MOLECULAR INTERACTION STUDIES OF BINARY LIQUID MIXTURES OF 2-METHYL CYCLOHEXANONE WITH 2-MEXOXY ANILINE IN TERMS OF THERMO-ACOUSTIC PARAMETERS AT DIFFERENT TEMPERATURES

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Abstract: In this present investigation, the thermos fundamental parameters such as density (ρ) and speed of sound(U) were measured experimentally for anisidine (2-methoxy aniline) with solvent agent such as 2-methyl cyclohexanone in various concentrations within temperatures from 303.15 to 313.15K (5K interval) at ambient atmospheric pressure. From these experimental determined values, various thermo-acoustic parameters of excess isentropic compressibility,K_s^E and excess molar volume, V_m^E are calculated. The calculated excess functions were correlated with reduced redlich-kister polynomial equation and results are analyzed in terms of structural molecular interactions between component molecules. Moreover, calibration of the partial molar volume's and partial isentropic compressibility's of 2-methyl cyclohexanone + 2-methoxy aniline at a temperature 303.15K shows strong interactions than any combination at any temperature. In addition to the FTIR characteristic spectrum of all combinations at different concentrations gives the more promising features such as interaction behavior that helps our analysis to guide the interactions of individual bonding strength of the molecules.

Keywords: 2-Methoxy Aniline,, Redlich-Kister Functions, Reduced Redlich-Kister Functions, Partial Molar Volumes, Partial Isentropic Compressibilities, FT-IR Spectrum.

Introduction: In this experimental framework, methoxy and aniline wing aromatic nature of 2-methoxy aniline(2MA) is independently blended with 2-methyl cyclohexanone(2MCH). This aniline aromatic ring and their derivatives are mostly used in the prevention of corrosions of iron in oil refinery rigs[1]. on the other hand the steric chair flip cycloalkane of 2MCH has been greatly used as solvent in many industrial and pharmaceutical sectors[2]. Several pioneers[3–6] eclectically researched the combination of aromatic aniline group with chiral cyclohexanone group. The present experimental work illustrates the binary liquid mixture of 2MA (1) + 2MCH (2) at regular intervals of constant temperature from 303.15K to 313.15K over a constant ambient atmospheric pressure. In order to evaluate molecular interactions, the extracted excess values such as excess volume,V_m^E and excess isentropic compressibility,K_s^E has been fitted to the Redlich Kister(RK) non-linear polynomial regression equation of the order 4[7]. Since the non-ideality combination of aromatic aniline group with methyl group of cyclohexanone are highly reactive at low concentration. Hence, this approach sporadically misguides the specific interactions at low concentrations. In order to illustrate intermolecular hydrogen bonding nature and strength, the excess values are fitted to Reduced Redlich Kister(RRK) non-linear polynomial regression equation[8,9]. Additionally, to promote extant of solvation behavior of composites partial molar volumes and partial isentropic compressibility's for composites have been conceived. The extracted results are reviewed on the basis of intermolecular interactions between component molecules with the help of FTIR spectrum, which is recorded at room temperature[10].

2. Experimental Course:

2.1 Materials Description: In the present sequence, the provenance, CAS number, purity and further purification under chromatography and drying methods of 2MA as well as 2MCH have been illustrated in Table-1. Further, the Table-2 illustrated the Purity of 2MA and 2MCH was gauged by comparison of experimental density and speed of sound with literature values.

Table 1: Specification of Provenance, CAS Number, Mass Fraction Purity and Further Purification.

Name of the chemical	Source	CAS number	mass fraction purity	Further Purification Methods
2-methoxy aniline	TCI Chemicals-India	90-04-0	>98.0%	*GLPC
2-methyl cyclohexanone	HiMedia Laboratories, India.	583-60-8	>99.70%	*GLPC

*Gas-Liquid Partition Chromatography carried through Inert gas Ar.

2.2 Evaluation Methodology: The binary mixture of systems such as 2MA(1)+2MCH(2) was prepared in different concentrations, i.e., molefractions of these systems carried out 12 subsequent values, on which solvation concentration varies from 0 to 1. The densities of pure samples and mixed samples were measured with 10mL specific gravity bottle in high accuracy

digital electronic balance supplied by Mettler Toledo, Company-India. Speed of sound measurements of samples were performed by using with 2MHz frequency single crystal ultrasonic interferometer supplied by Nunes, Company-India.

Table 2: Physical Properties of Pure Components of 2MCH and 2MA with Literature at Specific Temperatures

Sample	**parameter**	**Exp./Lit.**	**Temperatures**		
			303.15 K	**308.15 K**	**313.15 K**
2MCH	ρ (kg. m^{-3})	Expt.	920.80	911.22	907.45
	ρ (kg. m^{-3})	Lit.	920.84[a]	911.20[a]	907.44[a]
	U (m.s^{-1})	Expt.	1346.00	1324.3	1303.2
	U (m.s^{-1})	Lit.	1346.00[a]	1324.2[a]	1303.8[a]
2MA	ρ (kg. m^{-3})	Expt.	1091.80	1087.40	1083.80
	ρ (kg. m^{-3})	Lit.	1091.75[b]	1087.35[b]	1083.78[b]
	U (m.s^{-1})	Expt.	1595.44	1579.44	1466.32
	U (m.s^{-1})	Lit.	1595.4[b]	1579.2[b]	1466.3[b]

. [a]*Reference*[11] [b]*Reference*[12]

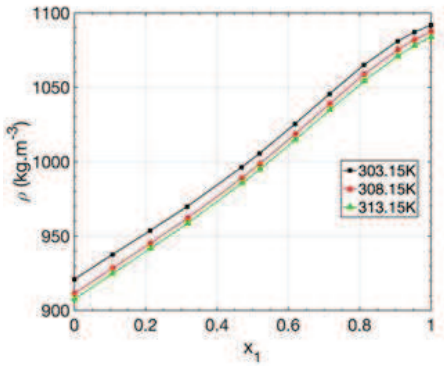

Figure 1: Density Variation of Combination 2MA(1)+2MCH(2) with Respect to Molefraction.

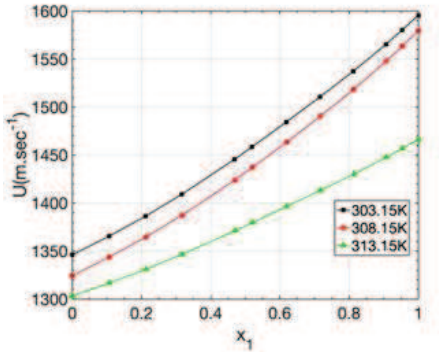

Figure 2: Speed of Sound variation of combination of 2MA(1)+2MCH(2) with respect to molefraction.

3 Results and Discussions: The experimentally calibrated parameters of density ρ and speed of sound U over entire compositions of 2MA(1)+2MCH(2) with temperature ranges 303.15K, 308.15K, 313.15 K are graphically illustrated in Figure 1 and Figure 2. The occurrent feature of all these attributes as regards to molefraction shows non-linear increasing trend, and also shows reduction as regards to increasing temperature in entire compositions. The non-linear abnormalities of trends of these liquid components implies molecular interactions are exists between them[3].

The excess thermodynamic acoustic parameters of binary solution have been esteemed with several peer reviewed journals. The eventual general expression was

$$Y^E = Y^r - Y^{id}$$----------(1)

Here, $Y^E = V_m^E, K_s^E$ and Y^r{= V_m*(molar volume),* K_s (isentropic compressibility)} is the real value of mixtures. And, the ideal component of thermodynamic acoustic parameters stands for

$$Y^{id} = x_1 Y_1 + (1 - x_1) Y_2$$----------(2)

Here, x_1 is the molefraction of component of 2MA with respect to 2MCH. Y_1 and Y_2 are the pure acoustic values of 2MA and 2MCH respectively.

3.1 Redlich-Kister Polynomial Analysis: The conventional non-linear curve fitting strategy for attributes of binary mixture pertains Redlich-Kister polynomial regression[7]. The standard deviation was calibrating from the consequence

$$Y_{RK}^E = x_1(1 - x_1) \sum_{p=0}^{p=N} A_{p,T}(2x_1 - 1)^p$$----(3)

Here, $Y_{RK}{}^E$ means excess attribute of any value (i.e., $V_m{}^E$, $K_s{}^E$) has been taken

$$\sigma(Y_{RK}^E) = \sqrt{\sum_{i=1}^{i=N} \frac{(Y_{i,exp} - Y_{i,cal})^2}{M - N}}$$---------(4)

Where *M* stands for the number of experimental values and *N* stands for the adjustable parameter. These excess values are examined with Redlich-Kister polynomial non-linear regression, and the values of $A_{i.T}$ (*i=0,1,2,3*) are determined along with standard deviation for experimental values and calibrated values. Table 3 catalogued the whole values of all composites.

The abnormality of thermodynamic acoustic excess parameters of V_m^E, K_s^E are portrayed in **Figure 3** & **Figure 4** respectively. Due to thermal agitations of all composites, temperature rise ushers to descend the excess parameters. The abnormality of excess molar volume at all temperatures has been illustrated in **Figure 3** over an entire concentration for all composites.

The values V_m^E are attributes positive for high concentrations of 2MCH and the trend turns to negative during the increasing concentration of 2MA in the respective temperatures.

The flipping sharpness of V_m^E from positive to negative was greater in 2MA(1) + 2MCH(2) at 303.15K. This is clearly visible in **Figure 3**, for the replicated sequence V_m^E . This clearly distinguishes the formation of H-bond[11], which is stronger at higher concentration and weaker in lower concentrations of composites. In addition to that, formation of H-bond is very weak at high concentrations of 2MCH.

Table 3: Coefficients of Redlich-Kister Equation and Standard Deviations for Excess Parameters of Various Binary Mixtures.

Combination	T/K	Redlich-kister equation coefficients				error
		$A_{0,T}$	$A_{1,T}$	$A_{2,T}$	$A_{3,T}$	$\sigma(Y^E_{RK})$
V_m^E (10^{-6} m^3.mol^{-1})						
2MA (1) + 2MCH(2)	303.15	0.5539	-4.3681	-6.3193	-1.0311	0.0254
	308.15	0.4977	-3.9161	-5.6926	-0.9524	0.0232
	313.15	0.4421	-3.4828	-5.0525	-0.8326	0.0217
K_s^E (10^{-12} m^2 .N^{-1})						
2MA (1)+ 2MCH(2)	303.15	-28.2441	-30.2306	-12.1652	11.9465	$4.7774x10^{-6}$
	308.15	-26.2670	-28.1145	-11.3136	11.1102	$4.9272x10^{-6}$
	313.15	-24.2900	-25.9985	-10.4620	10.2743	$7.6317x10^{-6}$

The abnormality of excess isentropic compressibility at all temperatures has been illustrated in **Figure 4** over an entire concentration for all composites. The K_s^E values are negative at all investigated temperatures for all composites. It also suggests interstitial accommodation and oriental ordering leading to more compact structure making, which enhances K_s^E to negative values. Fort and Moore indicated that the binary liquids having distinct molecular sizes and shapes mix well there by reducing the volume which causes values of K_s^E to be negative. The K_s^E of negative was greater 2MA(1)+2MCH(2) at 303.15K [12]. This is clearly visible in **Figure 4.** This clearly distinguishes a greater steric hindrance to the formation of hydrogen bonds in the respective composites.

3.2 Reduced Redlich-Kister Polynomial Analysis: The ineluctable Redlich Kister approach sporadically misguides the dissimilar composites. In conjunction to that it deceives interactions of molecules at low concentration regions in composites. Consequently, desnoyers suggested a contemporary befitted Reduced Redlich Kister(RRK) polynomial analysis to address more specific features in composites.[13]

$$Q_{Y^E_{RK},T}(x_1) = \frac{Y^E_{RK}(x_1)}{x_1(1-x_1)} \text{----------(5)}$$

The above specification is equivalent to apparent molar quantity of respective excess parameters in entire concentration ranges. Excess thermodynamic quantities have the convenience of showing the flipping sign, sharpness and magnitude of the dissimilarity composites, but the RRK polynomial specification elucidates a promising feature to lift the origin of the dissimilarity solutions[14].

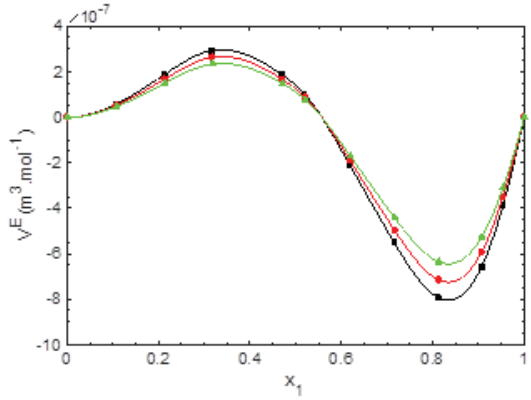

Figure 3: Excess Molar Volume variations against molefraction of solutions

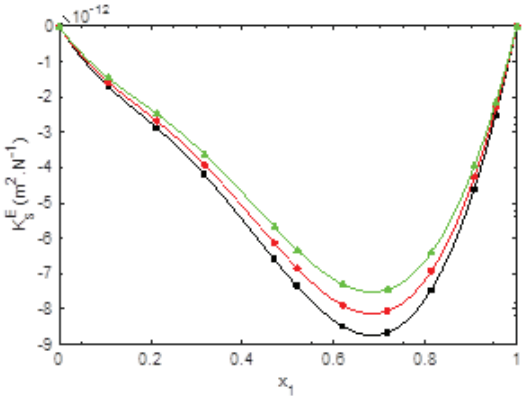

Figure 4: Excess Isentropic Compressibility Variations against Molefraction of Solutions.

On applying the reduced function on V_m^E & K_s^E the graphs of **Figure 3 & Figure 4** turn in to **Figure 5 & Figure 6** respectively. The abnormality of $Q_{V_m^E,T}(x_1)$ at all temperatures has been illustrated in Figure 5 over an entire concentration for all composites. The values $Q_{V_m^E,T}(x_1)$ are attributes positive (higher value) for high concentrations of 2MCH and the trend turns to negative (lower value) during the increasing concentration of 2MA. The decreasing trend of value from positive to negative was greater in 2MA(1)+2MCH(2) at 303.15K. This evidently distinguishes the hydrophobic interactions are present and stronger in the region of higher concentrations of methoxy aniline anisidine [15].

For the present scenario, the reduced functions values $Q_{K_s^E,T}(x_1)$ are higher value on 2MCH side and low value on 2MA. This clearly visible in **Figure 5**, for the replicated sequence of $Q_{K_s^E,T}(x_1)$. This result indicates composites are less compressible than the corresponding ideal mixtures. This strongly evident that strong interactions occur in these composites. This clearly indicates that the combination 2MA(1)+2MCH(2) at 303.15K sterically hindered higher than any other temperature.

3.3 Partial Molar Volumes and Partial Isentropic Compressibilities: The RRK functions of $Q_{V_m^E,T}(x_1)$ and $Q_{K_s^E,T}(x_1)$ at infinite dilution over a constant temperature and pressure was an addition tool to represents partial molar volumes and partial isentropic compressibilities at infinite dilutions. The above extrapolation expression (3) has modified as

$$Q_{V_m^E,T}(x_1 = 0) = A_{0,T} - A_{1,T} + A_{2,T} - A_{3,T} = \bar{V}_{1,p,m}^{E,\infty} = \bar{V}_{1,p,m}^{\infty} - V_{1,m} \text{----------(6)}$$

$$Q_{V_m^E,T}(x_1 = 1) = A_{0,T} + A_{1,T} + A_{2,T} + A_{3,T} = \bar{V}_{2,p,m}^{E,\infty} = \bar{V}_{2,p,m}^{\infty} - V_{2,m} \text{----------(7)}$$

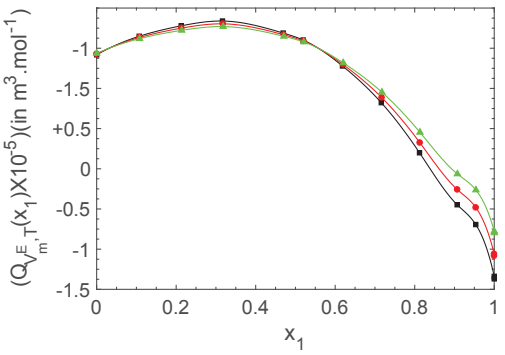

Figure 5: Reduced Excess Volume variations against molefraction of solutions.

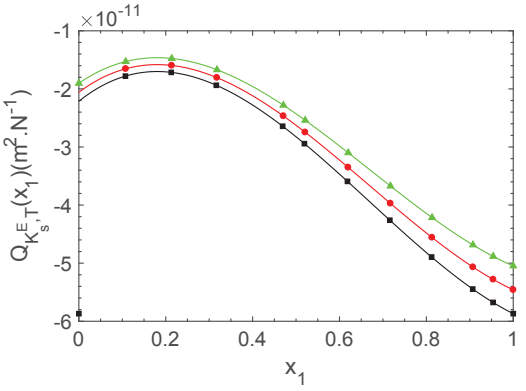

Figure 6: Reduced Excess Isentropic compressibility variations against molefraction of solutions.

The real-time analysis of partial molar volumes and partial isentriopc compressibilities over a molefraction concentration at constant pressure and temperature can be evaluated from the differential equation is[169,17]

$$\bar{V}_{i,p,m} = V_m(x_i) - x_j\left(\frac{\partial V_m(x_j)}{\partial x_j}\right)_{T,P} \text{---------(8)}$$

$$\bar{K}_{i,p,s} = K_s(x_i) - x_j\left(\frac{\partial K_s(x_j)}{\partial x_j}\right)_{T,P} \text{----------(9)}$$

Here x_i and x_j are the mole fractions of two components in the composite (*i=1,2 & j=i-1*). The intermolecular interactions in the composites can be interpreted in terms of packing efficiency of molecules with the help of partial molar volumes and partial isentropic compressibilities.

Because the domain influence of the components in the mixture changes with respect to the composition concentration and temperature. In this scenario, the partial molar volumes of components 2MA(1)+2MCH(2), at all temperatures has been shelled in **Figure 7** respectively.

For all combinations, the partial molar volumes of both components $\bar{V}_{1,p,m}$ *and* $\bar{V}_{2,p,m}$ are lower than of their individual values in the pure state, which reveals the domain influence of the individual components decreasing with their respective lower concentration regions[18]. The abnormality is examined for all constant interval of temperatures. This clearly suggests presence of solute-solvent interactions in between unlike molecules. Hence, from the representation of **Figure 7**, the effect of domain influence of volume is low for 2MA(1)+2MCH(2) at 303.15K This clearly suggests about, the solute-solvent interactions between molecules is high for 2MA(1)+2MCH(2) at 303.15K.

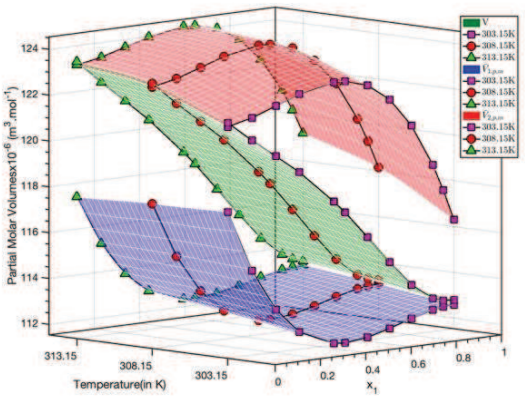

Figure 7: Plot of partial molar volumes against molefraction for the solutions 2MA(1)+2MCH(2) at studied range of temperatures 303.15K,308.15K & 313.15K.

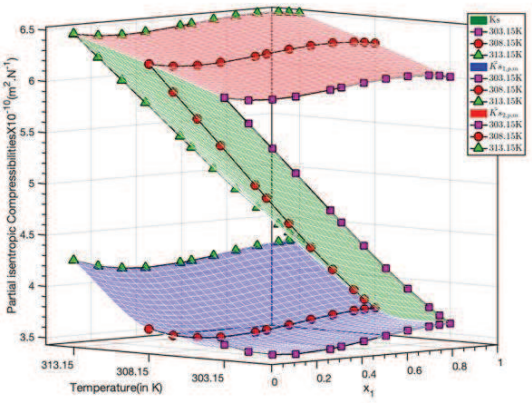

Figure 8 Plot of partial isentropic compressibilities against molefraction for the solutions 2MA(1)+2MCH(2) at studied range of temperatures 303.15K,308.15K & 313.15K.

Because the geometrical influence of the components in the mixture changes with respect to the composition concentration and temperature. In this scenario, the partial isentropic compressibilities of components 2MA(1)+2MCH(2) at all temperatures has been shelled in

Figure 8. The partial isentropic compressibilities $\bar{K}_{1,p,s} and\ \bar{K}_{2,p,s}$ are unchanged, negative and positive for the respective combinations of 2MA(1)+2MCH(2). This reveals the geometrical compressibility influence of the individual components increasing with their respective lower concentration regions in 2MA(1)+2MCH(2) combination at 303.15K[18]. The abnormality is examined for all constant interval of temperatures. This clearly suggests the strong dipole inclusions between 2MA(1)+2MCH(2) at 303.15K.

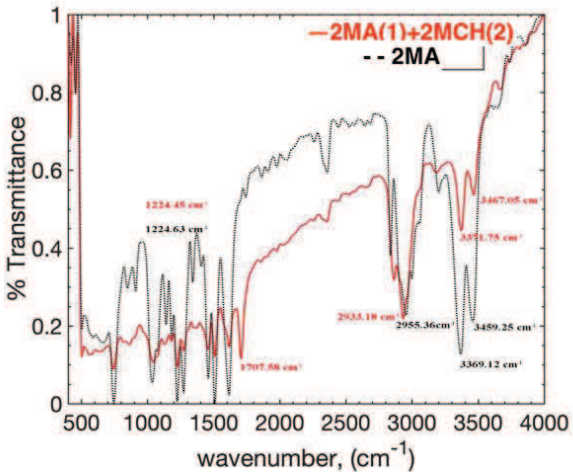

Figure 9: Normalized FT-IR spectra analysis for the binary mixture 2MA(1)+2MCH(2) over the range 400 to 4000 cm^{-1}

3.4 FT-IR Spectrum Analysis: The FT-IR spectrum of components 2MA+2MCH and their pure components are carried at room temperature 303.15K[10]. The peaks 3438.79cm^{-1}(N-H strong bond stretching), 3361.17cm^{-1}(O-H strong bond stretching), 2934.73cm^{-1}(C-H medium stretching) and 1706.10cm^{-1}(C=O strong stretching) are appeared. This contention was supported by the formation of intermolecular strong bonds.

4. Conclusion: In this frame work, the values of excess thermodynamic parameters have been calibrated for an entire composition of 2MA(1)+2MCH(2) with accustomed levels of temperatures. This is clearly elucidating a strong hydrogen bonding, dipole-inclusion interactions present in the component molecules. Moreover, the reduced excess thermodynamic parameters have been executed by using contemporary RRK polynomial over an entire composition with accustomed levels of temperatures. This reveals more specific features about, smaller molar mass of 2MCH molecules sterically hindered in larger molar mass of 2MA. These results of intermolecular interaction behavior also supported with FT-IR spectroscopy.

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