



MOLECULAR INTERACTIONS OF BINARY LIQUID MIXTURES OF DIOXANE BY EVALUATION OF EXCESS ACOUSTICAL PARAMETERS AT DIFFERENT TEMPERATURES

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Communicated: 16.06.21

Revision : 21.07.21 & 21.08.2021
Accepted: 26.08.2021

Published: 30.09.2021

ABSTRACT: Ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for binary mixtures of Dioxane with Anisole, Toluene and Ethylbenzene at 293-313 K temperatures. The experimental data have been used to evaluate acoustical parameters such as adiabatic compressibility (β), free length (L_f), acoustic impedance (Z) and molar volume (V_m). Excess values of above parameters have been also evaluated, excess molar volume (V_m^E), excess intermolecular free length (L_f^E), excess adiabatic compressibility (β^E) and excess acoustic impedance (Z^E) at each temperature. These values are useful to understand molecular interactions of binary liquid mixtures.

Key words: - Excess acoustical Parameters, Acoustical properties, Molecular Interactions, Ultrasonic Technique.

INTRODUCTION:

Ultrasonic velocity measurements find wide applications in characterizing the physico-chemical behavior of liquid mixtures. Molecular interactions play an important role in understanding the structures and properties of liquids. The molecular interaction study from the variation of acoustical parameters and their excess values with composition gives insight into the molecular process. In recent years, the theoretical and experimental investigations of excess and deviation functions are taken as interaction parameters to improve the results. This work is concerned to the systematic study of molecular interactions in the binary mixtures, which are important in many fields of industrial and biological processes. Mixed solvents find practical applications as they provide wide range of mixtures with desired properties.

In present work acoustical parameters of binary liquid mixtures of Dioxane with Anisole,

Toluene and Ethylbenzene are calculated at 293-313 K temperatures as a function of composition. A complete knowledge of thermodynamic and transport properties of these industrially imported mixtures are often required for their industrial applications. From the practical point of view the mixtures investigated are especially important because they are widely used as solvents for dyes, coloring raw materials in plastic industry used to make synthetic fibers and for aircraft and vehicles.

Recently various theories have been using for computing ultrasonic velocity in binary liquid mixtures and the deviation in theoretical velocities are mainly due to molecular interactions in the liquid mixtures. An attempt has been made to correlate the experimental findings with those predicted theoretically. It helps to understand properties of binary liquid mixtures.

MATERIALS AND METHODS:

All the chemicals were AR grade; purities of these chemicals were checked by density determination at 313 K which showed an accuracy of 0.0001 gm cm⁻³ as compared to reported values.

Binary liquid mixtures were prepared in measuring flask. The density, viscosity and velocity were measured as a function of composition of binary liquid mixture at 293-313 K. The density of sample was measured using digital densitometer (Rudolph) with an accuracy of 0.0001. An Ostwald's viscometer was used for the viscosity measurements. An ultrasonic interferometer having the frequency 2 MHz was used for ultrasonic velocity measurements. An electronically operated constant temperature bath was used to circulate water through measuring cell made up of steel containing experimental solution at 293-313 K temperature.

Theoretical

Various acoustical parameters were calculated from measured data by using following equations

Adiabatic compressibility

$$(\beta) = 1/U^2 \cdot \rho \dots\dots\dots (1)$$

Intermolecular

$$\text{Free length } (L_f) = K \cdot \beta^{1/2} \dots\dots\dots (2)$$

Where K is temperature dependant constant, value of K is 642 X 10⁻⁶ at 313 k.

Acoustic impedance

$$(Z) = U\rho \dots\dots\dots (3)$$

Molar Volume (V) =

$$(M_{\text{eff}} \cdot U / K \cdot \eta)^{3/2} \dots\dots\dots (4)$$

Where M is mean molecular weight. It is calculated as

$$M = X_1M_1 + X_2M_2$$

X₁ and X₂ are mole fractions and M₁, M₂ are molecular weights of constituent components of binary liquid mixtures.

Excess parameters were calculated from following equations

$$Y^E = Y_{\text{exp.}} - (X_1Y_1 + X_2Y_2) \dots\dots\dots (5)$$

Where,

Y_{exp.} = experimental values of mixtures

Y₁ & Y₂ = values of parameters for liquids 1 and 2 respectively.

X₁ & X₂ = mole fractions of liquid 1 and 2 respectively.

Graphs:

The excess values of the intermolecular free length, adiabatic compressibility, acoustic impedance and molar volume plotted against mole fraction of Dioxane (DOX) in the binary mixtures with Anisole (ANS), Toluene (TOL) and Ethylbenzene (ETB) at temperatures 293–313K

RESULT & DISCUSSION:

The excess values of intermolecular free length(L^E), adiabatic compressibility (β^E), acoustic impedance (Z^E) and molar volume (V_m^E) plotted against mole fraction of DOX binary mixtures at 293–313K.

For ideal solutions the excess values are expected to be zero. The deviations indicate the non-ideality of the solutions and are attributed mainly to different types of interactions. It can be summarized that excess values may be affected by several factors.

- The first factor is the specific forces between molecules such as hydrogen bonds, charge transfer complexes, breaking of hydrogen bonds and complexes bringing negative excess values.
- The second factor is the physical intermolecular forces including electrostatic forces between charged particles and a permanent dipole, induction forces between a permanent dipole and an induced dipole, forces of attraction and repulsion between non-polar molecules. Physical intermolecular forces are weak and the sign of excess value may be positive or negative.
- Third factor is the structural characteristics of the component arising from geometrical fitting of one component into other



structure due to the differences in shape and size of the components.

Positive deviations of L_r^E , V_m^E , Z^E and β^E in binary systems have been attributed to dispersion forces and negative deviation is due to dipole-dipole and induced dipole interactions. Dispersion forces are operative in all systems, but since more than one type of interactions are present between the components, the excess values are the net result of all type of contributions.

Sign and magnitude of excess adiabatic compressibility (β^E) can be used to study the type of interaction present in the binary mixtures. A negative value to the excess adiabatic compressibility indicates strong interaction and a positive value to excess compressibility indicates weak interaction. The strong interaction is attributed to charge transfer, dipole-dipole, dipole-induced dipole interactions and hydrogen bonding between unlike components and weak interaction is attributed to dispersion forces. The magnitude of the contributions made by these different types of interactions will vary with the components and the composition of the mixtures.

Fig.1, 5, 9 shows β^E values for all the binary mixtures of DOX. β^E exhibits negative behavior in all the systems throughout the concentration and temperature range studied, except for DOX + TOL, DOX + ETB and DMF + ANS where they possess variation of positive and negative values. β^E values of DOX + ANS are negative. The behaviors of DOX + TOL and DOX + ETB possess negative values at lower temperature and finally reach to positive values. The observed values indicate that dipole-dipole interactions decrease with increase of temperature. This fact indicates that the strength of complexation of DOX is greater in ANS than TOL and ETB. It has been observed that intermolecular interaction decreases with increase of temperature. The above fact confirms that weak dipole-induced dipole interactions dominate over complex

formation between unlike molecules. The change from positive to negative β^E values indicating the dissociation between the components and may be quantitatively interpreted in terms of detachment of unlike molecules leading to increase in compressibility and volume.

From the above discussion it can be concluded that, β^E values are negative for all the binary mixtures of DOX with ANS/TOL/ETB at all temperatures except for DOX+TOL, DOX+ETB, DMF+ANS. For binary mixtures of DOX+TOL and DOX+ETB β^E values are positive at lower temperature but negative at higher temperature. In the liquid mixtures, the intermolecular interaction might result in the decrease of the interspaces between molecules and this might lead to a decrease in intermolecular free length producing negative values for the excess intermolecular free length (L_r^E). S. Azhagiri indicates that the positive values of excess free length should be attributed to the dispersive forces and negative excess values should be due to charge transfer for all the systems.

Fig.2, 6, 10 show L_r^E values for all the binary mixtures of DOX. The values of L_r^E are negative for DOX + ANS and are positive for DOX + TOL and DOX + ETB. The observed fact indicates that DOX strongly interact with ANS than TOL and EBT. The strong interaction might have resulted in the decrease of interspaces between molecules. This might lead to decrease in intermolecular free length producing negative values for excess intermolecular free length.

Molar excess volumes (V_m^E) are found to be very sensitive towards mutual interactions between component molecules of the liquid mixtures. The sign and extent of deviation of these functions from ideality depend on the strength of interactions between unlike molecules.

A qualitative explanation is given for the change in V_m^E with composition and temperature. Thus, it is interesting to note that the results obtained so far suggest that the values of V_m^E , for the

present systems, are essentially influenced by different factors as given in the literature.

- Structure making dipole-dipole or dipole-induced dipole ($\pi \dots \pi$) type specific interactions.
- Geometrical fitting of smaller molecules into the voids created by larger molecules due to the difference in molar volumes.
- Disruption of dipolar association present in the liquid components tends to make V_m^E positive.

The observed negative V_m^E values suggest that the combined effect due to (i) and (ii) dominates over that of (iii).

The sign of V_m^E of a system depends upon the relative magnitude of expansion and contraction of the two liquids due to mixing. If the factors causing expansion dominate the contraction factors, the V_m^E becomes positive. On the other hand if the contraction factors dominate the expansion factors, then V_m^E become negative. The factors that are responsible for expansion in volume are as follows,

- Loss of dipolar association,
- The geometry of molecular structure, which does not allow fitting of one component into other component,
- Steric hindrance, which opposes the proximity of the constituent molecules.

The negative V_m^E values arise due to dominance of the following factors.

- Chemical interaction between constituent chemicals.
- Accommodation of molecules of one component into the interstitials of the molecules of the other component.
- Geometry of the molecular structure that favors fitting of the component molecules with each other. The negative V_m^E values in the mixtures under study indicate that interactions between molecules of the mixtures are stronger than interactions between molecules in the pure liquids and

that associative force dominate the behavior of the solution.

In case of binary mixtures of DOX with ANS/TOL/ETB an examination of **Fig. 4, 8, 12** reveal that the excess molar volume, V_m^E values are negative for DOX + ANS while the values are positive for DOX + TOL and DOX + ETB. The observed negative values of V_m^E for the binary mixture indicates the presence of specific interactions between DOX and ANS molecules. The negative V_m^E values are attributed to strong dipole-dipole interactions between unlike molecules in the mixtures. The negative values may arise due to interactions between the pi electrons of ANS with DOX. The structure making dipole-induced dipole interaction takes place resulting in negative V_m^E value. The positive values either may be due to interruption of dipolar association in the binary mixtures of DOX with TOL and ETB attributed to weak dipole-dipole interactions between unlike molecules in the mixtures. It is clear that the values of V_m^E shows negative deviation for the mixture of DOX with ANS and positive deviations for the mixtures of DOX with ETB & TOL and follows the sequence: Anisole > Ethylenebenzene > Toluene.

CONCLUSION

For the systems of DOX, the interactions between unlike molecules are quite obvious. In case of DOX + ANS system L_r^E , V_m^E and β^E are negative and the values of Z^E positive. In case of DOX + TOL and DOX + EBT systems L_r^E , V_m^E and β^E are positive and the values of Z^E negative. The observed negative deviation in Z^E and opposite behavior of L_r^E , V_m^E and β^E over the entire range of mole fraction of the system investigated again supports our view that the molecular interactions between the unlike molecules are quite obvious.

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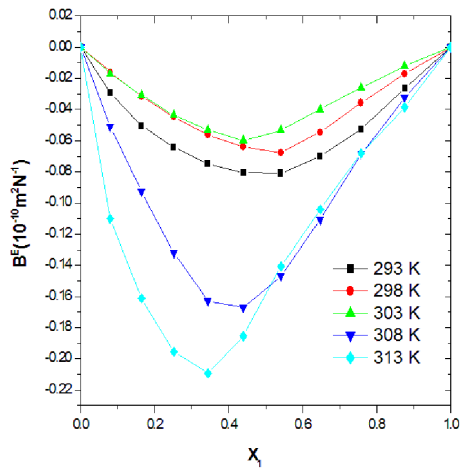


Fig. 1. Plots of β^E Vs. X_1 for DOX+ANS

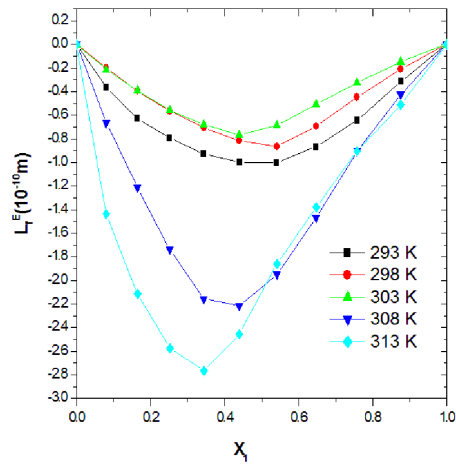


Fig. 2. Plots of L_f^E Vs. X_1 for DOX+ANS

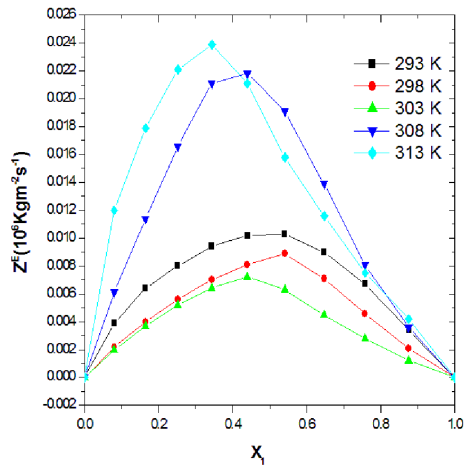


Fig. 3. Plots of Z^E Vs. X_1 for DOX+ANS

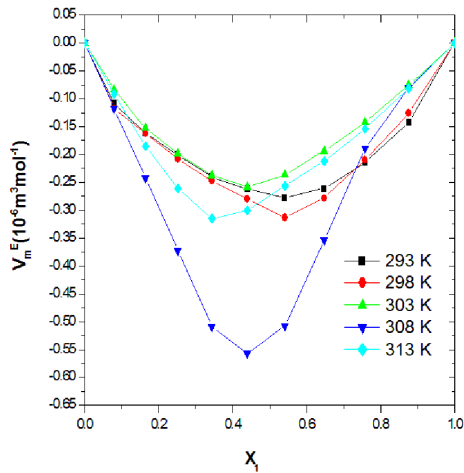


Fig. 4. Plots of V_m^E Vs. X_1 for DOX+ANS

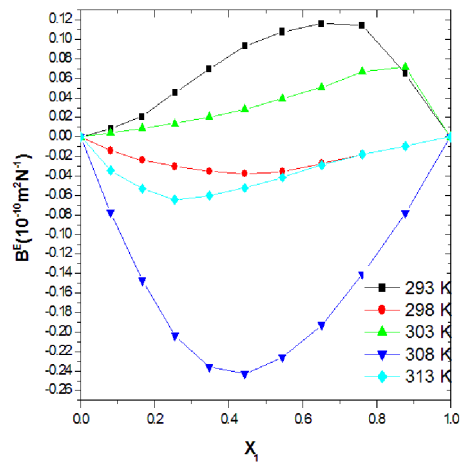


Fig. 5. Plots of β^E Vs. X_1 for DOX+TOL

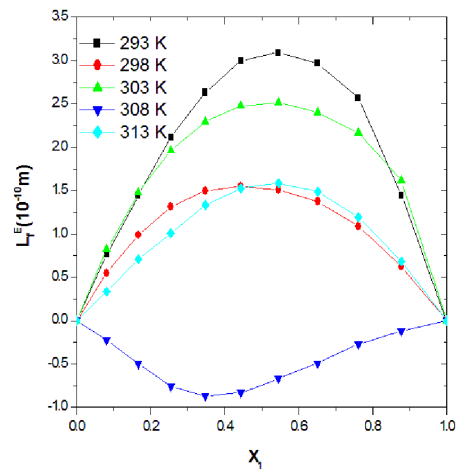


Fig. 6. Plots of L_f^E Vs. X_1 for DOX+TOL

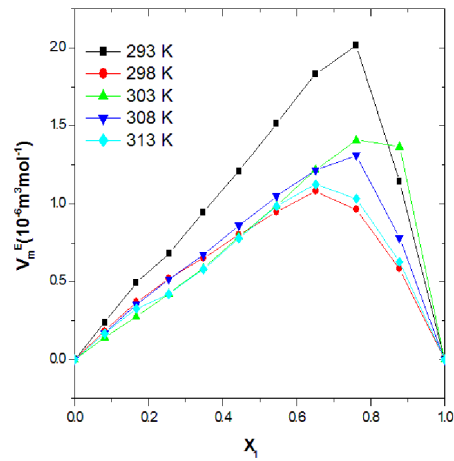
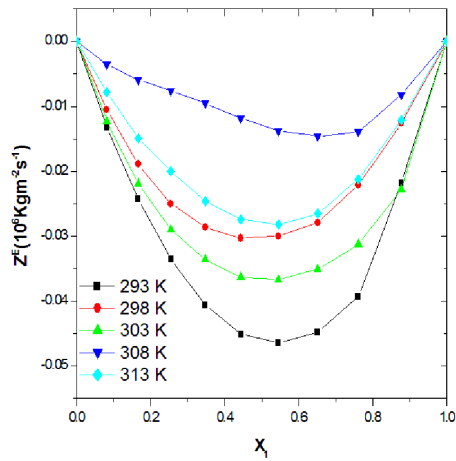


Fig.7. Plots of Z^E Vs. X_1 for DOX+ TOL **Fig.8. Plots of V_m^E Vs. X_1 for DOX+ TOL**

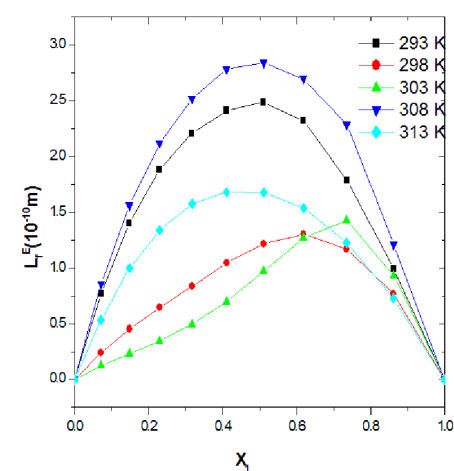
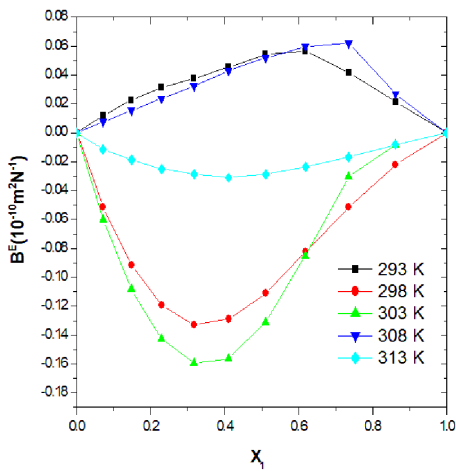


Fig.9. Plots of β^E Vs. X_1 for DOX+ ETB **Fig.10. Plots of L_T^E Vs. X_1 for DOX+ ETB**

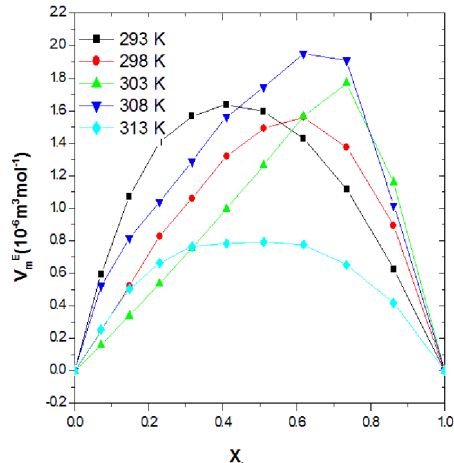
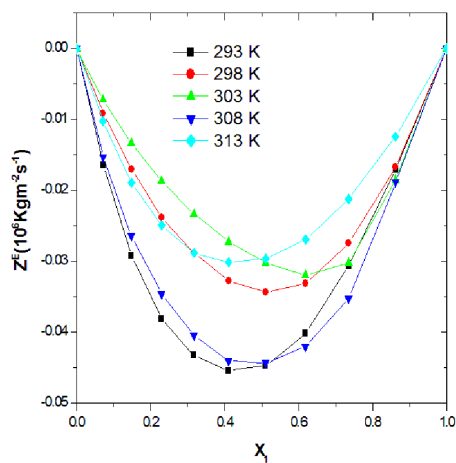


Fig.11. Plots of Z^E Vs. X_1 for DOX+ ETB

Fig.12. Plots of V_m^E Vs. X_1 for DOX+ ETB