP theory.

## 1. INTRODUCTION

When two liquids are mixed together, the resulting changes in physical and thermodynamic properties can be considered as a sum of several contributions due to free volume change, change in energy, change in molecular orientations and steric hindrances. The mixing of different compounds gives rise to solutions that generally do not behave as ideal solutions. In terms of interactions, when unlike interactions are equal to like interactions, then the resulting solution is said to be an ideal solution. The deviation from ideality is expressed by many thermodynamic variables particularly by excess or residual extensive properties [1,2]. Excess thermodynamic properties of mixtures are useful in the study of molecular interactions and arrangements. Thermodynamic properties derived from the measurement of speed of sound, density and viscosity for binary mixtures are useful in understanding the nature and type of intermolecular interactions between the component molecules [3,4].

The liquid components selected for binary liquid mixtures are known organic liquids with a wide range of applications in various fields of chemistry in addition to their use in industries and routine analytical work. In the present work, the binary blends of 2-methylaniline with diand tri- chloro substituted benzene are chosen for assessing the thermodynamic properties because these compounds assume wide utility. 2-methylaniline is a wellknownpolar solvent and is endowed with self-association
through hydrogen bonding of its amine group and it is used as an intermediate in the production of a number of products such as agricultural chemicals, azo dyes and pigments, bactericide or biocide and pharmaceuticals.1,2dichlorobenzene is used as an intermediate for dyes, and certain agriculture chemicals. 1,3-dichlorobenzene is widely used in the manufacture of polyresin, making deodorant block for garbage cans and in making mothballs. 1,2,4-trichlorobenzene is used in the manufacture of some the herbicide and pesticides and as a dye carrier in dielectric field. Further, it is used as an organic intermediate in the synthesis of some industrially important compounds and also a solvent in lubricants. Therefore, thermodynamic properties of 2-methylaniline + di- and tri- chlorosubstituted benzene are of interest because 2-methylanilineprovides an $-\mathrm{NH}_{2}$ group and diand tri - chloro substituted benzene provides a chloro group for interactions.

To gain some understanding about the nature of interactions in 2-methylaniline + di- and tri chlorosubstituted benzene mixtures, properties such as density ( $\rho$ ), speed of sound (u) and viscosity ( $\eta$ ) are measured in the temperature interval of $303.15-318.15 \mathrm{~K}$. Several researchers investigated density, speed of sound, and viscosity of binary mixtures of 2-methylanilinewith substituted benzene[5],o-toluidine with toluene + xylene [6], o-toluidine withxylenes[7] and o-toluidine with pyridine and picolines [8]. However, literature survey reveals hardly any study on excess thermodynamic
properties for the systems containing 2-methylaniline with di- and tri- chloro substituted benzene. The endeavour of the present work is to probe the influence of chloro group and its orientation in benzene molecules on the sign and magnitude of excess properties when di- and tri- chloro substituted benzene are mixed with 2 -methylaniline. .The present investigation is a continuation of our earlier research [9] on thermodynamic properties of binary liquid mixtures. In this paper, we report measurements of densities, speeds of sound and viscosities for three binary systems, 2 -methylaniline+ $\quad 1,2$-dichlorobenzene,2-methylaniline+1,3-dichlorobenzene and 2-methylaniline+ 1,2,4-trichlorobenzene at temperature (T) of 303.15318.15 K and atmospheric pressure0.1MPa.From the experimental data, various physicochemical parameters, $v i z ., V_{\mathrm{m}}^{\mathrm{E}}, \kappa_{\mathrm{s}}^{\mathrm{E}}, \Delta \eta$ and $G^{*}{ }^{E}$ of the mixtures; $\bar{V}_{\mathrm{m}, 1}, \bar{V}_{\mathrm{m}, 2}$, $\bar{K}_{\mathrm{s}, \mathrm{m}, 1}, \bar{K}_{\mathrm{s}, \mathrm{m}, 2}, \quad \bar{V}_{\mathrm{m}, 1}^{\mathrm{E}}$ and $\quad \bar{V}_{\mathrm{m}, 2}^{\mathrm{E}}, \bar{K}_{\mathrm{s}, \mathrm{m}, 1}^{\mathrm{E}}, \bar{K}_{\mathrm{s}, \mathrm{m}, 2}^{\mathrm{E}} \quad$ over whole composition range; $\bar{V}_{\mathrm{m}, 1}^{\circ}, \bar{V}_{\mathrm{m}, 2}^{\circ}, \bar{K}_{\mathrm{s}, \mathrm{m}, 1}^{\circ}, \bar{K}_{\mathrm{s}, \mathrm{m}, 2}^{\circ}$, $\bar{V}_{\mathrm{m}, 1}{ }^{\mathrm{E}}, \bar{V}_{\mathrm{m}, 2}{ }^{\mathrm{E}}, \bar{K}_{\mathrm{s}, \mathrm{m}, 1}^{\mathrm{O}}$ and $\bar{K}_{\mathrm{s}, \mathrm{m}, 2}{ }^{\mathrm{E}}$ of the components in the mixture at infinite dilution, have been calculated. The variations of these properties with composition of the binary mixtures are discussed in terms of molecular interactions between components and structural effects.

## 2. EXPERIMENTAL

Chemicals used in the present study were 2 methylaniline (Sigma Aldrich), 1,2-dichlorobenzene, 1,3dichlorobenzene, and 1,2,4-trichlorobenzeneand these chemicals were purchased from S.D. Fine Chemicals Ltd.1,2-dichlorobenzene was passed through alumina in a $30 \times 2 \mathrm{~cm}$ column and fractionally distilled.1,3dichlorobenzene was washed successfully with $10 \%$ sodium hydroxide solution and then with water until the washings were neutral, dried, and fractionated.1,2,4Trichlorobenzene was purified by repeated fractional distillation and stored in the dark with the vapor phase in contact with anhydrous magnesium perchlorate. 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 Karl-Fischer method. The details of the chemicals and pertaining purification methods were presented in Table-1.

### 2.2 Apparatus and procedure

All the binary liquid mixtures were prepared by weighing appropriate amount of pure liquids on an Afcoset-ER-120A electric balance-using syringe in narrow mouth stoppered bottle. The uncertainty of electronic balance was $\pm 0.05 \mathrm{mg}$ while the accuracy of the mole fraction was $\pm 1 \times 10^{-4}$

Density and speed of sound of the pure liquids as well as their binary mixtures were measured using an automatic digital vibrating tube density and speed of sound Analyzer (Anton Parr, DSA 5000M). The
instrument was first calibrated by comparing the density and speed of sound of the distilled water and dry air with the literature. The operating frequency for speed of sound measurements was 3 MHz . The uncertainties associated with the measurements for temperature, density and speed of sound were estimated to be within $\pm 0.01 \mathrm{~K}, \pm 0.5 \times 10$ ${ }^{3} \mathrm{~g} \cdot \mathrm{~cm}^{-3}$ and $\pm 0.5 \mathrm{~m} \cdot \mathrm{~s}^{-1}$ respectively. The viscosities of pure liquids and their mixtures were determined at atmospheric pressure at $\mathrm{T}=(303.15-318.15) \mathrm{K}$ by using an Ubbelohde viscometer, which was calibrated with benzene, carbon tetrachloride, acetonitrile and doubly distilled water.

The details of the methods and measurement techniques were described elsewhere [10]. An electronic digital stopwatch with an uncertainty of $\pm 0.01 \mathrm{~s}$ was used for flow time measurements. The experimental uncertainty of viscosity was estimated as $\pm 1.14 \%$ and the uncertainty of temperature $\pm 0.1 \mathrm{~K}$. The purity of all these solvents were compared with the measured densities, speeds of sound and viscosities of the pure liquids with the literature [11-15] and these were enlisted in the Table-2.

## 3. RESULTS AND DISCUSSIONS

The experimental densities and viscosities for all the binary systems at various compositions are used to calculate the excess thermodynamic functions using following equations:
$\mathrm{V}^{\mathrm{E}} / \mathrm{m}^{3} \cdot \mathrm{~mol}^{-1}=\left[\mathrm{x}_{1} \mathrm{M}_{1}+\mathrm{x}_{2} \mathrm{M}_{2}\right] / \rho-\left[\mathrm{x}_{1} \mathrm{M}_{1} / \rho_{1}+\mathrm{x}_{2} \mathrm{M}_{2} / \rho_{2}\right]$
$\Delta \eta / \mathrm{mPa} \cdot \mathrm{s}=\eta-\left(x_{1} \eta_{1}+x_{2} \eta_{2}\right)$
$\mathrm{G}^{* \mathrm{E}} / \mathrm{J} \cdot \mathrm{mol}^{-1}=\mathrm{RT}\left[\ln \eta \mathrm{V}-\left(\mathrm{x}_{1} \ln \eta_{1} \mathrm{~V}_{1}+\mathrm{x}_{2} \ln \eta_{2} \mathrm{~V}_{2}\right)\right]$
Where $\rho, \eta$ and $V$ are density, viscosity and molar volume of the binary mixture. $x_{1}, M_{1}, \rho_{1}, \eta_{1}, V_{l}$ and $x_{2}, M_{2}$, $\rho_{2}, \eta_{2}, V_{2}$ are the mole fraction, molar mass, density, viscosity and molar volume of pure components 1 and 2 respectively. $R$ is the gas constant and T is the absolute temperature

The experimental data is used to compute isentropic compressibility $\left(\kappa_{s}\right)$ by using the following relation:
$\kappa_{s}=\left(u^{2} \rho\right)^{-1}$
The method used for calculating $\kappa_{s}^{E}$ (Benson Kiyohara approach) is outlined previously [16].
$\mathrm{V}^{\mathrm{E}}, \kappa_{s}^{E}$ and $\Delta \eta$ values are fitted to a Redlich Kister[17] polynomial equation,
$Y^{\mathrm{E}}=x_{1} x_{2} \sum_{i=0}^{j} A_{i}\left(1-2 x_{1}\right)^{i}$
Where $Y^{E}$ is the $\mathrm{V}^{\mathrm{E}}, \kappa_{s}^{E}$ and $\Delta \eta$. Values of the coefficients $A_{i}$ have been determined by using the method of least - squares. The standard deviations $\sigma\left(Y^{E}\right)$ have been calculated by using the formula
$\sigma\left(\mathrm{Y}^{\mathrm{E}}\right)=\left[\Sigma\left(\mathrm{Y}_{\text {exp }}^{\mathrm{E}}-\mathrm{Y}_{\text {cal }}^{\mathrm{E}}\right)^{2} /(\mathrm{m}-\mathrm{n})\right]^{1 / 2}$
where m is the total number of experimental points and n is the number of parameters. The coefficients, $A_{i}$ and corresponding standard deviation values $(\sigma)$ are presented in Table-5.

The experimental values of density ( $\rho$ ), viscosity $(\eta)$ and speed of sound $(u)$ of the binary liquid mixtures of 2-methylaniline with di- and tri- chloro substituted benzene at temperatures $\mathrm{T}=(303.15$ to 318.15$) \mathrm{K}$ are given in Table-3. The excess molar volume ( $\mathrm{V}^{\mathrm{E}}$ ), excess isentropic compressibility ( $\kappa_{\mathrm{s}}^{\mathrm{E}}$ ), deviation in viscosity $(\Delta \eta)$, and excessGibbs energy of activation of viscous flow $\left(G^{* E}\right)$ values are given in Table-4. The plots of $V^{\mathrm{E}}$, $\kappa_{\mathrm{S}}^{\mathrm{E}}, \Delta \eta$ and $G^{* E}$ against mole fraction $\left(\mathrm{x}_{1}\right)$ at 303.15 K are presented in Figures 1-4, respectively. The excess or deviation values reflect the interaction between the mixing species and the extent of interaction is mainly depend upon the composition, different molecular sizesand shapes of the components and temperatures.

In general, the sign of $V^{E}$ depends upon the relative magnitude of contractive and expansive effects that arise on mixing of the components. The factors that cause contraction on mixing are:
a) Free volume and $\mathrm{P}^{*}$ effects
b) Strong physical interactions, such as dipole-dipole interactions, charge-transfer complexes
c) Favourable geometrical fitting of one component into other
d) Occupation of void spaces of one component by the other

This is expected when the molecular sizes of the compounds differ by a large magnitude.

The factors that cause expansion of volume on mixing of the components are:
a) Dissociation of one component or both of the components.
b) Steric hindrance
c) Disruption of homo molecular associations
d) Formation of weaker solute-solvent bonds than solutesolute and solvent-solvent bonds

The experimental data in the present study suggest that the factors, which are responsible for contraction in volume, are dominant in all the binary mixtures over the entire composition range at temperature from 303.15 K to 318.15 K .

An examination of data in the Table-4 (Figure-1) suggests that the excess molar volume $\left(\mathrm{V}^{\mathrm{E}}\right)$ data for all binary systems are negative over the entire composition range at temperatures from 303.15 K to 318.15 K and at atmospheric pressure.

It is clear that the negative values of $\mathrm{V}^{\mathrm{E}}$ for all binary mixtures is due to the free volume and $\mathrm{P}^{*}$ effects, which include size and shape of the components. The negative value of $\mathrm{V}^{\mathrm{E}}$ than the free volume and $\mathrm{P}^{*}$ effects values for the present mixtures suggest that the dipoledipole interactions between the component liquids of the mixtures resulting in the formation of electron donoracceptor complexes[18] and further, the hetero molecular association between unlike molecules dominate over the homo molecular association between like molecules.

The difference in $\mathrm{V}^{\mathrm{E}}$ values observed between diand tri- chloro substituted benzene is probably because of the difference in their shapes, which lead to different alignments in the liquid mixtures. Further, the chlorine atom at the $4^{\text {th }}$ position in $1,2,4$ - trichlorobenzene offers, the least steric hindrance to 2-methylanilinemolecules and thus the electron donor - acceptor interactions in it are lower than those of 1, 2-dichlorobenzene and 1, 3dichlorobenzene.

The values of $\mathrm{V}^{\mathrm{E}}$ for the binary mixtures of 2methylanilinewith di- and tri - chloro substituted benzene fall in the following order:
1,2-dichlorobenzene < 1,3-dichlorobenzene < 1, 2, 4trichlorobenzene

The $\pi$ - electron density in derivatives of benzene ring depends upon the group that is attached to it. The hetero molecular interactions between the component molecules depend upon the net electron density in the ring. Further, these interactions seem to depend upon therelative orientation of the two groups in the ring. As the separation between the two groups' increases, the intermolecular interaction is expected to decrease. The intermolecular interaction in ortho isomer causes a large strain in the ring, causing an opposite pole at ortho side of the ring and thus giving a dipolar character, than Meta and para derivatives. Thus, the intermolecular interactions in ortho position become stronger than the Meta and para isomers due to stronger polar character. Hence, theabove order is justified.

A perusal of Table-4 shows that the $\mathrm{V}^{\mathrm{E}}$ values become more negative as the temperature is increased from 303.15 K to 318.15 K . This indicates a gradually decreasing trend in the degree of the inter hydrogen bonds in the associated 2-methylaniline molecules as the experimental temperature increases and dipole-dipole interactions between the hetero molecules are increased leading to greater contraction in the mixture volumes[19].

In general, $\kappa_{\mathrm{s}}^{\mathrm{E}}$ values depend upon two factors: (i) increase in free length, defined by Jacobson [20] due to loss of dipolar association, breaking up of hydrogen bonding and difference in size and shapes of the component molecules and (ii) decrease in free-length as a result of dipole-dipole interactions, hydrogen bonding association and complex formation between the component molecules [21,22]. The first effect contributes
to the increase in interspaces between molecules in mixtures. Consequently, sound waves cover smaller distances in mixtures than as pure components. This would result in negative deviation in speed of sound and positive deviation in isentropic compressibility. The second effect contributes to the decrease in interspaces between molecules in mixtures. Consequently, sound waves cover larger distances in mixtures than in pure components. This would result in positive deviation in speed of sound and negative deviation in isentropic compressibility. The experimental value indicates that the negative contribution predominates in these mixtures.

The excess isentropic compressibility is negative over the entire range of composition, as indicated by curves in Figure-2 and the data included in Table-4. Itis observed that the negative values of $\kappa_{s}^{E}$ for all binary mixtures can be explained on the basis of strong hetero molecular associations, complex formation through dipole-dipole interactions between unlike molecules, structural reorganization that leads to close packing, etc. [23].In the present investigation, there is a possibility of electron donor - acceptor interactions leading to complex formation between nitrogen atom of amino group of 2methoxyaniline molecule, which acts as donor, and the $\pi$ electrons of benzene ring of aromatic hydrocarbons, which act as acceptor resulting in negative $\kappa_{s}^{E}$ values [24].

The values of $\kappa_{\mathrm{s}}{ }^{\mathrm{E}}$ for the binary mixtures of 3chloroaniline with di / tri chlorobenzenes fall in the order: 1,2-dichlorobenzene < 1,3-dichlorobenzene < 1, 2, 4trichlorobenzene

The above order suggests that the dipole moments of the pure solvents are influencing the $V^{\mathrm{E}}$ data of the binary liquid mixtures. The dipole moments are 2methylaniline: $1.60 \mathrm{D}, 1,2$-dichlorobenzene: $2.77 \mathrm{D}, 1,3-$ dichlorobenzene: 1.89 D and 1, 2, 4-trichlorobenzene: 0.8109 D. The more negative $\mathrm{V}^{\mathrm{E}}$ data of $1,2-$ dichlorobenzene when compared with other chloro substituted benzenes are due to its high dipole moment that leads to stronger dipole - dipole interactions. This type of behaviour is reported earlier [25].Hence, the above order may be justified [26, 27].

A perusal of Table- 4 shows that the values of $\Delta \eta$ are positive over the entire range of composition in all the binary mixtures at temperatures from 303.15 K to 318.15 K. These may be attributed to the irregular shape, size and packing of molecules between unlike molecules, for which the molecular interactions increases [28].Further, the viscosity of a mixture [29] depends on the molecular interactions between the components mixture with strong interactions between different molecules show positive viscosity deviations, while for mixtures without specific interactions, viscosity deviations are negative. The positive viscosity deviations in the present investigation suggest the involvement of specific interactions between component molecules over the entire composition range in all the binary mixtures [30]. The positive $\Delta \eta$ values for 2methylaniline + isomeric chlorobenzenes increase with increase in temperature, suggesting an increase in specific
molecular interaction between unlike molecules due to thermal energy.

The data presented in Figure-4 and Table4,indicate that excess Gibbs energy of activation of viscous flow values is positive for three binary mixtures over the entire composition range at all investigated temperatures. The positive values of excess Gibbs energy of activation of viscous flow for the binary systems investigated suggest the intermolecular association through dipole-dipole interactions between isomeric chlorobenzenes and2-methylaniline molecules. The positive values of excess Gibbs energy of activation of viscous flow decrease with the increase in temperature in all these systems.

## 4. PARTIAL MOLAR PROPERTIES

The interpretations of excess partial molar properties $\left(\bar{V}_{\mathrm{m}, 1}^{\mathrm{E}}, \bar{V}_{\mathrm{m}, 2}^{\mathrm{E}}, \bar{K}_{\mathrm{s}, \mathrm{m}, 1}^{\mathrm{E}}\right.$ and $\left.\bar{K}_{\mathrm{s}, \mathrm{m}, 2}^{\mathrm{E}}\right)$ and excess partial molar properties at infinite dilution $\left(\bar{V}_{\mathrm{m}, 1}{ }^{\mathrm{E}}, \bar{V}_{\mathrm{m}, 2}{ }^{\mathrm{E}}\right.$ $\bar{K}_{\mathrm{s}, \mathrm{m}, 1}{ }^{\mathrm{E}}$ and $\bar{K}_{\mathrm{s}, \mathrm{m}, 2}{ }^{\mathrm{E}}$ ) of components 2 havepreviously been described [10].

A close perusal of Table-6 indicates that the values of $\bar{V}_{\mathrm{m}, 1}^{\mathrm{E}}$ and $\bar{V}_{\mathrm{m}, 2}^{\mathrm{E}}$ are negative for all the binary mixtures over the whole composition range. This indicates the formation of hydrogen bond complexes (NH.... $\pi$ ) between unlike molecules in the mixtures.

From the Table-6, it may be inferred that the values of $\bar{K}_{s, m, 1}^{\mathrm{E}}$ and $\bar{K}_{\mathrm{s}, \mathrm{m}, 2}^{\mathrm{E}}$ are negative for all the binary mixtures over the whole composition range. The negative values indicate that the $n-\pi$ interactions between unlike molecules in binary liquid mixtures.

From the Table-7, it can be seen that the values of $\bar{V}_{\mathrm{m}, 1}{ }^{\mathrm{E}}$ and $\bar{V}_{\mathrm{m}, 2}{ }^{\mathrm{E}}$ are negative for all the binary mixtures over the whole composition range. The negative $\bar{V}_{\mathrm{m}, 1}{ }^{\mathrm{E}}$ and $\bar{V}_{\mathrm{m}, 2}{ }^{\mathrm{E}}$ $V_{\mathrm{m}, 2}$ values indicate that the donor-acceptor interactions between unlike molecules in binary liquid mixtures.

It is seen from the Table-7 that the values of $\bar{K}_{\mathrm{s}, \mathrm{m}, 1}{ }^{\mathrm{E}}$ and $\bar{K}_{\mathrm{s}, \mathrm{m}, 2}{ }^{\mathrm{E}}$ are negative for all the binary systems at each investigated temperature. The negative values may be due to complex formation through dipole-dipole or electron donor-acceptor interactions between unlike molecules in the binary mixtures [29,30].

### 4.1Prigogine-Flory-Patterson theory

The Prigogine-Flory-Patterson theory considers excess thermodynamic properties of binary mixtures to be the sum of different contributions [33-35]. The excess molar volume can be expressed as: an interactional term which is proportional to the interaction parameter, $\chi_{12}$ a free volume contribution which arises from the dependence of the reduced volume upon the reduced temperature as a result of the differences between the degrees of thermal expansion of the components and an
www.arpnjournals.com
internal pressures and of the reduced volumes of the components.
$\frac{V^{E}}{x_{1} V_{1}^{*}+x_{2} V_{2}^{*}}=\cdot \frac{\left(\tilde{V}^{1 / 3}-1\right) \tilde{V}^{2 / 3}}{\left[(4 / 3) \tilde{V}^{-1 / 3}-1\right]} \Psi_{1} \theta_{2}\left(\frac{\chi_{12}}{P_{1}^{*}}\right)$
int.contribution $)-\frac{\left(V_{1}-V_{2}\right)^{2}\left[(14 / 9) \tilde{V}^{-1 / 3}-1\right] \Psi_{1} \Psi_{2}}{\left[(4 / 3) \tilde{V}^{-1 / 3}-1\right) \tilde{V}}$
(fv.contribution) $+\frac{\left(\tilde{V}_{1}-\tilde{V}_{2}\right)\left(P_{1}^{*}-P_{2}^{*}\right)}{P_{1}^{*} \Psi_{2}+P_{2}^{*} \Psi_{1}} \Psi_{1} \Psi_{2}$
( $P^{*}$ contribution)
The reduced volume of pure component $\tilde{V}_{i}$ was calculated from the isobaric thermal expansively $\alpha_{i}$ by equation:
$\tilde{\mathrm{V}}_{i}=\left(\frac{1+\left(\frac{4}{3}\right) \alpha_{i} T}{1+\alpha_{i} T}\right)$
The $\tilde{V}$ of mixture is approximated in equation (8)
by
$\tilde{V}=\Psi_{1} \tilde{V}_{1}+\Psi_{2} \tilde{V}_{2}$
The molecular contact energy fraction of components $\Psi_{1}$ is given by
$\Psi_{1}=1-\Psi_{2}=\frac{\phi_{1} P_{1}^{*}}{\phi_{1} P_{1}^{*}+\phi_{2} P_{2}^{*}}$
The characteristic volume is $V_{i}^{*}=V_{i}^{*} / \tilde{V}_{i}$ and the characteristic pressure is given by
$P_{i}^{*}=\frac{T \tilde{v}_{2}^{2} \alpha_{i}}{\mathrm{~K}_{T i}}$
where $\kappa_{T i}$ is the isothermal compressibility of pure component $i$.

The hard-core volume fractions of the components 1 and $2\left(\phi_{1}\right.$ and $\left.\phi_{2}\right)$ are defined by
$\phi_{1}=1-\phi_{2}=\frac{x_{1} V_{1}^{*}}{x_{1} V_{1}^{*}+x_{2} V_{2}^{*}}$

The $\kappa_{T}$ values were calculated from the following expression,
$\kappa_{T}=\kappa_{S}+\frac{T V \alpha^{2}}{C_{P}}$
The $\chi_{12}$ parameter required for the calculation of $V^{E}$ using Flory-Patterson theory are derived by fitting the $V^{E}$ expression to the experimental equimolar value of $V^{E}$ for each system investigated. The calculated equimolar value of the three contributions together with the $\chi_{12}$ parameter for each system is listed in Table-8. The comparison of experimental $V^{E}$ values with those calculated from PFP is shown graphically in Figure-5.

An analysis of each of the three contributions to $V^{E}$ has shown that the interactional contribution is positive for all systems, the free volume and $\mathrm{P}^{*}$ contributions are negative for all the mixtures. It is clear from Table-7 that the dominant role is played by the free volume and $\mathrm{P}^{*}$ contributions and these are the main parameters for deciding the sign and magnitude of excess volumes for 2methoxyaniline + di- and tri - chlorosubstituted benzene mixtures.

## 5. CONCLUSIONS

This paper reports experimental data of densities, speeds of sound and viscosities of binary blends of 2 methoxyaniline with di- and tri- chlorosubstituted benzene (1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,2,4trichlorobenzene) over the entire composition range at $\mathrm{T}=$ (303.15 - 318.15) K with 5 K intervals. From the experimental data, various physicochemical parameters, $v i z ., V_{\mathrm{m}}^{\mathrm{E}}, \kappa_{\mathrm{S}}^{\mathrm{E}}$ and $\Delta \eta$ of the mixtures, the excess partial molar properties $\left(\bar{V}_{\mathrm{m}, 1}^{\mathrm{E}}, \bar{V}_{\mathrm{m}, 2}^{\mathrm{E}}, \quad \bar{K}_{\mathrm{s}, \mathrm{m}, 1}^{\mathrm{E}}\right.$ and $\left.\bar{K}_{\mathrm{s}, \mathrm{m}, 2}^{\mathrm{E}}\right)$ and excess partial molar properties at infinite dilution $\left(\bar{V}_{\mathrm{m}, 1}{ }^{\mathrm{E}}\right.$, $\bar{V}_{\mathrm{m}, 2}{ }^{\mathrm{E}} \bar{K}_{\mathrm{s}, \mathrm{m}, 1}{ }^{\mathrm{E}}$ and $\bar{K}_{\mathrm{s}, \mathrm{m}, 2}{ }^{\mathrm{E}}$ ) of components are calculated. The results are analyzed in terms of intermolecular interactions through dipole-dipole and donor-acceptor interactions between 2-methoxy aniline and di- and tri chlorosubstituted benzene molecules. Moreover, the $V^{E}$ values are analyzed with Prigogine- Flory-Patterson theory and shown that the free volume and $\mathrm{P}^{*}$ contributions is the main factor for negative values of excess molar quantities.
www.arpnjournals.com


Figure-1. Curves of excess volume $\left(V^{E}\right)$ with mole fraction for the binary mixtures of 2-methylaniline + 1, 2, 4-trichlorobenzene (!); 1, 3-dichlorobenzene (,) and

1, 2-dichlorobenzene ( $\mathbf{\Delta}$ ) at 303.15 K


Figure-2. Curves of excess isentropic compressibility ( $\kappa_{s}^{E}$ ) with mole fraction for the binary mixtures of 2-methylaniline + 1, 2, 4-trichlorobenzene (!); 1, 3-dichlorobenzene(,) and $\quad 1,2$-dichlorobenzene $(\mathbf{\Delta})$ at 308.15 K
www.arpnjournals.com


Figure-3. Curves of deviation in viscosity $(\Delta \eta)$ with mole fraction for the binary mixtures of 2-methylaniline + 1, 2, 4-trichlorobenzene (!); 1, 3-dichlorobenzene (,) and

1, 2-dichlorobenzene ( $\mathbf{\Delta}$ ) at 303.15 K


Figure-4. Excess Gibbs energy of activation of viscous flow $\left(G^{* E}\right)$ with mole fraction $\left(\mathrm{x}_{1}\right)$ of 2-methylaniline + 1, 2, 4-trichlorobenzene (!); 1, 3-dichlorobenzene (,) and

1, 2-dichlorobenzene ( $\mathbf{\Delta}$ ) at 303.15 K
www.arpnjournals.com


Figure-5. Curves of excess volume $\left(V^{E}\right)$ with mole fraction for the binary mixtures of
2-methylaniline + 1, 2, 4-trichlorobenzene (!); 1, 3-dichlorobenzene (,);
1,2 -dichlorobenzene $(\boldsymbol{\Delta})$ and (-----) calculated with PFP theory at 303.15 K
Table-1. Provenance and purity of the materials used in this work.

| Chemical name | CAS Number | Source | $* *$ Water <br> content <br> $\%$ | Purification <br> method | *Analysis <br> method | Purity in <br> mass fraction |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2-methylaniline | $95-53-4$ | Sigma Aldrich India | 0.042 | no purification | GC | 0.9975 |
| 1,2-dichlorobenzene | $95-50-1$ | S.D. fine Chemicals, <br> India | 0.035 | fractional <br> distillation | GC | 0.9960 |
| 1,3-dichlorobenzene | $541-73-1$ | S.D. Fine Chemicals, <br> India | 0.040 | fractional <br> distillation | GC | 0.9955 |
| $1,2,4$-trichlorobenzene | $120-82-1$ | S.D. Fine Chemicals, <br> India | 0.038 | fractional <br> distillation | GC | 0.9970 |

*Gas Chromatography;
** Karl-Fischer method
Table-2. Comparison of experimental and literature values of density ( $\rho$ ), speed of sound (u) and viscosity ( $\eta$ ) data of pure components at $T=303.15$ Kand 0.1MPa pressure.
*298.15 K

|  | density $(\mathbf{\rho}) \mathbf{g} \cdot \mathbf{c m}^{-3}$ |  | Viscosity $(\boldsymbol{\eta}) / \mathbf{m P a} \cdot \mathbf{s}$ |  | speed of <br> sound $(\mathbf{u}) / \mathbf{m} \cdot \mathbf{s}^{\mathbf{- 1}}$ |  | $\mathbf{C p /} / \mathbf{J ~ K}^{-\mathbf{1}} \mathbf{m o l}^{-\mathbf{1}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Pure <br> components | Experimental | Literature | Experimental | Literature | Experimental | Literature |  |
| 2-methylaniline | 0.99019 | $0.9901[12]$ | 3.258 | $3.31 *[13]$ | 1578.5 | $1579.0[12]$ | $218.43[11]$ |
| $1,2-$ <br> dichlorobenzene | 1.29540 | $1.29472[14]$ | 1.238 | $1.235[14]$ | 1263.0 | $1265.0[14]$ | $171.76[15]$ |
| $1,3-$ <br> dichlorobenzene | 1.27778 | $1.27779[14]$ | 0.945 | $0.946[14]$ | 1235.0 | $1238.0[14]$ | $171.25[15]$ |
| $1,2,4-$ <br> trichlorobenzene | 1.44242 | $1.44243[14]$ | 1.762 | $1.760[14]$ | 1255.0 | $1256.0[14]$ | $195.92[15]$ |

The standard uncertainties are $u(\rho)= \pm 0.5 \times 10^{-3} \mathrm{~g} \cdot \mathrm{~cm}^{-3}, \mathrm{u}(\mathrm{u})= \pm 0.5 \mathrm{~m} \cdot \mathrm{~s}^{-1} \mathrm{u}(\eta) \pm 1.14 \%, \mathrm{u}(\mathrm{T})=0.01 \mathrm{~K}$ for density, speed of sound, $u(T)=0.1 \mathrm{~K}$ for viscosity and $u(p)=1 \mathrm{kPa}$.

ARPN Journal of Engineering and Applied Sciences
www.arpnjournals.com
Table-3. Density ( $\rho$ ), Viscosity $(\eta)$ and speed of sound $(u)$ of binary liquid mixtures of 2-methylaniline with 1,2dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzeneat $\mathrm{T}=$ (303.15 to 318.15) Kand 0.1 MPa pressure.

| $x_{1}$ | $\rho / \mathrm{g} \cdot \mathrm{cm}^{-3}$ |  |  |  | $\eta / \mathrm{m} \mathrm{Pa} \cdot \mathrm{s}$ |  |  |  | $u / \mathrm{m} \cdot \mathrm{s}^{-1}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 303.15K | 308.15K | 313.15K | 318.15K | 303.15K | 308.15K | 313.15K | 318.15K | 303.15K | 308.15K | 313.15K | 318.15K |
|  |  |  |  |  | 2-methylaniline (1)+ 1,2-dichlorobenzene(2) |  |  |  |  |  |  |  |
| 0.0000 | 1.29540 | 1.28938 | 1.28356 | 1.27785 | 1.238 | 1.150 | 1.060 | 0.974 | 1263.0 | 1243.0 | 1222.0 | 1203.0 |
| 0.0895 | 1.26975 | 1.26393 | 1.25828 | 1.25277 | 1.431 | 1.319 | 1.205 | 1.097 | 1291.3 | 1271.8 | 1251.3 | 1232.6 |
| 0.1795 | 1.24353 | 1.23788 | 1.23240 | 1.22705 | 1.622 | 1.483 | 1.345 | 1.212 | 1319.9 | 1300.4 | 1280.0 | 1261.1 |
| 0.3125 | 1.20415 | 1.19876 | 1.19349 | 1.18834 | 1.899 | 1.721 | 1.546 | 1.378 | 1362.2 | 1342.2 | 1321.6 | 1302.2 |
| 0.4256 | 1.17016 | 1.16498 | 1.15985 | 1.15489 | 2.130 | 1.920 | 1.712 | 1.514 | 1397.9 | 1377.5 | 1356.8 | 1337.2 |
| 0.5169 | 1.14238 | 1.13736 | 1.13237 | 1.12755 | 2.315 | 2.078 | 1.845 | 1.622 | 1426.4 | 1406.1 | 1385.5 | 1365.8 |
| 0.6254 | 1.10897 | 1.10416 | 1.09935 | 1.09471 | 2.531 | 2.263 | 1.999 | 1.747 | 1460.1 | 1440.2 | 1420.0 | 1400.5 |
| 0.7145 | 1.08123 | 1.07657 | 1.07190 | 1.06740 | 2.707 | 2.413 | 2.124 | 1.848 | 1487.7 | 1468.3 | 1448.6 | 1429.5 |
| 0.8102 | 1.05109 | 1.04661 | 1.04207 | 1.03774 | 2.893 | 2.571 | 2.256 | 1.954 | 1517.5 | 1498.6 | 1479.4 | 1460.6 |
| 0.9012 | 1.02209 | 1.01776 | 1.01335 | 1.00914 | 3.069 | 2.719 | 2.379 | 2.052 | 1546.3 | 1527.3 | 1508.3 | 1489.3 |
| 1.0000 | 0.99019 | 0.98599 | 0.98169 | 0.97759 | 3.258 | 2.878 | 2.508 | 2.153 | 1578.5 | 1558.2 | 1538.5 | 1518.5 |
|  |  |  |  |  | 2-methylaniline (1) + 1,3-dichlorobenzene(2) |  |  |  |  |  |  |  |
| 0.0000 | 1.27778 | 1.27225 | 1.26683 | 1.26131 | 0.945 | 0.896 | 0.848 | 0.799 | 1235.0 | 1221.0 | 1206.0 | 1192.0 |
| 0.1053 | 1.24958 | 1.24422 | 1.23895 | 1.23361 | 1.200 | 1.117 | 1.037 | 0.957 | 1267.9 | 1254.0 | 1239.0 | 1225.0 |
| 0.2011 | 1.22347 | 1.21825 | 1.21309 | 1.20789 | 1.430 | 1.316 | 1.205 | 1.097 | 1299.3 | 1285.0 | 1269.7 | 1255.3 |
| 0.3045 | 1.19484 | 1.18975 | 1.18471 | 1.17966 | 1.676 | 1.528 | 1.384 | 1.243 | 1334.1 | 1319.0 | 1303.3 | 1288.2 |
| 0.4064 | 1.16616 | 1.16121 | 1.15626 | 1.15135 | 1.916 | 1.734 | 1.557 | 1.385 | 1368.7 | 1352.9 | 1336.7 | 1320.9 |
| 0.5070 | 1.13743 | 1.13260 | 1.12777 | 1.12300 | 2.149 | 1.934 | 1.724 | 1.521 | 1403.0 | 1386.5 | 1369.8 | 1353.4 |
| 0.6062 | 1.10864 | 1.10397 | 1.09925 | 1.09462 | 2.376 | 2.128 | 1.887 | 1.654 | 1436.7 | 1419.7 | 1402.6 | 1385.8 |
| 0.7041 | 1.07985 | 1.07529 | 1.07069 | 1.06621 | 2.598 | 2.318 | 2.045 | 1.782 | 1470.1 | 1452.6 | 1435.2 | 1418.0 |
| 0.8007 | 1.05102 | 1.04659 | 1.04210 | 1.03776 | 2.814 | 2.502 | 2.198 | 1.905 | 1503.6 | 1485.6 | 1467.8 | 1450.2 |
| 0.9060 | 1.01912 | 1.01482 | 1.01044 | 1.00623 | 3.049 | 2.702 | 2.362 | 2.037 | 1541.7 | 1522.9 | 1504.4 | 1485.9 |
| 1.0000 | 0.99019 | 0.98599 | 0.98169 | 0.97759 | 3.258 | 2.878 | 2.508 | 2.153 | 1578.5 | 1558.2 | 1538.5 | 1518.5 |
|  |  |  |  |  | 2-methylaniline (1) + 1,2,4-trichlorobenzene(2) |  |  |  |  |  |  |  |
| 0.0000 | 1.44242 | 1.43644 | 1.43045 | 1.42449 | 1.762 | 1.617 | 1.472 | 1.329 | 1255.0 | 1240.2 | 1224.6 | 1209.0 |
| 0.0917 | 1.40665 | 1.40083 | 1.39500 | 1.38924 | 1.908 | 1.743 | 1.579 | 1.418 | 1280.2 | 1265.8 | 1250.7 | 1235.5 |
| 0.2069 | 1.36023 | 1.35462 | 1.34896 | 1.34339 | 2.090 | 1.898 | 1.708 | 1.523 | 1313.3 | 1298.6 | 1283.2 | 1267.8 |
| 0.3198 | 1.31311 | 1.30766 | 1.30218 | 1.29678 | 2.265 | 2.047 | 1.832 | 1.623 | 1346.8 | 1331.5 | 1315.5 | 1299.3 |
| 0.4254 | 1.26749 | 1.26221 | 1.25688 | 1.25167 | 2.427 | 2.184 | 1.945 | 1.713 | 1379.1 | 1363.1 | 1346.5 | 1329.7 |
| 0.5207 | 1.22497 | 1.21986 | 1.21469 | 1.20966 | 2.570 | 2.305 | 2.044 | 1.792 | 1408.9 | 1392.5 | 1375.5 | 1358.3 |
| 0.6352 | 1.17213 | 1.16724 | 1.16227 | 1.15746 | 2.739 | 2.446 | 2.160 | 1.884 | 1445.7 | 1429.0 | 1411.9 | 1394.4 |
| 0.7412 | 1.12144 | 1.11677 | 1.11201 | 1.10740 | 2.892 | 2.575 | 2.265 | 1.967 | 1481.2 | 1464.2 | 1447.2 | 1429.5 |
| 0.8552 | 1.06500 | 1.06052 | 1.05597 | 1.05161 | 3.054 | 2.710 | 2.375 | 2.053 | 1521.7 | 1504.0 | 1486.6 | 1468.6 |
| 0.9501 | 1.01635 | 1.01208 | 1.00770 | 1.00352 | 3.188 | 2.821 | 2.463 | 2.120 | 1558.1 | 1539.0 | 1520.5 | 1501.4 |
| 1.0000 | 0.99019 | 0.98599 | 0.98169 | 0.97759 | 3.258 | 2.878 | 2.508 | 2.153 | 1578.5 | 1558.2 | 1538.5 | 1518.5 |

Table-4. Excess molar volume ( $V^{E}$ ) and excess isentropic compressibility ( $\kappa_{s}^{E}$ ), deviation in viscosity ( $\Delta \eta$ ) andexcess Gibbs energy of activation of viscous flow $\left(G^{* E}\right)$ ofliquid mixtures of 2-methylaniline with 1,2-dichlorobenzene, 1,3dichlorobenzene and 1,2,4-trichlorobenzeneat $\mathrm{T}=(303.15$ to 318.15$) \mathrm{K}$.

|  | $V^{E} / \mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}$ |  |  |  | $\Delta \boldsymbol{\eta} / \mathrm{mPa} \cdot \mathrm{s}$ |  |  |  | $\kappa_{s}^{E} / \mathrm{TPa}^{-1}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | 2-methylaniline (1) + 1,2-dichlorobenzene <br> (2) |  |  |  |  |  |  |  |
| $\mathrm{x}_{1}$ | 303.15 K | 308.15 K | $\begin{gathered} 313.15 \\ \text { K } \end{gathered}$ | 318.15 K | 303.15 K | 308.15 K | $\begin{gathered} 313.15 \\ \mathrm{~K} \end{gathered}$ | $\begin{gathered} 318.15 \\ \mathrm{~K} \end{gathered}$ | 303.15 K | $\begin{gathered} 308.15 \\ \text { K } \end{gathered}$ | $\begin{gathered} 313.15 \\ \mathrm{~K} \end{gathered}$ | $\begin{gathered} 318.15 \\ \mathrm{~K} \end{gathered}$ |
| $\begin{gathered} 0.000 \\ 0 \end{gathered}$ | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $\begin{gathered} 0.089 \\ 5 \end{gathered}$ | -0.0457 | -0.0492 | -0.0526 | -0.0580 | 0.012 | 0.014 | 0.016 | 0.017 | -4.869 | -5.634 | -6.339 | -6.997 |
| $\begin{gathered} 0.179 \\ 5 \end{gathered}$ | -0.0735 | -0.0785 | -0.0850 | -0.0929 | 0.021 | 0.023 | 0.025 | 0.027 | -8.765 | -9.744 | -10.70 | -11.57 |
| $\begin{gathered} 0.312 \\ 5 \end{gathered}$ | -0.0975 | -0.1034 | -0.1114 | -0.1182 | 0.030 | 0.031 | 0.034 | 0.036 | -12.60 | -13.44 | -14.36 | -15.17 |
| $\begin{gathered} 0.425 \\ 6 \\ \hline \end{gathered}$ | -0.1081 | -0.1144 | -0.1201 | -0.1267 | 0.033 | 0.034 | 0.036 | 0.038 | -14.03 | -14.74 | -15.55 | -16.29 |
| $\begin{gathered} 0.516 \\ 9 \end{gathered}$ | -0.1093 | -0.1156 | -0.1212 | -0.1283 | 0.033 | 0.034 | 0.036 | 0.038 | -14.01 | -14.72 | -15.53 | -16.29 |
| $\begin{gathered} 0.625 \\ 4 \end{gathered}$ | -0.1037 | -0.1102 | -0.1176 | -0.1256 | 0.030 | 0.032 | 0.034 | 0.036 | -12.69 | -13.57 | -14.49 | -15.40 |
| $\begin{gathered} 0.714 \\ 5 \\ \hline \end{gathered}$ | -0.0930 | -0.1001 | -0.1073 | -0.1148 | 0.026 | 0.028 | 0.030 | 0.032 | -10.66 | -11.75 | -12.78 | -13.85 |
| $\begin{gathered} 0.810 \\ 2 \end{gathered}$ | -0.0739 | -0.0805 | -0.0875 | -0.0955 | 0.019 | 0.021 | 0.023 | 0.024 | -7.677 | -8.870 | -9.937 | -11.06 |
| $\begin{gathered} 0.901 \\ 2 \\ \hline \end{gathered}$ | -0.0455 | -0.0511 | -0.0566 | -0.0624 | 0.011 | 0.012 | 0.014 | 0.015 | -4.220 | -5.186 | -6.013 | -6.895 |
| $\begin{gathered} 1.000 \\ 0 \\ \hline \end{gathered}$ | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |

2-methylaniline (1) + 1,3-dichlorobenzene (2)

| 0.000 <br> 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0.105 <br> 3 | -0.0430 | -0.0468 | -0.0501 | -0.0540 | 0.012 | 0.013 | 0.014 | 0.015 | -4.582 | -5.194 | -5.785 | -6.418 |
| 0.201 <br> 1 | -0.0703 | -0.0757 | -0.0809 | -0.0860 | 0.020 | 0.022 | 0.023 | 0.025 | -8.324 | -9.114 | -9.915 | -10.72 |
| 0.304 <br> 5 | -0.0902 | -0.0956 | -0.1018 | -0.1071 | 0.027 | 0.029 | 0.030 | 0.032 | -11.41 | -12.19 | -13.03 | -13.82 |
| 0.406 <br> 4 | -0.1019 | -0.1080 | -0.1127 | -0.1178 | 0.031 | 0.032 | 0.034 | 0.035 | -13.15 | -13.85 | -14.67 | -15.41 |
| 0.507 <br> 0 | -0.1046 | -0.1099 | -0.1155 | -0.1205 | 0.031 | 0.033 | 0.034 | 0.036 | -13.45 | -14.10 | -14.90 | -15.62 |
| 0.606 <br> 2 | -0.0981 | -0.1063 | -0.1111 | -0.1163 | 0.029 | 0.031 | 0.032 | 0.034 | -12.36 | -13.03 | -13.83 | -14.61 |
| 0.704 <br> 1 | -0.0876 | -0.0933 | -0.0992 | -0.1048 | 0.024 | 0.026 | 0.028 | 0.029 | -10.10 | -10.81 | -11.62 | -12.49 |
| 0.800 <br> 7 | -0.0680 | -0.0725 | -0.0790 | -0.0844 | 0.017 | 0.019 | 0.020 | 0.022 | -7.023 | -7.727 | -8.484 | -9.376 |
| 0.906 <br> 0 | -0.0374 | -0.0409 | -0.0446 | -0.0484 | 0.009 | 0.010 | 0.010 | 0.011 | -3.212 | -3.723 | -4.241 | -4.895 |
| 1.000 <br> 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |

ARPN Journal of Engineering and Applied Sciences
www.arpnjournals.com

| 0.000 <br> 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0.091 <br> 7 | -0.0325 | -0.0353 | -0.0385 | -0.0429 | 0.009 | 0.010 | 0.012 | 0.013 | -3.626 | -4.303 | -5.037 |
| 0.206 <br> 9 | -0.0632 | -0.0682 | -0.0726 | -0.0774 | 0.018 | 0.020 | 0.022 | -5.804 |  |  |  |
| 0.319 <br> 8 | -0.0860 | -0.0892 | -0.0932 | -0.0965 | 0.025 | 0.027 | 0.029 | 0.030 | -10.30 | -11.22 | -12.07 |
| 0.425 <br> 4 | -0.0971 | -0.0994 | -0.1029 | -0.1064 | 0.029 | 0.030 | 0.032 | 0.033 | -11.77 | -12.64 | -13.39 |
| 0.520 <br> 7 | -0.0980 | -0.1011 | -0.1045 | -0.1088 | 0.029 | 0.031 | 0.033 | 0.034 | -12.06 | -12.96 | -13.74 |
| 0.635 <br> 2 | -0.0887 | -0.0928 | -0.0968 | -0.1008 | 0.027 | 0.028 | 0.030 | 0.032 | -11.09 | -12.12 | -13.09 |
| 0.741 <br> 2 | -0.0711 | -0.0770 | -0.0815 | -0.0859 | 0.021 | 0.023 | 0.025 | 0.027 | -8.965 | -10.12 | -11.29 |
| 0.855 <br> 2 | -0.0464 | -0.0494 | -0.0536 | -0.0588 | 0.013 | 0.015 | 0.017 | 0.019 | -12.32 |  |  |
| 0.950 <br> 1 | -0.0156 | -0.0197 | -0.0219 | -0.0251 | 0.005 | 0.006 | 0.007 | 0.008 | -2.025 | -2.558 | -3.157 |
| 1.000 <br> 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | -3.692 |


|  | $\begin{gathered} \text { 2-methylaniline }(1)+1,2,4- \\ \text { trichlorobenzene(2) } \\ \hline \end{gathered}$ |  |  |  | $\begin{gathered} \text { 2-methylaniline }(1)+1,3- \\ \text { dichlorobenzene(2) } \\ \hline \end{gathered}$ |  |  |  | $\begin{gathered} \hline \text { 2-methylaniline (1)+1,2- } \\ \text { dichlorobenzene(2) } \\ \hline \end{gathered}$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{G}^{* \mathrm{E}} / \mathrm{J} \cdot \mathrm{mol}^{-1}$ |  |  |  | $\mathrm{G}^{* \mathrm{E}} / \mathrm{J} \cdot \mathrm{mol}^{-1}$ |  |  |  | $\mathrm{G}^{*} \mathrm{E} / \mathrm{J} \cdot \mathrm{mol}^{-1}$ |  |  |  |  |  |
| $\mathrm{X}_{1}$ | $\begin{gathered} 303.15 \\ \mathrm{~K} \end{gathered}$ | $\begin{gathered} 308.15 \\ \mathrm{~K} \end{gathered}$ | $\begin{gathered} 313.15 \\ \mathrm{~K} \end{gathered}$ | $\begin{gathered} 318.15 \\ \mathrm{~K} \end{gathered}$ | $\mathrm{X}_{1}$ | $\begin{gathered} 303.15 \\ \mathrm{~K} \end{gathered}$ | $\begin{gathered} 308.15 \\ \mathrm{~K} \end{gathered}$ | 313.15 K | $\begin{gathered} 318.15 \\ \mathrm{~K} \end{gathered}$ | $\mathrm{X}_{1}$ | $\begin{gathered} 303.15 \\ \mathrm{~K} \end{gathered}$ | $\begin{gathered} 308.15 \\ \text { K } \end{gathered}$ | $\begin{gathered} 313.15 \\ \mathrm{~K} \end{gathered}$ | $\begin{gathered} 318.15 \\ \mathrm{~K} \end{gathered}$ |
| $\begin{gathered} 0.000 \\ 0 \end{gathered}$ | 0.000 | 0.000 | 0.000 | 0.000 | $\begin{gathered} 0.000 \\ 0 \end{gathered}$ | 0.000 | 0.000 | 0.000 | 0.000 | $\begin{gathered} 0.000 \\ 0 \end{gathered}$ | 0.000 | 0.000 | 0.000 | 0.000 |
| $\begin{gathered} 0.091 \\ 7 \\ \hline \end{gathered}$ | 0.597 | 0.571 | 0.558 | 0.544 | $\begin{gathered} 0.105 \\ 3 \\ \hline \end{gathered}$ | 2.701 | 2.471 | 2.225 | 1.978 | $\begin{gathered} 0.089 \\ 5 \\ \hline \end{gathered}$ | 1.441 | 1.375 | 1.315 | 1.239 |
| $\begin{gathered} 0.206 \\ 9 \end{gathered}$ | 1.110 | 1.068 | 1.022 | 0.991 | $\begin{gathered} 0.201 \\ 1 \end{gathered}$ | 4.107 | 3.781 | 3.413 | 3.052 | $\begin{gathered} 0.179 \\ 5 \end{gathered}$ | 2.385 | 2.254 | 2.124 | 1.981 |
| $\begin{gathered} 0.319 \\ 8 \end{gathered}$ | 1.405 | 1.349 | 1.286 | 1.224 | $\begin{gathered} 0.304 \\ 5 \end{gathered}$ | 4.875 | 4.506 | 4.085 | 3.647 | $\begin{gathered} 0.312 \\ 5 \end{gathered}$ | 3.104 | 2.937 | 2.765 | 2.572 |
| $\begin{gathered} 0.425 \\ 4 \\ \hline \end{gathered}$ | 1.514 | 1.445 | 1.378 | 1.310 | $\begin{gathered} 0.406 \\ 4 \\ \hline \end{gathered}$ | 5.059 | 4.693 | 4.272 | 3.823 | $\begin{gathered} 0.425 \\ 6 \\ \hline \end{gathered}$ | 3.241 | 3.068 | 2.888 | 2.682 |
| $\begin{gathered} 0.520 \\ 7 \end{gathered}$ | 1.478 | 1.419 | 1.357 | 1.296 | $\begin{gathered} 0.507 \\ 0 \end{gathered}$ | 4.819 | 4.483 | 4.092 | 3.677 | $\begin{gathered} 0.516 \\ 9 \end{gathered}$ | 3.112 | 2.949 | 2.778 | 2.582 |
| $\begin{gathered} 0.635 \\ 2 \end{gathered}$ | 1.311 | 1.258 | 1.204 | 1.163 | $\begin{gathered} 0.606 \\ 2 \end{gathered}$ | 4.264 | 3.978 | 3.647 | 3.293 | $\begin{gathered} 0.625 \\ 4 \end{gathered}$ | 2.725 | 2.592 | 2.446 | 2.282 |
| $\begin{gathered} \hline 0.741 \\ 2 \\ \hline \end{gathered}$ | 1.031 | 0.999 | 0.968 | 0.936 | $\begin{gathered} 0.704 \\ 1 \\ \hline \end{gathered}$ | 3.467 | 3.244 | 2.985 | 2.703 | $\begin{gathered} 0.714 \\ 5 \\ \hline \end{gathered}$ | 2.250 | 2.147 | 2.033 | 1.903 |
| $\begin{gathered} 0.855 \\ 2 \end{gathered}$ | 0.635 | 0.616 | 0.604 | 0.602 | $\begin{gathered} 0.800 \\ 7 \end{gathered}$ | 2.484 | 2.331 | 2.149 | 1.956 | $\begin{gathered} 0.810 \\ 2 \end{gathered}$ | 1.605 | 1.534 | 1.463 | 1.377 |
| $\begin{gathered} 0.950 \\ 1 \end{gathered}$ | 0.236 | 0.232 | 0.231 | 0.230 | $\begin{gathered} 0.906 \\ 0 \end{gathered}$ | 1.244 | 1.170 | 1.075 | 0.982 | $\begin{gathered} 0.901 \\ 2 \end{gathered}$ | 0.885 | 0.848 | 0.816 | 0.775 |
| $\begin{gathered} 1.000 \\ 0 \\ \hline \end{gathered}$ | 0.000 | 0.000 | 0.000 | 0.000 | $\begin{gathered} 1.000 \\ 0 \\ \hline \end{gathered}$ | 0.000 | 0.000 | 0.000 | 0.000 | $\begin{gathered} 1.000 \\ 0 \\ \hline \end{gathered}$ | 0.000 | 0.000 | 0.000 | 0.000 |

## www.arpnjournals.com

Table-5. Coefficients of Redlich - Kister equation and standard deviation ( $\sigma$ ) values for liquid mixtures of 2-methylaniline with 1,2dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene at $\mathrm{T}=(303.15-318.15) \mathrm{K}$.

| Binary mixtures | Functions | $\mathrm{A}_{1}$ | $\mathrm{A}_{2}$ | $\mathrm{A}_{3}$ | $\sigma$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 303.15 K |  |  |  |  |  |
| 2-methylaniline + 1,2-dichlorobenzene | $V^{E} / \mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}$ | -0.434 | 0.019 | -0.149 | 0.001 |
|  | $\kappa_{s}^{E} / \mathrm{TPa}^{-1}$ | -56.36 | 7.690 | 4.338 | 0.001 |
|  | $\Delta \eta / \mathrm{mPa} \cdot \mathrm{s}$ | 0.132 | -0.016 | 0.004 | 0.001 |
| 2-methylaniline + 1,3-dichlorobenzene | $V^{E} / \mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}$ | -0.416 | 0.011 | -0.049 | 0.001 |
|  | $\kappa_{s}^{E} / \mathrm{TPa}^{-1}$ | -53.88 | 6.447 | 16.59 | 0.001 |
|  | $\Delta \eta / \mathrm{mPa} \cdot \mathrm{s}$ | 0.125 | -0.014 | -0.020 | 0.001 |
| 2-methylaniline + 1,2,4-trichlorobenzene | $V^{E} / \mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}$ | -0.394 | 0.022 | 0.041 | 0.001 |
|  | $\kappa_{s}^{E} / \mathrm{TPa}^{-1}$ | -48.33 | -0.107 | 7.048 | 0.001 |
|  | $\Delta \eta / \mathrm{mPa} \cdot \mathrm{s}$ | 0.116 | -0.001 | -0.015 | 0.001 |
| 308.15 K |  |  |  |  |  |
| 2-methylaniline + 1,2-dichlorobenzene | $V^{E} / \mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}$ | -0.458 | 0.009 | -0.191 | 0.001 |
|  | $\kappa_{s}^{E} / \mathrm{TPa}^{-1}$ | -59.15 | 6.580 | -6.788 | 0.001 |
|  | $\Delta \eta / \mathrm{mPa} \cdot \mathrm{s}$ | 0.139 | -0.019 | 0.019 | 0.001 |
| 2-methylaniline + 1,3-dichlorobenzene | $V^{E} / \mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}$ | -0.440 | 0.012 | -0.071 | 0.001 |
|  | $\kappa_{s}^{E} / \mathrm{TPa}^{-1}$ | -56.52 | 6.884 | 10.95 | 0.001 |
|  | $\Delta \eta / \mathrm{mPa} \cdot \mathrm{s}$ | 0.132 | -0.012 | -0.011 | 0.001 |
| 2-methylaniline + 1,2,4-trichlorobenzene | $V^{E} / \mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}$ | -0.403 | 0.010 | -0.019 | 0.001 |
|  | $\kappa_{s}^{E} / \mathrm{TPa}^{-1}$ | -51.87 | -1.233 | -1.202 | 0.001 |
|  | $\Delta \eta / \mathrm{mPa} \cdot \mathrm{s}$ | 0.123 | 0.001 | -0.002 | 0.001 |
| 313.15 K |  |  |  |  |  |
| 2-methylaniline + 1,2-dichlorobenzene | $V^{E} / \mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}$ | -0.484 | 0.001 | -0.233 | 0.001 |
|  | $\kappa_{s}^{E} / \mathrm{TPa}^{-1}$ | -62.38 | 6.026 | -15.52 | 0.001 |
|  | $\Delta \eta / \mathrm{mPa} \cdot \mathrm{s}$ | 0.144 | -0.019 | 0.042 | 0.001 |
| 2-methylaniline + 1,3-dichlorobenzene | $V^{E} / \mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}$ | -0.462 | -0.008 | -0.103 | 0.001 |
|  | $\kappa_{s}^{E} / \mathrm{TPa}^{-1}$ | -59.72 | 7.105 | 6.297 | 0.001 |
|  | $\Delta \eta / \mathrm{mPa} \cdot \mathrm{s}$ | 0.138 | -0.017 | -0.002 | 0.001 |
| 2-methylaniline + 1,2,4-trichlorobenzene | $V^{E} / \mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}$ | -0.417 | 0.009 | -0.059 | 0.001 |
|  | $\kappa_{s}^{E} / \mathrm{TPa}^{-1}$ | -54.93 | -2.599 | -11.51 | 0.001 |
|  | $\Delta \eta / \mathrm{mPa} \cdot \mathrm{s}$ | 0.129 | 0.001 | 0.018 | 0.001 |
| 318.15 K |  |  |  |  |  |
| 2-methylaniline + 1,2-dichlorobenzene | $V^{E} / \mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}$ | -0.512 | 0.001 | -0.292 | 0.001 |
|  | $\kappa_{s}^{E} / \mathrm{TPa}^{-1}$ | -65.38 | 4.726 | -24.63 | 0.001 |
|  | $\Delta \eta / \mathrm{mPa} \cdot \mathrm{s}$ | 0.152 | -0.022 | 0.056 | 0.001 |
| 2-methylaniline + 1,3-dichlorobenzene | $V^{E} / \mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}$ | -0.482 | 0.006 | -0.139 | 0.001 |
|  | $\kappa_{s}^{E} / \mathrm{TPa}^{-1}$ | -62.60 | 6.656 | -0.431 | 0.001 |
|  | $\Delta \eta / \mathrm{mPa} \cdot \mathrm{s}$ | 0.144 | -0.019 | 0.014 | 0.001 |
| 2-methylaniline + 1,2,4-trichlorobenzene | $V^{E} / \mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}$ | -0.428 | 0.007 | -0.122 | 0.001 |
|  | $\kappa_{s}^{E} / \mathrm{TPa}^{-1}$ | -57.79 | -2.981 | -21.47 | 0.001 |
|  | $\Delta \eta / \mathrm{mPa} \cdot \mathrm{s}$ | 0.134 | 0.003 | 0.037 | 0.001 |

www.arpnjournals.com
Table-6. The values $\bar{V}_{m, 1}^{E} \bar{V}_{m, 2}^{E} \bar{K}_{\mathrm{s}, \mathrm{m}, 1}^{\mathrm{E}}, \quad \bar{K}_{\mathrm{s}, \mathrm{m}, 2}^{\mathrm{E}}$ of liquid mixtures of 2-methylaniline with di- and tri- chloro substituted benzeneat T= (303.15 to 318.15 ) K.

| 2-methylaniline (1)+ 1,2-dichlorobenzene(2) |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 303.15 K |  | 308.15 K |  | 313.15 K |  | 318.15 K |  | 303.15 K |  | 308.15 K |  | 313.15 K |  | 318.15 K |  |
| x1 | $\bar{V}_{m, 1}^{E}$ | $\bar{V}_{m, 2}^{E}$ | $\bar{V}_{m, 1}^{E}$ | $\bar{V}_{m, 2}^{E}$ | $\bar{V}_{m, 1}^{E}$ | $\bar{V}_{m, 2}^{E}$ | $\bar{V}_{m, 1}^{E}$ | $\bar{V}_{m, 2}^{E}$ | $\bar{K}_{\mathrm{s}, \mathrm{m}, \mathrm{l}}^{\mathrm{E}}$ | $\bar{K}_{\mathrm{s}, \mathrm{m}, 2}^{\mathrm{E}}$ | $\bar{K}_{\mathrm{s}, \mathrm{m}, 1}^{\mathrm{E}}$ | $\bar{K}_{\mathrm{s}, \mathrm{~m}, 2}^{\mathrm{E}}$ | $\bar{K}_{\mathrm{s}, \mathrm{m}, 1}^{\mathrm{E}}$ | $\bar{K}_{\mathrm{s}, \mathrm{m}, 2}^{\mathrm{E}}$ | $\bar{K}_{\mathrm{s}, \mathrm{m}, \mathrm{l}}^{\mathrm{E}}$ | $\bar{K}_{\mathrm{s}, \mathrm{m}, 2}^{\mathrm{E}}$ |
| 0.0000 | $0.564$ | 0.000 | -0.640 | 0.000 | -0.716 | 0.000 | $0.803$ | 0.000 | $50.43$ | 0.000 | $67.66$ | 0.000 | -82.29 | 0.000 | -98.15 | 0.000 |
| 0.0895 | $0.415$ | $0.007$ | -0.459 | $0.009$ | -0.503 | $0.011$ | $0.552$ | -0.013 | $46.85$ | -0.186 | $54.38$ | $0.605$ | -61.27 | -0.940 | -68.63 | $1.309$ |
| 0.1795 | $0.307$ | $0.025$ | -0.330 | $0.030$ | -0.354 | $0.034$ | $0.380$ | -0.040 | $41.65$ | -1.012 | $43.90$ | $2.220$ | -46.52 | -3.194 | -49.15 | $4.270$ |
| 0.3125 | $0.201$ | $0.056$ | -0.209 | $0.065$ | -0.219 | $0.074$ | $0.229$ | -0.083 | $32.33$ | -4.109 | $32.02$ | $6.072$ | -32.45 | -7.694 | -32.61 | $9.504$ |
| 0.4256 | $0.143$ | $0.084$ | -0.147 | $0.093$ | -0.152 | $0.103$ | $0.159$ | -0.112 | $23.97$ | -9.030 | $24.01$ | $10.75$ | -24.59 | -12.27 | -24.87 | $13.98$ |
| 0.5169 | $0.107$ | $0.109$ | -0.111 | $0.117$ | -0.115 | $0.125$ | $0.122$ | -0.132 | $17.56$ | -14.76 | $18.39$ | $15.77$ | -19.47 | -16.83 | -20.33 | $18.03$ |
| 0.6254 | $0.073$ | $0.148$ | -0.076 | $0.154$ | -0.081 | $0.161$ | $0.087$ | -0.164 | $10.84$ | -23.73 | $12.38$ | $23.82$ | -13.88 | -24.34 | -15.24 | $24.87$ |
| 0.7145 | $0.048$ | $0.197$ | -0.051 | $0.203$ | -0.055 | $0.211$ | $0.061$ | -0.216 | $6.368$ | -32.83 | $7.972$ | $32.82$ | -9.419 | -33.47 | -10.80 | $33.99$ |
| 0.8102 | $0.025$ | $0.280$ | -0.027 | $0.292$ | -0.029 | $0.305$ | $0.033$ | -0.320 | $2.818$ | -44.22 | $3.960$ | $45.79$ | -4.950 | -47.99 | -5.923 | $49.90$ |
| 0.9012 | $0.008$ | $0.402$ | -0.009 | $0.428$ | -0.009 | $0.456$ | $0.011$ | -0.494 | $0.757$ | -56.44 | $1.203$ | $62.32$ | -1.581 | -68.28 | -1.959 | $73.88$ |
| 1.0000 | 0.000 | $0.603$ | 0.000 | $0.659$ | 0.000 | $0.718$ | 0.000 | -0.805 | 0.000 | -70.93 | 0.000 | $86.26$ | 0.000 | -100.2 | 0.000 | $113.8$ |

2-methylaniline (1) +1,3-dichlorobenzene(2)

| 0.0000 | $0.453$ | 0.000 | -0.500 | 0.000 | -0.572 | 0.000 | $0.615$ | 0.000 | $35.10$ | 0.000 | $44.24$ | 0.000 | $53.28$ | 0.000 | -65.17 | 0.000 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0.1053 | $0.345$ | $0.006$ | -0.373 | $0.007$ | -0.411 | $0.009$ | $0.434$ | -0.010 | $41.37$ | 0.258 | $45.32$ | $0.003$ | $49.70$ | -0.239 | -54.73 | $0.586$ |
| 0.2011 | $0.268$ | $0.020$ | -0.285 | $0.023$ | -0.304 | $0.029$ | $0.317$ | -0.032 | $39.96$ | -0.058 | $41.61$ | $0.719$ | $43.81$ | -1.333 | -45.71 | $2.224$ |
| 0.3045 | $0.200$ | $0.042$ | -0.211 | $0.047$ | -0.219 | $0.056$ | $0.228$ | -0.060 | $33.84$ | -2.195 | $34.62$ | $3.131$ | $35.88$ | -4.051 | -36.53 | $5.342$ |
| 0.4064 | $0.147$ | $0.070$ | -0.155 | $0.076$ | -0.157 | $0.086$ | $0.166$ | -0.089 | $25.61$ | -6.785 | $26.40$ | -7.70 | $27.50$ | -8.70 | -28.09 | $10.01$ |
| 0.5070 | $0.104$ | $0.104$ | -0.110 | $0.110$ | -0.111 | $0.120$ | $0.119$ | -0.121 | $17.25$ | -13.84 | $18.33$ | $14.51$ | $19.52$ | -15.43 | -20.47 | $16.43$ |
| 0.6062 | $0.069$ | $0.145$ | -0.074 | $0.152$ | -0.075 | $0.161$ | $0.083$ | -0.161 | $10.08$ | -22.84 | $11.34$ | $23.30$ | $12.57$ | -24.17 | -13.81 | $24.82$ |
| 0.7041 | $0.041$ | $0.197$ | -0.045 | $0.206$ | -0.046 | $0.214$ | $0.052$ | -0.217 | $4.813$ | -32.82 | $5.974$ | $33.49$ | $7.038$ | -34.70 | -8.243 | $35.43$ |
| 0.8007 | $0.020$ | $0.264$ | -0.022 | $0.278$ | -0.023 | $0.288$ | $0.027$ | -0.300 | $1.629$ | -42.39 | $2.413$ | $44.26$ | $3.110$ | -46.62 | -3.954 | $48.51$ |
| 0.9060 | $0.005$ | $0.361$ | -0.006 | $0.388$ | -0.006 | $0.405$ | $0.007$ | -0.439 | $0.187$ | -50.45 | $0.439$ | $55.56$ | $0.658$ | -60.83 | -0.935 | $66.18$ |
| 1.0000 | 0.000 | $0.476$ | 0.000 | $0.523$ | 0.000 | $0.557$ | 0.000 | -0.627 | 0.000 | -53.25 | 0.000 | $63.88$ | 0.000 | -73.94 | 0.000 | $85.41$ |

2-methylaniline (1) + 1,2,3-trichlorobenzene(2)

| 0.0000 | $0.331$ | 0.000 | -0.413 | 0.000 | -0.466 | 0.000 | $0.544$ | 0.000 | $46.00$ | 0.000 | $60.98$ | 0.000 | -78.08 | 0.000 | -93.86 | 0.000 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0.0917 | $0.296$ | $0.002$ | -0.336 | $0.004$ | -0.364 | $0.005$ | $0.402$ | -0.007 | $43.48$ | -0.149 | $50.57$ | $0.499$ | -58.09 | -0.922 | -64.90 | $1.319$ |

www.arpnjournals.com
$\left.\begin{array}{|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|}\hline 0.2069 & - & - & -0.254 & -- & -0.265 & - & - & -0.029 & - & -1.344 & - & - & -40.68 & -3.916 & -42.08 & - \\ 5.0 .199\end{array}\right]$

## www.arpnjournals.com

Table-7. The values of $\bar{V}_{\mathrm{m}, 1}^{\circ}, V_{\mathrm{m}, 1}^{*}, \bar{V}_{\mathrm{m}, 1}{ }^{\mathrm{E}}, \bar{V}_{\mathrm{m}, 2}^{\circ}, V_{\mathrm{m}, 2}^{*}, \bar{V}_{\mathrm{m}, 2}^{\circ} \mathrm{E} \bar{K}_{\mathrm{s}, \mathrm{m}, 1}^{\circ}, K_{\mathrm{s}, \mathrm{m}, 1}^{*}, \bar{K}_{\mathrm{s}, \mathrm{m}, 1,}^{{ }^{\mathrm{E}}} \bar{K}_{\mathrm{s}, \mathrm{m}, 2}^{\circ}, K_{\mathrm{s}, \mathrm{m}, 2}^{*}$ and $\bar{K}_{\mathrm{s}, \mathrm{m}, 2 \text { of the }}^{\circ} \mathrm{E}$ components for 2-methylaniline + di- and tri- chloro substituted benzenebinary mixtures at $\mathrm{T}=(303.15$ to 318.15$) \mathrm{K}$.

www.arpnjournals.com

Table-8. PFP interaction parameter, $\chi_{12}$, and calculated values of the three contributions from the PFP theory with experimental excess molar volumes at $x_{1}=0.5$ at 303.15 K .

| Binary mixtures | $\chi_{12} \mathbf{1 0}^{\mathbf{6}}$ | Calculated contributions |  |  | $\mathrm{V}_{m}^{E}(\boldsymbol{x}=\mathbf{0 . 5})$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Interactional $\mathbf{1 0}^{-\mathbf{8}}$ | Free volume | $\mathbf{P}^{*}$ effect | $\mathbf{E X P}$ | $\mathbf{P F P}$ | $\delta / \mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}$ |
| 3-chloroaniline+1,2-dichlorobenzene | -4.860 | 1.056 | -0.0100 | -0.0482 | -0.1095 | -0.1090 | -0.0005 |
| 3-chloroaniline+1,3-dichlorobenzene | -6.806 | 1.078 | -0.0012 | -0.0297 | -0.1042 | -0.1040 | -0.0002 |
| 3-chloroaniline+1,2,4-trichlorobenzene | -9.251 | 1.041 | -0.0001 | -0.0022 | -0.0984 | -0.0981 | -0.0003 |

## REFERENCES

[1] J. Ortega. , J. Chem. Eng. Data 30 (1985) 465-467.
[2] N.V. Sastry, M.K. Valand, Int. J. Thermophys. 18 (1997) 1387-1403.
[3] S. Singh, V.K. Rattan, S. Kapoor, R. Kumar, A. Rampal, J. Chem. Eng. Data 50 (2005) 288-292.
[4] M.N. Roy, B. Sinha, V.K. Dakua. 2006. J. Chem. Eng. Data. 51: 590-594.
[5] Dimple, S. J. Yadav, K. C. Singh, V. K Sharma, 54 (2009) 2109-2112.
[6] Dimple, S. J. Yadav, K. C. Singh, V. K Sharma, 53 (2008) 1935-1939.
[7] Dimple, S. J. Yadav, K. C. Singh, V. K Sharma, ThermochimicaActa 468 (2008) 108-115.
[8] N. Saini, J. S. Yadav, S. K. Jangra, D. Sharma and V. K. Sharma, J. Chem. Thermodyn. 43 (2011) 782-795.
[9] M. Gowrisankar, A. Venkatesulu, T. Srinivasa Krishna K. Ravindhranath, J. Chem. Thermodyn., 107, 104-113 (2017).
[10]P.Venkateswara Rao, M. Gowrisankar, L. Venkatramana,T. Srinivasa Krishna, K. Ravindhranath, J. Chem. Thermodyns.101, 92-101 (2016).
[11]MilanZábranský, Jr. VlastimilRiviviča,J. Phys. Chem. Ref. Data 33 1071-1081 (2004).
[12] V. Pandiyan, S. L. Oswal, N. I. Malek, P. Vasantharani, ThermochimicaActa 524 140-150 (2011).
[13] N.A. Lange, Handbook of chemistry, $9^{\text {th }}$ ed. McGraw Hill Handboo publishers Inc., Sandusky, Ohio, 1956.
[14] S.C. Bhatia, R. Rani, J. Sangwan, R. Bhatia, Int. J. Thermophys. 32 (2011)1163-1174.
[15] S.C. Bhatia, N. Tripathi, G.P. Dubey, Indian J. Chem. 42(2003) 2513-2517.
[16] G.C. Benson, O. Kiyohara, J. Chem. Thermodyn. 11 (1979) 1061-1064.
[17]O. Redlich, A.T. Kister, Ind. Eng. Chem., 40, 345348 (1948).
[18]P. Jain, M. Singh. 2004. J. Chem. Eng. Data 49: 12141217.
[19]G.V.A. Rama Rao, V. Sarma, C. Rambabu. 2004. Indian J. Chem. 43A (2004) 2518-2528.
[20] B. Jacobson. 1952. J. Chem. Phys. 20: 927.
[21]M.V. Rathnam, R.T. Sayed, K.R. Bhanushali, M.S.S. Kumar, M.S.S. 2012. J. Mol. Liq. 166: 9.
[22] A. Ali, Abida, S. Hyder. 2004. Phys. Chem. Liq, 42: 411.
[23]M.V. Rathnam, M. Sudhir, M.S.S. Kumar, J. soln. Chem. 39, 1735-1748 (2010).
[24]M.M. Palaiologou, I.E. Molinou, J. Chem. Eng. Data 40, 880-882 (1995).
[25] M.M. Palaiologou, I.E. Molinou, J. Chem. Eng. Data 40 (1995) 880-882.
[26] M.P. Reddy, K. Sivakumar, P. Venkatesu, Fluid Phase Equilibra. 310 (2011) 74-81.
[27] V. Syamala, K.Siva Kumar, P.Venkateswarlu, J Chem. Thermodyn. 38 (2006) 1553-1562.
[28]K. Tiwari Mf., C. Patra, V. Chakravarthy, Acoust. Lett., 19 (1995) 53-59.
www.arpnjournals.com
[29] I.Gascon, A.M. Mainer, M.R. Felix, J.S. Urieta, L.A. Cerdeirina, J. Chem. Eng. Data 40(2000) 151-155.
[30] A. Ali, A.K. Nain, D. Chand, B. Lal. 2005. Indian J. Chem. 44a: 511-515.
[31]H.T. Van, D. Patterson. 1982. J. Soln.Chem. 11, 793805.
[32]D. Patterson, G. Delma. 1970. Corresponding states theories and liquid models, discuss Faraday Soc. 49: 98-105.
[33] I. Prigogine. 1957. The Molecular Theory of Solution. North Holland Corp, Amesterdam.

