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Experimental Investigation of Solute – Solvent Interactions of Liquid Mixtures of Anisole with 2-alkoxyalkanols through Thermophysicochemical Properties and ATR-FT IR Spectral Studies

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Abstract:

Thermophysical parameters such as density (p) of binary liquid mixtures of Anisole (methoxy benzene) with 2 -Methoxy ethanol, 2-Ethoxyethanol, and 2-Butoxy Ethanol have been calculated at temperatures of 303.15 K, 308.15 K & 313.15 K and speed of sound (u) measured at 303.15 K, 313.15 K. The excess molar volumes (V^E) and excess isentropic compressibilities ($\kappa_s{}^E$) of all the studied temperatures have been determined using the data measured from density and speed of sound. Redlich-Kister polynomial equation was fitted to the calculated V^E and $\kappa_s{}^E$ values. Additionally, the estimated speed of sound data were compared with Jacobson's Free Length theory (FLT), and Schaff's Collision factor theory (CFT) to test their predictive capability. The results were analyzed in terms of physicochemical interactions occurred due to the solute- solvent components in the binary liquid mixtures. The existence of hydrogen bonding between Anisole and 2 -Methoxy ethanol, 2-Ethoxyethanol, and 2-Butoxyethanol was experimentally confirmed by using AT FT-IR Spectroscopic studies.

Keywords: Density; Speed of sound; Excess molar volume; FT-IR spectrum.

1. Introduction

In general in a chemical design and effective chemical process optimization, the molecular interactions prevailing process fluids and thermodynamic properties like densities and speed of sounds play a major role. These two properties are very important for engineering designs involving chemical separations, heat transfer, mass transfer, and fluid flow. Basically, sound speed data have acquired the status of an important place for the study of structure and properties of matter. Moreover, sound speed data plays an important role in the establishing intermolecular interactions between component molecules. The structural arrangements are influenced by the shape of the molecule as well as by their mutual interactions. Role of mixed solvents are always essential in the chemical industry in the fields ranging from petro chemistry to pharmaceutical chemistry. Anisole is one of aromatic ethers that is widely used for a number of practical applications in various fields such as dyes, pigment, and perfumery and as a starting point for preparation of different derivatives. Thus, a study of physical properties of the binary mixtures containing anisole has attracted a substantial interest in the literature [1-7]. Anisole is a precursor to insect pheromones and pharmaceuticals [8]. Anisole is one of the important phenolic ether and is used as the starting-point for the preparation of various derivatives.

Alkoxyalkanols are oxygenated compounds are increasingly used as additives to gasoline due their octane enhancing and pollution reducing properties [9, 10]. Moreover, hydroxyl ethers are non-ionic amphiphile molecule, very effective as surfactants with a large number of applications [11, 12]. Moreover, 2-alkoxyalkanols are a very interesting class of solvent having ether i.e. oxygen (-O-) or hydroxyl (-OH) group and is noted for its donating and accepting ability. In this article an investigation was undertaken of the systems containing the binary mixtures of anisole and Alkoxyalkanols, which makes the possible study of self-association via inter and intra molecular hydrogen bonding through the -OH (Hydroxyl) and -O- (ether) groups in the same molecule. [13-16].

In the present study an attempt has been made to provide insight into the nature of molecular interactions occurring between anisole and alkoxyalkanols by measuring the densities (ρ) at 303.15 K to 313.15 K and speeds of sound (u) at 303.15K and 313.15 K. Further, the present work will provide that an increasing chain length of alkoxyalkanols from methoxy to butoxy may three influence both the sign and magnitude of excess thermodynamic functions. Moreover, the measured values of the speed of sound are also analyzed in terms of Schaaff's collision factor theory (CFT) [17] and Jacobson's free length theory (FLT).[18,19]. FT-IR Spectroscopic data are also collected in the present investigation to learn of the existence of intermolecular hydrogen bonding between anisole and Alkoxyalkanols molecules. To the best of our knowledge no experimental data on density and speed of sound is available in the literature for the binary mixtures of anisole with 2-Methoxy ethanol, 2-Ethoxy ethanol,and 2-Butoxy ethanol.

2. Experimental Section

2.1. Materials

All the chemicals (A.R. grade) used in the present work supplied by S.D. Fine Chem. Ltd., India. The purities of all the experimental liquids were analyzed by Gas Chromatography and the water content of samples were measured by Analab (Micro Aqua Cal 100) Karl Fischer Titrator and these were mentioned in Table1. The purity of chemicals was checked by comparing the measured densities and speed of sound, which were in good agreement with literature values [20-44] at T= 303.15K to 313.15K was reported in Table 2.

2.2. Methods

2.2.1. Sample preparation

The homogeneous binary liquid mixtures of anisole with isomeric cresols were prepared over the entire range of composition by syringing known weights of pure liquids into air tight screw capped glass vials. The required properties of the binary systems were measured on the same day to prevent loss due to evaporation and minimize the absorption of atmospheric moisture. The mass measurements were performed on digital

electronic balance (ATY 224, Shimadzu, India) with an uncertainty of ±1× 10^{-4} g. The uncertainty in the estimated mole fraction of mixtures was found to be less than ±1 × 10^{-4}.

2.2.2. Density (ρ) and speed of sound (u) measurements:

The density (ρ) and speed of sound (u) measurements of pure components and the binary liquid mixtures of anisole with Alkoxyalkanols were carried at temperatures ranging from 303.15 K to 313.15 K, and at 0.1 MPa pressure, using digital densimeter (Rudolph Research Analytical, DDM-2911, USA) and ultrasonic interferometer (Mittal Enterprises, F-05, India) respectively. The working frequency for the speed of sound (u) measurement is 2MHz The desired temperature of the sample is maintained by a thermostat within u(T) = ±0.02 K. Further details about the experimental apparatus and procedure can be found in our previous work [45]The uncertainty in density (ρ) measurements and excess volumes (V^E) calculated from densities is estimated to be ± 6x10^{-4} g. cm^{-3} and ± 5x$10^{-3}$$cm^3$.$mol^{-1}$ respectively. The uncertainty in the measured speeds of sound (u) and the derived excess isentropic compressibility (κ_s^E) values are found to be ± 0.5 m s^{-1} and ± 0.05 TPa^{-1} respectively.

The working of the interferometer was tested by comparing the measured speed of sound of pure samples of anisole and Alkoxyalkanols, which are in good agreement with literature values [20-44] reported in Table -2. FTIR spectra have been measured by an ALPHA FT-IR Spectrometer (Bruker) to study the existence of intermolecular hydrogen bonding between anisole and 2-alkoxyalkanols.

3. Results and discussion

3.1. Excess volumes (V^E)

The non-ideal behavior between binary mixtures of Anisole with 2-Methoxyethanol, 2-Ethoxyethanol and 2-Butoxy ethanol represented interms of excess molar volume (V^E), which is computed from the experimentally determined density data using following equation

$$V^E/cm^3.mol^{-1} = [[X_1 M_1 + X_2 M_2]/\rho_m - [X_1 M_1/\rho_1 + X_2 M_2/\rho_2]] \quad (1)$$

Where, X_i is the mole fraction of component i (i=1, 2) in the mixture; M_i is the molar mass. $\rho_m$and ρ_i are the measured density of the mixture and the pure component i(i=1,2) respectively. Further, the V^E data were also graphically represented in Figure -1 at 303.15K of all the mixtures.

The calculated V^E values were fitted to Redlich-Kister [46] equation and these were given in Table- 3.

Redlich-Kister equation is:

$$V^E/cm^3.mol^{-1} = X_1(1-X_1)[a_0+a_1(2X_1-1)+a_2(2X_1-1)^2] \quad (2)$$

where a_0, a_1 and a_2 are adjustable parameters and $x_1$is the mole fraction of anisole .The values of parameters were obtained by the least-square method and these values of the parameters were given in Table 6. Excess volume (V^E) data of liquid mixtures is a result of different contributions arising from the structural changes undergone by the pure solvent molecules.

An examination of V^E values in figure-1 shows that negative values are present at all temperatures over the entire composition for binary mixtures of anisole with 2- alkoxyalkanols. The sign of the excess molar volume of the system depends on the relative six magnitude of expansion and contraction of mixing two liquids [47-54]. The values of V^E become more negative as the length of the alkyl chain length of the alkoxyalkanols molecules decreases and show the following effects.

The contraction in values of V^E is the result of contributions from several factors such as:

i) The rupture of self-associated structure of the alkoxyalkanol molecule,
ii) The intermolecular hydrogen bond formation between alkoxyalkanols and anisole molecules,
iii) Existence of specific interaction between alkoxyalkanols and the anisole molecules. This interaction may be considered as the reaction between alkoxyalkanols as a Lewis acid and anisole as a Lewis base [55].

The factors that cause expansion in volume are

(a) Dispersion forces can be attributed to the declustering of the structure of one or both of the component molecules in a solution, i.e. the loss of dipolar interaction between the molecules.
(b) The geometry of molecular structures that prevents molecules from one component from fitting into voids produced by molecules from the other component.
(c) Steric hindrance between the molecules that make up the component.

The factors that cause volume contraction were prevalent in binary liquid mixtures including anisole with 2-Methoxyethanol, 2-Ethoxyethanol and 2-Butoxy ethanol, according to the V^E data in Figures 1 to 3.

Over the full composition range for the examined mixtures, the observed values of excess molar volume (V^E) data support the existence of hydrogen bonding connections between the O-atom of the $–OCH_3$ group of anisole molecule and the H-atom of the -OH group of alkoxyalkanols.

The algebraic V^E values of anisole with 2-alkoxyalkanols follow the order:

(A+2-ME) > (A+2-EE) > (A+2-BE)

The above order indicates the magnitude of V^E becomes less negative as the alkyl chain length of the alkoxyalkanol molecule increases (figure-1). The more negative excess volume in the system (A+2-ME) reveals that a more efficient packing and/or attractive interaction is occurring between these two components when mixed together. Moreover, the negative values of V^E may be ascribed to the formation of hydrogen bond between the oxygen atom of the $–OCH_3$ group of anisole and the hydrogen atom of the hydroxyl group of alkoxyalkanol molecules. The decreasing V^E values in all mixtures studied suggest that with the increase in carbon chain length of the alkoxyalkanol, the effect of formation of hydrogen bonding decreases [56, 57]. The negative excess molar volumes shown in table 3 indicate that a more efficient packing and/or attractive interaction occurs in the mixed state. Generally the high negative deviations from ideality in these binary systems are due to the interstitial accommodation and strong intermolecular interactions such as chemical or specific interaction of the molecules like hydrogen bonding, dipole-dipole interaction between the unlike molecules. The negative values of V^E for the alkoxyalkanols under investigation may be attributed to the existence of the hydrogen bond of the type -OH…O- between the –O- group of anisole and -OHgroup of alkoxyalkanols. The strength of hydrogen bonding decreases as the chain length of the alkoxyalkanols increases due to the increased +I effect of the alkyl group [58]. An study of the V^E data in Figures .1 to 3 reveals that the property is negative for all mixtures over the whole composition range at temperatures ranging from 303.15K to 313.15K.

Further, the curves in figure 1 show that V^E becomes less negative as the carbon chain length of 2-alkoxyalkanol molecule increases from 2-methoxyethanol to 2-butoxyethanol. This is due to the fact that increase in chain length of the alkoxyalkanols (hence decrease the strength of hydrogen bond) facilitates the disruption of associated structures in alkoxyalkanols on addition of anisole leading to less negative V^E values. The less negative V^E is observed for the system of anisole with 2-butoxyethanol suggests that weak association is expected since the $–OCH_3$group in the anisole molecule provides a lesser surface area and volume fraction. Moreover, the closer approach of unlike molecules in these is sterically hindered as the size of alkyl group becomes more bulky, resulting in weak hydrogen bonding between unlike molecules [59-61].

3.2. Excess isentropic compressibilities (κ_s^E)

The speed of sound (u) data of pure liquids and binary mixtures generated by combining anisole with 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol were measured at 303.15K and 313.15K spanning the whole composition range in this study. The measured sound speed (u) and density (ρ) data were utilised to construct isentropic compressibilities (κ_s) and excess isentropic compressibilities (κ_s^E).
Table 4. includes the mole fraction of anisole (x_1), mixture density (ρ), speed of sound (u), isentropic compressibility (κ_s), and excess isentropic compressibility (κ_s^E), as well as the κ_s^E data graphically presented in figures 4 to 5.
The following equation was used to calculate the isentropic compressibility (κ_s) using the experimental density (ρ) and speed of sound (u) data:

$$\kappa_s = \frac{1}{u^2 \rho} \quad (3)$$

and the κ_s^E were estimated by adopting the following equation:

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \quad (4)$$

where, κ_s^{id} represents the ideal value of the isentropic compressibility which was calculated from the Benson and Kiyohara equation [62].

$$\kappa_s^{id} = \sum_{i=1}^{2} \phi_i \left[\kappa_{s,i} + TV_i\left(\alpha_i^2\right)/C_{p,i}\right] - \left\{T\left(\sum_{i=1}^{2} x_i V_i\right)\left(\sum_{i=1}^{2} \phi_i \alpha_i\right)^2 / \sum_{i=1}^{2} x_i C_{p,i}\right\} \quad (5)$$

Here, C_{pi} and α_i are the molar heat capacity and the thermal expansion coefficient of the i^{th}component respectively. The value of C_{pi} and α_i obtained and evaluated from literature [63-67]
The property is negative over the whole composition range at 303.15K and 313.15K, according to κ_s^E data in table- 4 for mixtures of anisole with 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol. This could be explained by the relative strength of effects on the free space between component molecules.
The sign and amplitude of κ_s^E are important in predicting molecular interactions between pure components and mixtures. Furthermore, Kiyohara and Benson [62] have proposed that κ_s^E data is the result of numerous opposing effects. Charge exchange, dipole–induced dipole and dipole–dipole interactions, interstitial convenience, and creation of H-bonding all contribute to negative κ_s^E values, but dissociation of liquid order structure generates positive excess isentropic compressibility. As a result, the magnitude and sign of various kinds are mostly determined by the molecular composition of component liquids.
The values of κ_s^E become more negative as the number of $–CH_2–$ units in the alkoxyethanol moleculesincreases (the more negative κ_s^E values have been found for the (A+ BE) mixture). The variation of κ_s^E with the size of the alkoxy ethanol is consistent with that of the excess molar volume (V^E). In general, the values of κ_s^E can be considered as arising from two types of interaction between the component molecules:

(i) a physical interaction, consisting of dispersion forces or weak dipole-dipole interaction making a positive contribution
(ii) a chemical or specific interaction, which include charge-transfer forces, forming H-bonds and other complex forming interactions, resulting in a negative contribution to the κ_s^E

Apart from these interactions, negative contribution may also be due to the differences in size and shape of component molecules, which might allow them to fit into each other's structure, reducing volume and compressibility and resulting in negative the κ_s^E

values. The negative values of the κ_s^E are also an indication that the mixture is less compressible than the corresponding ideal mixture and suggest strong chemical and specific interactions between the components of binary mixtures analysed, which are greatest in the case of the (anisole +2-butoxyethanol) system. For an internal structure of binary mixtures containing alkoxyalkanol and protic solvent like anisole we can suggest that the addition of pure anisole to alkoxyalkanols would disrupt their self-associated structure their by releasing free Anisole, 2-methoxyethanol,2-ethoxyethanol and 2-butoxyethanol molecules may mix by specific interactions and intermolecular hydrogen bonds form the mixed intermolecular complexes. The decrease in volume and compressible might arise also from interstitial accommodation and hydrophobic interactions in the investigated binary mixtures. The binary mixtures the algebraic values of anisole with 2-alkoxyalkanols κ_s^E will be in the following order:

Anisole +2- methoxyethanol < Anisole + 2-ethoxyethanol < Anisole + 2-butoxyethanol

The more negative κ_s^E indicate that liquid combinations of anisole with 2- methoxyethanol are less compressible than the comparable ideal mixtures [68] and also the other mixtures, namely 2-ethoxyethanol, 2-butoxyethanol, as shown in Figures 4 to 5.
At 303.15K and 313.15K temperatures, the κ_s^E values are negative over the whole mole fraction range, suggesting the prevalence of interstitial of component effect accommodation, which can be attributed to the relative strength between component molecules as indicated in the literatures [69,70] Finally, it is concluded that in all systems, excess volume and excess isentropic compressibilities data are negative, and that the properties decrease as temperature increases.
Experimental speed of sound were analyzed in terms of collision factor theory (CFT) [17], free length theory (FLT) [18,19] and these were also included in Table-4 along with experimental speed of sound. A comparison between experimental sound speed and theoretical values suggest that the model proposed by Schaaff's CFT gives better estimation of sound speed data. The merits of these theories were compared in terms of relative root mean deviation (RMSD) by using the following formula [71, 72 ,73].

$$\text{RMSD} = \left[\frac{1}{n}\sum_{i=1}^{n}\left[\frac{y_{exp}-y_{cal}}{y_{exp}}\right]^2\right]^{1/2} \quad (6)$$

The RMSD for all the binary system values are given in Table-5. And shows that Schaaff's CFT model gives better estimation in speed of the sound for the binary mixtures under the investigation.

The experimental data of anisole with, 2- methoxyethanol, 2-ethoxyethanol, 2-butoxyethanols were fitted to Redlich-Kister [45] equation. The values of parameters were obtained by the least-square method and these values of the parameters were given in Table 6. The corresponding standard deviations σ (Y^E) are calculated by applying the following formula:

$$\sigma\left(Y^E\right) = [\,\Sigma(Y^E_{exp} - Y^E_{cal})^2/(m-n)]^{1/2} \quad (7)$$

where σ (Y^E) is V^E/κ_S^E. 'm' is the total number of experimental points and 'n' is the number of coefficients. A perusal of curves in Figures 4 and 5 shows that the values of excess isentropic compressibility (κ_s^E) for anisole with 2- methoxyethanol , 2-ethoxyethanol, 2-butoxyethanols mixtures were negative over the entire mole fraction range at temperature from 303.15 K to 313.15K. This indicates the predominance of interstitial accommodation of the component molecules and this may be ascribed to the relative strength between component molecules as defined in the literatures [74] The values of κ_s^E becomes more negative as the strength of interaction between component molecules increases, due to dissociation of associated structure between anisole and 2- methoxyethanol forms strong O···H bond than the other anisole with 2-ethoxyethanol, 2-butoxyethanols. We can suggest that the addition of pure anisole, 2- methoxyethanol , 2-ethoxyethanol, 2-butoxyethanols

would disrupt their self-associated structures there by releasing free anisole and 2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol molecules may mix through by specific interactions and intermolecular hydrogen bonds forming the mixed intermolecular complexes.

3.3. FT-IR Studies

FT-IR spectra changes are broadly utilized in investigation of intermolecular H-bonding presence between the binary liquid mixtures of Anisole and 2-methoxyethanol , 2-ethoxyethanol, 2-butoxyethanol The spectroscopic studies used for the formation of strong hydrogen-bonding between C-O-C stretching of Anisole and OH stretching of 2-methoxyethanol , 2-ethoxyethanol. However, compared to the other liquid mixtures containing Anisole with , 2-butoxyethanol had a weaker solute-solvent interactions. The values of vibration frequencies and spectra's were included in Table -7 and Figures. 6,7 and 8.

Furthermore, an examination of FT-IR spectral data for the equimolar binary liquid mixtures have Hydrogen bonding interaction between 2-Alkoxyalkanols and ether functional groups This band (hydrogen bonded –O- stretching) can be seen in the pure liquids [75] Anisole exhibit band –O− stretching at 1239.68cm^{-1} (ASym) and 1035.37 cm^{-1} (Sym) in the experimental FT-IR spectrum of the pure components' absorption bands: The 2-alkoxyalkanols, namely 2-Methoxyethanol (ME), 2- Ethoxyethanol (EE), 2-Butoxyethanol (BE). Anisole exhibit some characteristic absorption bands 3412.85 cm^{-1} (O-H str), 3411.98 cm^{-1} (O-H str)and 3410.37cm^{-1}(OH str) respectively. In the present investigation, the FT-IR spectrum considered at room temperature and equimolar concentration, the resultant absorption bands of (A+2-ME), (A+2-EE) and (A+2- BE) are 3435.38 cm^{-1},3427.84 cm^{-1} and 3417.63 cm^{-1} respectively, that indicates formation of weak intermolecular interactions between component molecules as the chain length of 2-alkoxyalkanols increases, the absorption band shifted to lower frequency. The frequency shifts are caused by the strong intermolecular interaction like hydrogen bonding between the hydrogen in the hydroxyl group of 2-alkoxyalkanols with Oxygen in anisole. These shows in figures 6,7,8. Finally, concluded that experimental FT-IR Spectroscopy analysis concur with those of the experimental, theoretical studies.

4. Conclusions

In the present study the experimental data for density and speed of sound for the binary liquid mixtures of anisole and 2-Methoxyethanol (ME), 2- Ethoxyethanol (EE), 2-Butoxyethanol (BE)at temperatures 303.15K to 313.15K.were studied The experimental results for were used to compute excess volume and excess isentropic compressibility results analysed in terms of Redlich-Kister equation and the experimental speed sound for compared with theoretical models namely CFT and FLT . The CFT models give better the results and The FT-IR analysis and excess thermodynamic properties can be interpreted by considering the intermolecular hydrogen bonding, molecular size and shapes of the components.

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Table 1: Name of the chemical, source, CAS number, purity in mass fraction, purity analysis method and water content in mass fraction of the chemicals used in this work.

Component	Source	CAS number	Purity in mass fraction (as received from supplier	Purity in mass fraction (after purification)	*Analysis method	Water content in mass fraction
Anisole	S.D.Fine Chemicals.Ltd	64-17-5	>0.99	0.989	GC	0.0003
2-Methoxy ethanol	S.D.Fine Chemicals. Ltd	109-86-4	>0.99	0.993	GC	0.0004
2-Ethoxy ethanol	S.D.Fine Chemicals. Ltd	110-80-5	>0.98	0.987	GC	0.0004
2- Butoxy ethanol	S.D.Fine Chemicals. Ltd.	111-76-2	>0.98	0.994	GC	0.0005

*GC=Gas Chromatography

Table 2: Density (ρ) and sound speed (u) values for the pure components along with literature values at temperatures studied and at 0.1 MPa pressure.

T/K	ρ/(g.cm^3)		u/(m.s^{-1})	
	Exp.	Lit.	Exp.	Lit.
Anisole				
303.15	0.98458	0.98459 [a] 0.98460 [b] 0.98420 [c]	1386.68	1386.57[a] 1387.00[d]
308.15	0.98032	0.98031[a] 0.97971[d]		
313.15	0.97568	0.97566[a] 0.97570[c] 0.97500 [c]	1349.88	1349.87[a] 1349.66[e]
2-Methoxy Ethanol				
303.15	0.95586	0.98554 f 0.9558 g 0.95547 h	1324.56	1324.50 [m] 1324.72 [k] 1324.29 [n]
308.15	0.95114	0.95116 f 0.95154 j		
313.15	0.94646	0.94649 [f] 0.94642 [k] 0.94656 [l]	1290.64	1290.60 [m] 1290.05 [k]
2- Ethoxy Ethanol				
303.15	0.92182	0.9210 [o] 0.9231 [p] 0.92077 [q] 0.92145 [r]	1288.21	1287.08 [o] 1286.70 [p] 1285.10 [q] 1285.40 [s]
308.15	0.91614	0.9170 [o] 0.91641 [q] 0.91686 [s]		
313.15	0.91146	0.9120 [o] 0.9138 [p] 0.91180 [q] 0.91224 [s]	1252.46	1252.0 [o] 1250.2 [p] 1249.60 [q]
2-Butoxy Ethanol				
303.15	0.89224	0.8923[f] 0.8924[w] 0.89217[t] 0.89213[u] 0.89268[v]	1290.06	1294.00 [y]
308.15	0.88795	0.88797[f] 0.88809[j] 0.88705 [u] 0.88810[w] 0.88891[x]		
313.15	0.88346	0.88346 [y] 0.88340 [y]	1273.16	1273.06[y]

Standard uncertainties are $u(\rho)$ ±5x10^{-5}g.cm^{-3}, u (u) ± 0.5 m.s^{-1}, u (p) = 1kPa, u (T) ± 0.02 and ±0.05 K for ρ and u measurements respectively.

(a) -ref-20 ,(b)-ref-21(c)-ref-22, (d)-ref-23,(e)-ref-24, (f)-ref-25,(g) ref-26,(h)ref-27,(i)-ref-28 ,(j)-ref-29,(k)-ref-30,(l)-ref-31,(m) ref-32,(n)ref-33,(o).ref-34,(p) ref-35,(q)-ref-36,(r)-ref-37,(s)-ref-38.(t)-ref- 39 (u)-ref-40 (v)- ref-41 (w)-ref-42(x)-ref-43(y)-ref-44**,**

Table 3: Mole fraction of Anisole (x_1), densities (ρ), experimental excess volumes (V^E) and predicted excess volumes (Redlich-Kister) at T= 303 K to 313.15 K and 0.1M Pa pressure for the binary mixtures of Anisole (1) with 2-Methoxy ethanol , 2-Ethoxyethanol, 2-Butoxy Ethanol (2)[a]

x_1	Density(ρ) (g.cm^{-3})	V^E/cm^3.mol^{-1}	
		Experimental	Redlich-Kister
Anisole *(1) + 2-Methoxy ethanol (2)*			
T=303.15K			
0.0746	0.96116	-0.207	-0.205
0.1535	0.96583	-0.368	-0.369
0.2372	0.96989	-0.484	-0.489
0.3260	0.97343	-0.558	-0.562
0.4205	0.97645	-0.588	-0.588
0.5211	0.97892	-0.567	-0.565
0.6287	0.98094	-0.500	-0.493
0.7437	0.98245	-0.375	-0.374
0.8672	0.98363	-0.206	-0.208
T=308.15K			
0.0746	0.95721	-0.271	-0.270
0.1535	0.96218	-0.458	-0.459
0.2372	0.9663	-0.578	-0.579
0.3260	0.96972	-0.640	-0.641
0.4205	0.97257	-0.652	-0.657
0.5211	0.97514	-0.638	-0.636
0.6287	0.97739	-0.590	-0.582
0.7437	0.97913	-0.486	-0.486
0.8672	0.98031	-0.315	-0.316
T=313.15K			
0.0746	0.95293	-0.308	-0.305
0.1535	0.95798	-0.504	-0.508
0.2372	0.96205	-0.621	-0.626
0.3260	0.96535	-0.674	-0.678
0.4205	0.96818	-0.684	-0.685
0.5211	0.97072	-0.667	-0.661
0.6287	0.97297	-0.619	-0.614
0.7437	0.97487	-0.532	-0.531
0.8672	0.97606	-0.361	-0.363
Anisole (1) + *2-Ethoxyethanol*(2)			
T=303.15K			
0.0901	0.92890	-0.085	-0.086
0.1823	0.93581	-0.152	-0.153
0.2765	0.94261	-0.208	-0.203
0.3728	0.94919	-0.241	-0.241
0.4714	0.95572	-0.27	-0.264
0.5722	0.96197	-0.268	-0.272
0.6754	0.96813	-0.258	-0.261
0.7810	0.97401	-0.216	-0.220
0.8892	0.97960	-0.142	-0.139
T=308.15K			
0.0901	0.92376	-0.130	-0.130
0.1823	0.93099	-0.218	-0.218
0.2765	0.93795	-0.277	-0.277
0.3728	0.94474	-0.319	-0.315
0.4714	0.95139	-0.346	-0.340
0.5722	0.95777	-0.343	-0.351
0.6754	0.96414	-0.340	-0.342
0.7810	0.97017	-0.298	-0.299
0.8892	0.97567	-0.198	-0.197
T=313.15K			

0.0901	0.91957	-0.184	-0.183
0.1823	0.92703	-0.298	-0.297
0.2765	0.93397	-0.356	-0.362
0.3728	0.94070	-0.391	-0.394
0.4714	0.94731	-0.413	-0.405
0.5722	0.95362	-0.403	-0.401
0.6754	0.95978	-0.376	-0.378
0.7810	0.96570	-0.322	-0.324
0.8892	0.97113	-0.212	-0.212
Anisole (1) + *2-Butoxyethanol* (2)			
T=303.15K			
0.1208	0.90211	-0.061	-0.063
0.2361	0.91181	-0.102	-0.101
0.3463	0.9214	-0.132	-0.126
0.4518	0.93084	-0.146	-0.142
0.5528	0.94017	-0.151	-0.152
0.6496	0.94938	-0.148	-0.153
0.7426	0.9585	-0.138	-0.142
0.8318	0.96745	-0.115	-0.116
0.9175	0.97618	-0.072	-0.070
T=308.15K			
0.1208	0.89794	-0.079	-0.081
0.2361	0.90768	-0.125	-0.125
0.3463	0.91728	-0.156	-0.151
0.4518	0.92674	-0.173	-0.169
0.5528	0.93611	-0.182	-0.180
0.6496	0.94534	-0.179	-0.183
0.7426	0.95446	-0.168	-0.174
0.8318	0.9634	-0.142	-0.145
0.9175	0.97208	-0.092	-0.089
T=313.15K			
0.1208	0.89388	-0.116	-0.116
0.2361	0.90375	-0.186	-0.188
0.3463	0.91348	-0.238	-0.235
0.4518	0.92304	-0.27	-0.264
0.5528	0.93241	-0.282	-0.280
0.6496	0.94157	-0.273	-0.279
0.7426	0.95062	-0.254	-0.257
0.8318	0.95937	-0.208	-0.208
0.9175	0.96776	-0.126	-0.125

The standard uncertainties are u (x) ± 1x10^{-4}, u (ρ) ± 5x10^{-5} g.cm^{-3}, u (T) = 0.02K and u(p) = 1 kPa, and u (V^E) = ±0.002 cm^3.mol^{-1}.respectively.

Table 4: Mole fraction (x_1) of Anisole Experimental sound speed(u), isentropiccompressibilities (κ_s), excess isentropic compressibilities (κ_s^E) and predicted excess isentropic compressibilities (Redlich-Kister) theoretical sound speed values of Anisole (1) with *2-Methoxy ethanol* , *2-Ethoxyethanol*, *2-Butoxy Ethanol* (2) at 303.15K and 313.15 K and 0.1M Pa pressure.

x_1	u(exp) (m.s^{-1})	κ_s (TPa^{-1})	u_{FLT}	u_{CFT}	κ_s^E/(TPa^{-1})	
			(m.s^{-1})		Exp.	Redlich-Kister
Anisole(1)+ *2-Methoxy ethanol* (2)						
T=303.15 K						
0.0746	1329.13	588.94	1350.76	1329.36	-1.174	-1.120
0.1535	1333.82	581.98	1372.29	1334.40	-1.834	-1.879
0.2372	1338.87	575.18	1388.93	1339.72	-2.210	-2.320
0.326	1344.34	568.43	1401.23	1345.33	-2.396	-2.495
0.4205	1350.30	561.68	1408.98	1351.25	-2.441	-2.459
0.5211	1356.78	554.92	1411.87	1357.52	-2.354	-2.268
0.6287	1363.68	548.19	1410.73	1364.16	-2.083	-1.963
0.7437	1371.06	541.47	1405.16	1371.21	-1.627	-1.549
0.8672	1378.69	534.85	1396.81	1378.70	-0.896	-0.961
T=313.15K						
0.0746	1287.16	633.4	1318.17	1291.40	-2.084	-2.055
0.1535	1297.07	620.5	1340.40	1296.59	-3.580	-3.569
0.2372	1303.02	612.2	1355.63	1302.05	-4.480	-4.586
0.326	1309.40	604.2	1365.10	1307.80	-5.081	-5.157
0.4205	1315.97	596.4	1370.97	1313.86	-5.313	-5.335
0.5211	1322.58	588.9	1374.61	1320.26	-5.185	-5.161
0.6287	1329.33	581.6	1375.98	1327.02	-4.740	-4.651
0.7437	1336.04	574.7	1374.69	1334.17	-3.879	-3.761
0.8672	1342.66	568.3	1368.01	1341.78	-2.263	-2.330

Anisole+*2-Ethoxyethanol*(2)						
T=303.15 K						
0.0901	1296.51	640.4	1304.80	1296.98	-2.257	-2.354
0.1822	1305.44	627.0	1319.98	1305.97	-4.335	-4.095
0.2764	1314.01	614.4	1334.24	1315.18	-5.342	-5.281
0.3728	1322.96	601.9	1346.69	1324.61	-5.886	-5.965
0.4714	1332.39	589.4	1358.61	1334.29	-6.140	-6.184
0.5722	1342.20	577.0	1368.22	1344.22	-5.854	-5.955
0.6754	1352.59	564.6	1376.99	1354.41	-5.261	-5.276
0.781	1363.45	552.3	1383.45	1364.87	-4.134	-4.112
0.8892	1374.76	540.1	1387.48	1375.63	-2.405	-2.392
T=313.15K						
0.0901	1262.22	682.6	1275.36	1261.09	-3.350	-3.280
0.1822	1271.77	666.9	1293.39	1269.95	-5.445	-5.432
0.2764	1281.15	652.3	1307.43	1279.04	-6.487	-6.700
0.3728	1290.67	638.1	1319.75	1288.36	-7.073	-7.300
0.4714	1300.41	624.2	1330.98	1297.93	-7.325	-7.391
0.5722	1310.40	610.7	1339.79	1307.76	-7.175	-7.067
0.6754	1320.53	597.5	1347.31	1317.86	-6.609	-6.337
0.781	1330.44	585.0	1352.89	1328.23	-5.277	-5.101
0.8892	1340.04	573.4	1354.64	1338.91	-2.988	-3.122
Anisole (1) + *2-Butoxyethanol* (2)						
T=303.15 K						
0.1208	1304.71	651.20	1307.89	1305.13	-3.931	-4.018
0.2361	1315.27	633.97	1320.48	1315.72	-7.034	-6.790
0.3463	1324.93	618.26	1332.29	1325.88	-8.627	-8.554
0.4518	1334.30	603.42	1342.96	1335.64	-9.352	-9.462
0.5528	1343.53	589.25	1352.89	1345.00	-9.414	-9.608
0.6496	1352.69	575.66	1361.99	1353.99	-8.923	-9.045
0.7426	1361.79	562.58	1370.42	1362.65	-7.895	-7.798
0.8318	1370.45	550.36	1377.71	1370.96	-6.026	-5.878
0.9175	1378.54	539.05	1383.43	1378.97	-3.233	-3.283
T=313.15K						
0.1208	1283.63	678.96	1287.87	1282.46	-5.578	-5.542
0.2361	1292.28	662.58	1300.18	1291.33	-8.351	-8.417
0.3463	1300.13	647.63	1311.54	1299.81	-9.737	-9.806
0.4518	1307.83	633.40	1321.68	1307.92	-10.392	-10.369
0.5528	1315.44	619.80	1330.51	1315.67	-10.446	-10.403
0.6496	1323.08	606.70	1337.88	1323.10	-9.987	-9.961
0.7426	1330.55	594.20	1344.47	1330.23	-8.935	-8.934
0.8318	1337.77	582.44	1349.03	1337.05	-7.136	-7.114
0.9175	1344.28	571.81	1351.09	1343.59	-4.219	-4.235

The standard uncertainties are $u\,(X_1) = \pm\, 1\times10^{-4}$, $u(u)$ = 0.5m.s^{-1}, $u\,(T)$ = 0.02 K for speed of sound and $u\,(p) = \pm 5\text{x}10^{-5}$g.cm^{-1}, U($K_S^E$)=0.03TPa^{-1}.

Table 5: RMSD of speed of sound (u) of anisole (1) with *2-Methoxy ethanol*, *2-Ethoxyethanol*, and + *2-Butoxy Ethanol* (2) at T= 303.15K and 313.15 K from CFT, FLT models.

	RMSD
Anisole(1) + *2-Methoxy ethanol* (2) T=303.15K	
CFT	0.00043
FLT	0.02942
	T=313.15K
CFT	0.00147
FLT	0.03224
Anisole (1) + *2-Ethoxyethanol* (2) T=303.15K	
CFT	0.00096
FLT	0.01289
	T=313.15K
CFT	0.00413
FLT	0.0185
Anisole(1) + *2-Butoxy Ethanol* (2) T=303.15K	
CFT	0.00064
FLT	0.00434
	T=313.15K
CFT	0.00043
FLT	0.00817

Table 6: Standard deviation σ (V^E) and σ (κ_s^E) values of constants (a_0, a_1, a_2; b_0, b_1, b_2) for Redlich-Kister, Eq. (2) et al. for Anisole (1) with 2-Methoxy ethanol, 2-Ethoxyethanol, and + 2-Butoxy Ethanol at 303.15K to 313.15K

Temperature	Redlich-Kister			
	a_0	a_1	a_2	$\sigma(V^E)$
	$cm^{-3}.mol^{-1}$			
Anisole(1) +*2-Methoxy ethanol* (2)				
303.15K	-2.295	0.726	-0.082	0.004
308.15K	-2.572	0.598	-1.140	0.004
313.15K	-2.670	0.599	-1.711	0.004
Anisole(1)+ *2-Ethoxyethanol* (2)				
303.15K	-1.073	-0.239	-0.256	0.004
308.15K	-1.378	-0.282	-0.661	0.004
313.15K	-1.621	0.0191	-0.892	0.004
Anisole(1)+ *2-Butoxy Ethanol* (2)				
303.15K	-0.590	-0.190	-0.254	0.004
308.15K	-0.698	-0.231	-0.413	0.004
313.15K	-1.094	-0.315	-0.418	0.004

Table 7: Experimental FT-IR Frequencies with wavenumbers (cm^{-1}) and Shifting of bands of Anisole (1) 2 -*Methoxy ethanol*, *2-Ethoxyethanol*, and + *2-Butoxy Ethanol* (2) binary mixtures at 298.15K.

Compound	Band	Experimental
		ν ($c.m^{-1}$)
Anisole	C-O-C	1239.68 (Asym) and 1035.37 (Sym)
2-Methoxy ethanol	$-OH^a$	3412.85
2-Ethoxyethanol	$-OH^b$	3411.98
2-Butoxy Ethanol	$-OH^c$	3410.37
Anisole+2-Methoxy ethanol	$-OH^d$	3435.38
Anisole + 2-Ethoxyethanol	$-OH^e$	3427.84
Anisole +2-Butoxyethanol	$-OH^f$	3417.63
Shift in wavenumbers with respect to Aromatic anilines values		$\delta\nu(c.m^{-1})$
Anisole +2-Methoxyethanol	$-OH^d$ –-OH^a	22.53
Anisole + 2-Ethoxyethanol	$-OH^e$ –-OH^b	15.66
Anisole +2-Butoxy ethanol	$-OH^f$ – -OH^c	7.26

FIGURE CAPTIONS:

Figure 1: Variation of excess molar volume (V^E) with mole fraction (x_1) of Anisole for the binary liquid mixtures of Anisole with 2 -*Methoxy ethanol* (■); *2-Ethoxyethanol* (●); and *2-Butoxy Ethanol* (▲) at 303.15 K

Figure 2: Variation of excess molar volume (V^E) with mole fraction (x_1) of Anisole for the binary liquid mixtures of Anisole with 2 -*Methoxy ethanol* (■); *2-Ethoxyethanol* (●); and *2-Butoxy Ethanol* ((▲) at 308.15 K

Figure 3: Variation of excess molar volume (V^E) with mole fraction (x_1) of Anisole for the binary liquid mixtures of Anisole with 2 -*Methoxy ethanol* (■); *2-Ethoxyethanol* (●); and *2-Butoxy Ethanol* ((▲) at 313.15 K

Figure 4: Excess isentropic compressibility (κ_s^E) with mole fraction (x_1) of Anisole for the binary liquid mixtures of Anisole with 2 -*Methoxy ethanol* (■); *2-Ethoxyethanol* (●); and *2-Butoxy Ethanol* ((▲) at 303.15 K

Figure 5: Excess isentropic compressibility (κ_s^E) with mole fraction (x_1 of Anisole for the binary liquid mixtures of Anisole with 2 -*Methoxy ethanol* (■); *2-Ethoxyethanol* (●); and *2-Butoxy Ethanol* ((▲) at 313.15 K

Figure 6: Normalized FT-IR Spectra of (Anisole + 2 -*Methoxy ethanol*) binary mixture over the range (3500- 1000 cm^{-1}). peak a: Anisole (A); peak b: 2 -*Methoxy ethanol* (A); peak c: Anisole with 2 -*Methoxy ethanol* (A+2-ME).

Figure 7: Normalized FT-IR Spectra of (Anisole + *2-Ethoxyethanol*) binary mixture over the range (3500- 1000 cm^{-1}). peak a: Anisole (A); peak b: *2-Ethoxyethanol* (2-EE); peak c: Anisole with *2-Ethoxyethanol* (A +2-EE).

Figure 8: Normalized FT-IR Spectra of (Anisole + *2-Butoxy Ethanol*) binary mixture over the range (3500- 1000 cm^{-1}). peak a: Anisole (A); peak b: *2-Butoxy Ethanol* (2-BE); peak c: Anisole with *2-Butoxy Ethanol* (A +2-BE).

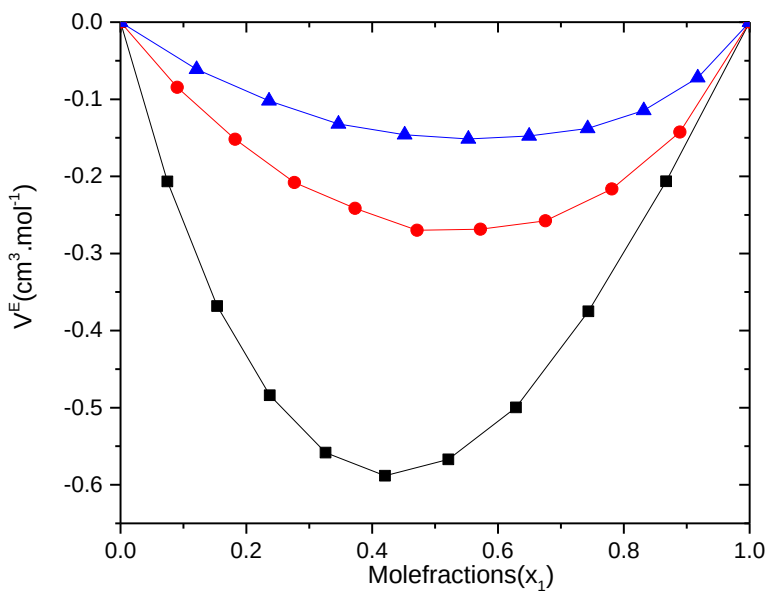

Figure 1: Variation of excess molar volume (V^E) with mole fraction (x_1) of Anisole for the binary liquid mixtures of Anisole with 2 -*Methoxy ethanol* (■); *2-Ethoxyethanol* (●); and *2-Butoxy Ethanol* (▲) at 303.15 K

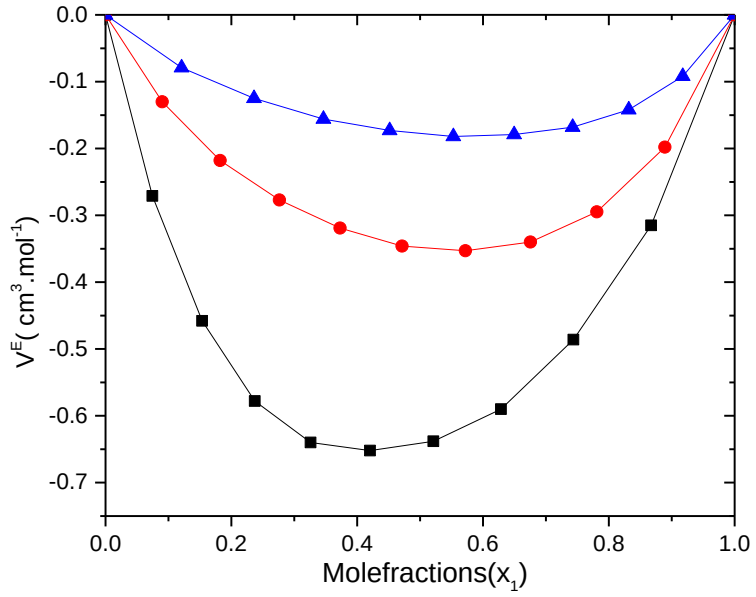

Figure 2: Variation of excess molar volume (V^E) with mole fraction (x_1) of Anisole for the binary liquid mixtures of Anisole with 2 -*Methoxy ethanol* (■); *2-Ethoxyethanol* (●); and *2-Butoxy Ethanol* ((▲) at 308.15 K

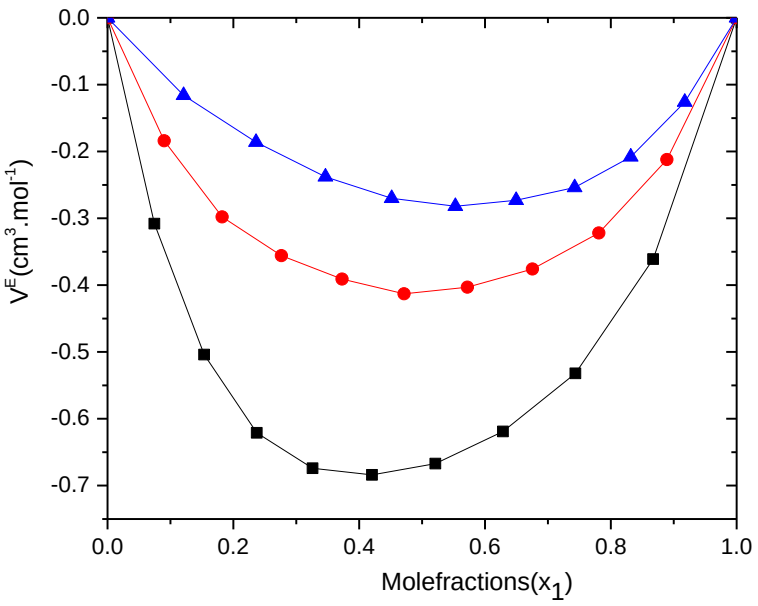

Figure 3 : Variation of excess molar volume (V^E) with mole fraction (x_1) of Anisole for the binary liquid mixtures of Anisole with 2 -*Methoxy ethanol* (■); *2-Ethoxyethanol* (●); and *2-Butoxy Ethanol* ((▲) at 313.15 K

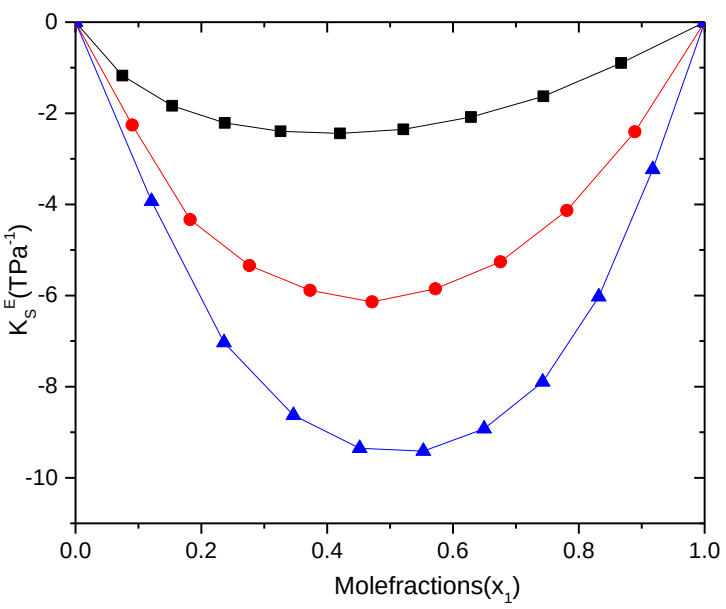

Figure 4 : Excess isentropic compressibility (κ_s^E) with mole fraction (x_1) of Anisole for the binary liquid mixtures of Anisole with 2 -*Methoxy ethanol* (■); *2-Ethoxyethanol* (●); and *2-Butoxy Ethanol* ((▲) at 303.15 K

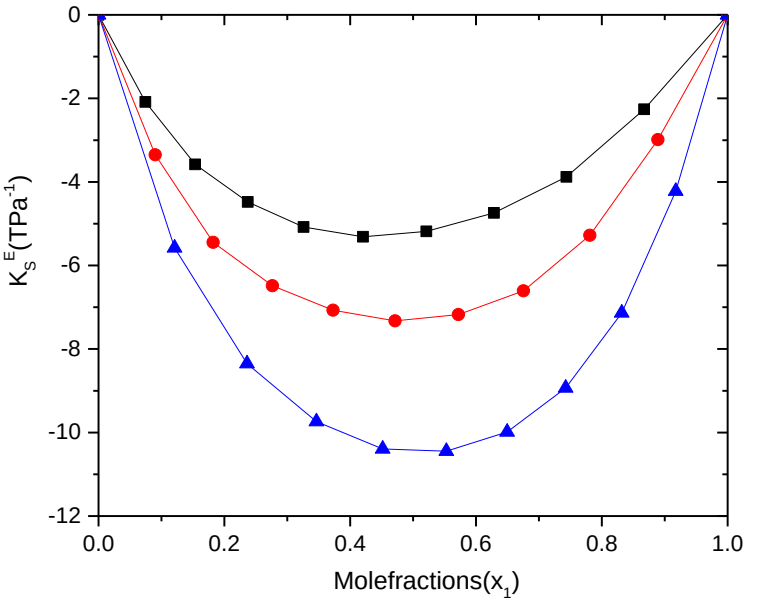

Figure 5 : Excess isentropic compressibility (κ_s^E) with mole fraction (x_1 of Anisole for the binary liquid mixtures of Anisole with 2 -*Methoxy ethanol* (■); *2-Ethoxyethanol* (●); and *2-Butoxy Ethanol* ((▲) at 313.15 K

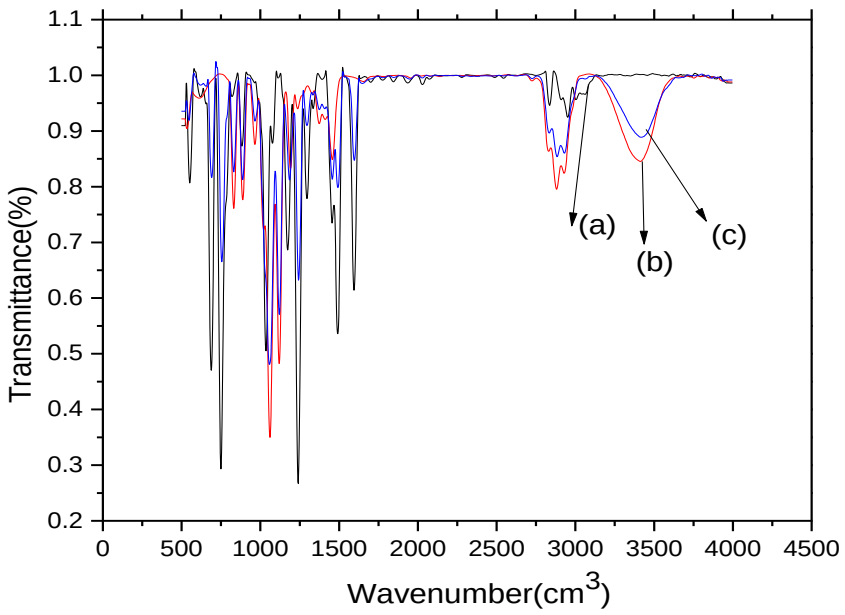

Figure 6: Normalized FT-IR Spectra of (Anisole + 2 -*Methoxy ethanol*) binary mixture over the range (3500- 1000 cm^{-1}). peak a: Anisole (A); peak b: 2 -*Methoxy ethanol* (2-ME); peak c: Anisole with 2 -*Methoxy ethanol* (A+2-ME).

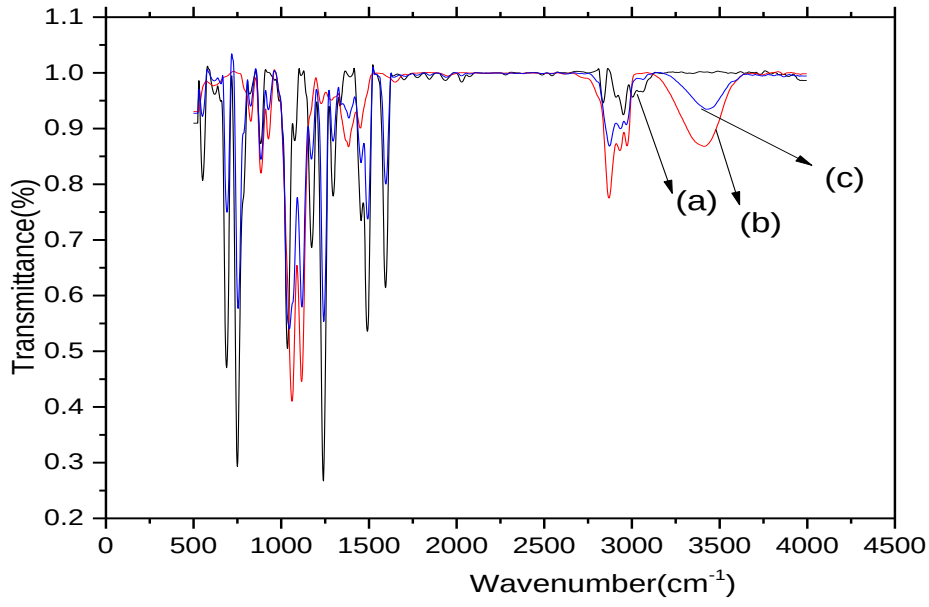

Figure 7: Normalized FT-IR Spectra of (Anisole + 2- Ethoxy ethanol) binary mixture over the range (3500- 1000 cm^{-1}). peak a: Anisole (A); peak b: 2- Ethoxy ethanol(2-EC); peak c: Anisole with 2- Ethoxy ethanol (A +2-EC).

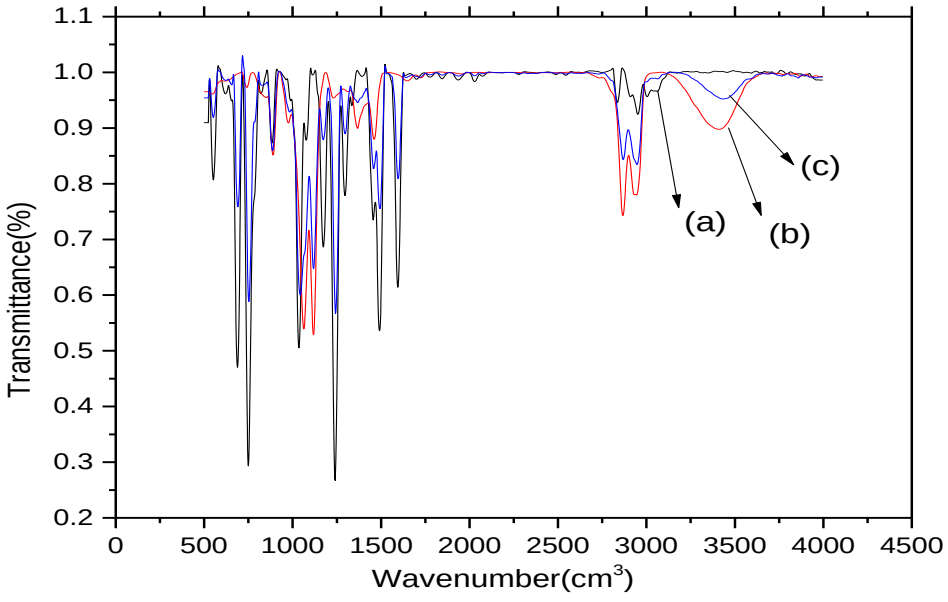

Figure 8: : Normalized FT-IR Spectra of (Anisole + 2 -*Butoxy ethanol*) binary mixture over the range (3500- 1000 cm^{-1}). peak a: Anisole (A); peak b: 2 -*Butoxy ethanol* (A); peak c: Anisole with 2 -*Butoxy ethanol* (A+2-BE).