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Molecular Interactions of Binary Liquid Mixtures of Dimethylsulfoxide by Evaluation of Excess Acoustical Parameters at Different Temperatures

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Abstract

Ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for binary mixtures of Dimethylsulfoxide 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 (Vm). 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. Positive deviations of Lf^E, V_m^E, Z^E and β^E in binary systems have been attributed to dispersive forces and negative deviation is due to dipole-dipole and induced dipole interactions. Dispersive forces are operative in all systems, but since more than one type of interactions are present between the components, the excess values is the net result of all type of contributions. The binary mixture of Dimethylsulfoxide and Anisole show the large value of deviations of excess parameters β^E, L_f^E Z^E, V_m^E. These results suggest that Anisole has strong molecular interactions with Dimethylsulfoxide than Ethylbenzene and Toluene. The strong molecular interaction of Dimethylsulfoxide with Anisole may attribute to strong dipole-dipole interactions between these molecules. The greater interaction of Anisole may be due to more positive Inductive effect of OCH_3 group. It has been found that, molecular interactions in the binary systems of Dimethylsulfoxide with Anisole, Ethylbenzene and Toluene follow the order of Anisole> Ethylbenzene> Toluene.

Keywords: *Acoustical properties Ultrasonic Technique, DMSO, Anisole, Toluene and Ethylbenzene.*

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 **[1]**. 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 **[2]**. 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 **[3]**.

In view of their industrial importance, the present study reports the experimental values of densities (ρ), viscosities (η) and ultrasonic speeds (U) of binary mixtures of Dimethylsulfoxide (DMSO) with Anisole (ANS), Toluene (TOL) and Ethylbenzene (ETB) over the entire composition range and at 293–313 K. The above experimental data were used to evaluate the 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. The excess values are important to unerstand molecular interactions in the liquid mixtures and elucidation of the structural properties of the molecules **[4–6]**.

Experimental:

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 **[7-8]**. 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

$$\text{Adiabatic compressibility } (\beta) = 1/U^2.\rho \quad \ldots\ldots\ldots (1)$$

$$\text{Intermolecular Free length } (L_f) = K.\ \beta^{1/2} \quad \ldots\ldots\ldots (2)$$

Where K is temperature dependant constant, value of K is 642 X 10^{-6} at 313 k.

$$\text{Acoustic impedance } (Z) = U\rho \quad \ldots\ldots\ldots (3)$$

$$\text{Molar Volume } (V) = (M_{eff}.\ U/K.\eta)^{3/2} \quad \ldots\ldots\ldots (4)$$

Where M is mean molecular weight. It is calculated as

$$M = X_1M_1 + X_2M_2$$

X_1 and X_2 are mole fractions and M_1, M_2 are molecular weights of constituent components of binary liquid mixtures.

Excess parameters were calculated from following equations

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

Where,

$Y_{exp.}$ = experimental values of mixtures

Y_1 & Y_2 = values of parameters for liquids 1 and 2 respectively.

X_1 & X_2 = mole fractions of liquid 1 and 2 respectively.

Results and Discussion:

The excess values of intermolecular free length (L_f^E), adiabatic compressibility (β^E), acoustic impedance (Z^E) and molar volume (V_m^E) plotted against mole fraction of DMSO 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 **[9 - 12]**.

Fig. 1, 5 and 9 shows β^Evalues for all the binary mixtures of DMSO. The values of β^E for DMSO+ ANS, DMSO+TOL and DMSO+EBT are negative. 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 [13-15].

Fig.2, 6 and 10 show L_f^E values for all the binary mixtures of DMSO. The values of L_f^E are positive for all binary liquid mixtures DMSO with ANS, TOL and ETB. The positive values are attributed to the fact that the dispersive forces developed in the binary mixtures of DMSO.

Fig.3, 7 and 11 show Z^E values are negative for all DMSO + ANS, DMSO + TOL, DMSO + EBT. Negative values of Z^E attributed to weak interactions [16-18].

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 [19-21]. V_m^E values are negative for all binary mixtures of DMSO with ANS, TOL and EBT. The negative V_m^E values are attributed to strong dipole-dipole interactions between the unlike molecules in the mixtures. It is clear from Fig.4, 8 and 12 that the values of Vm^E show negative deviation for the mixture of DMSO with ANS, ETB and TOL.

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

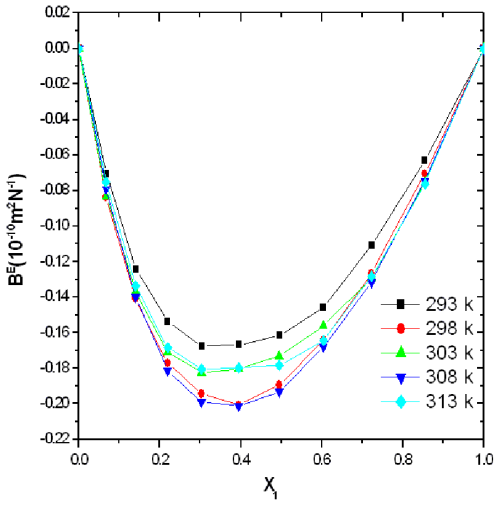

Fig.1. Plots of β^E Vs. $X_1$for DMSO+ANS

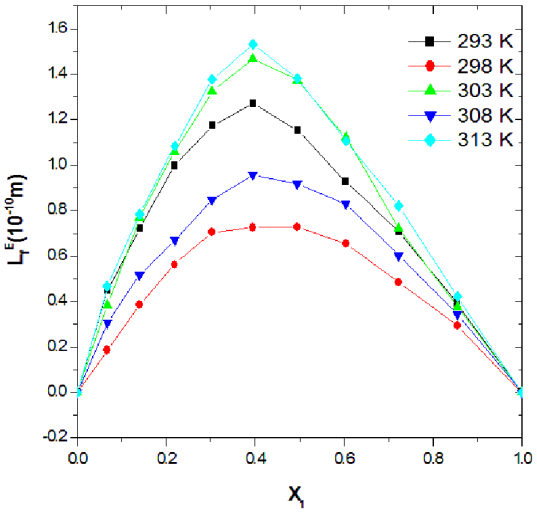

Fig.2. Plots of L_f^E Vs. $X_1$for DMSO+ANS

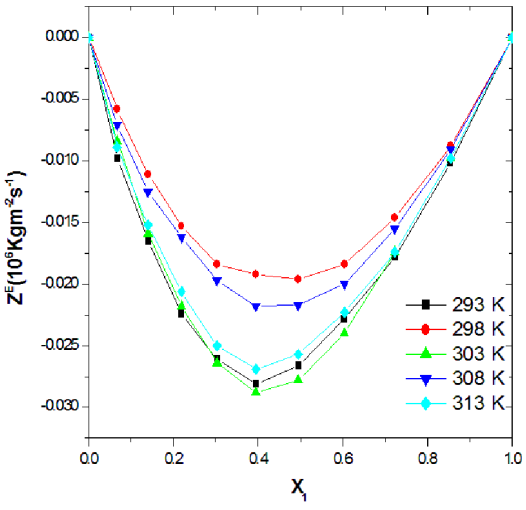

Fig.3. Plots of Z^E Vs. $X_1$for DMSO+ANS

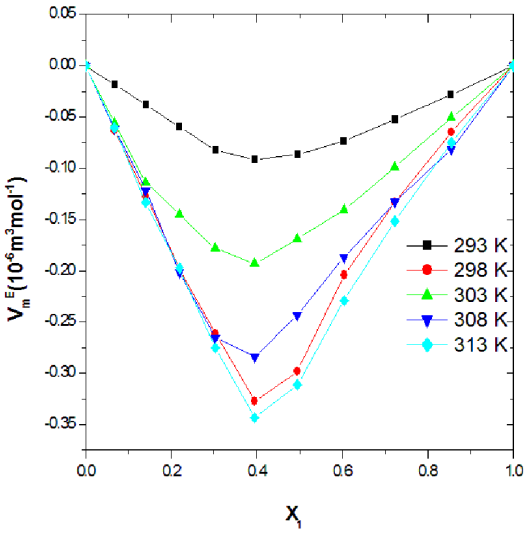

Fig.4. Plots of V_m^E Vs. $X_1$for DMSO+ANS

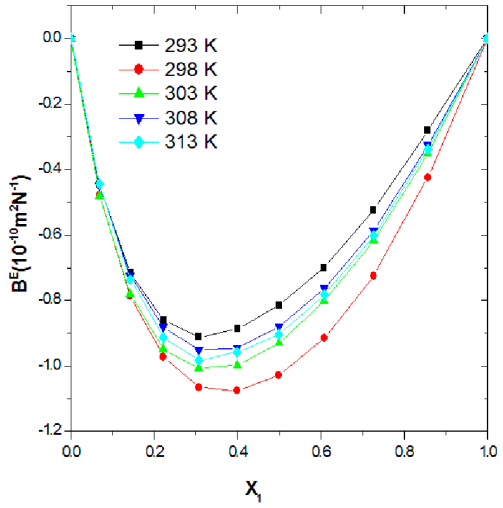

Fig.5. Plots of β^E Vs. $X_1$for DMSO+TOL

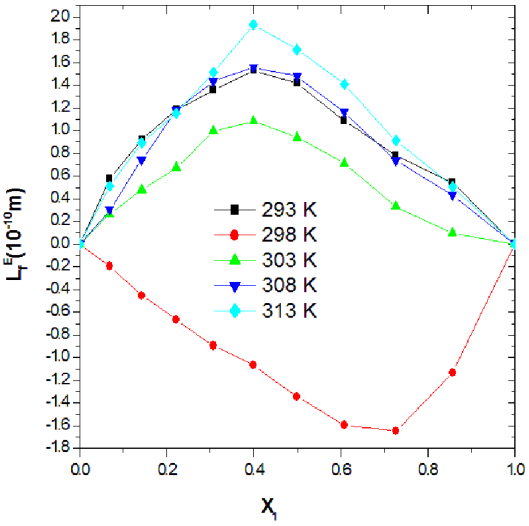

Fig.6. Plots of L_f^E Vs. $X_1$for DMSO+ TOL

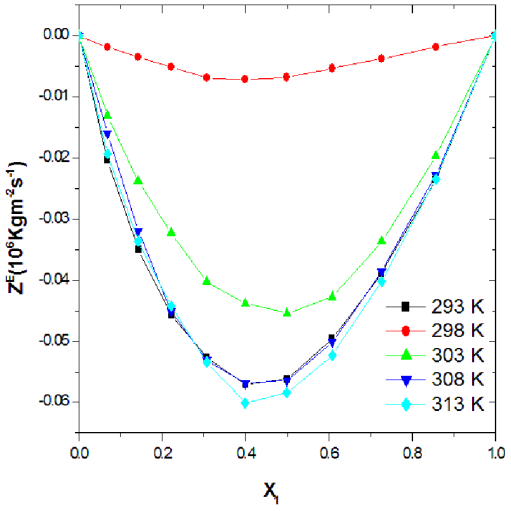

Fig.7. Plots of Z^E Vs. $X_1$for DMSO+ TOL

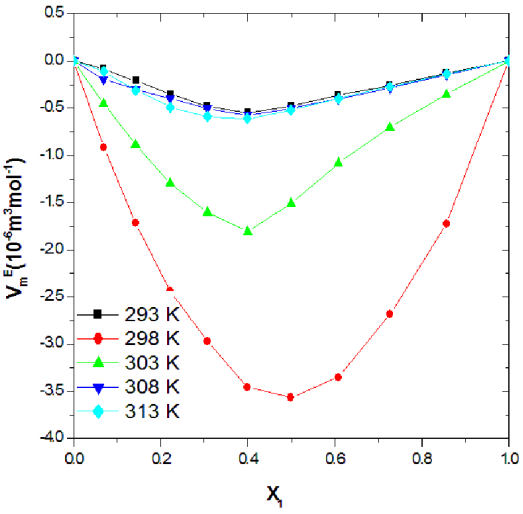

Fig.8. Plots of V_m^E Vs. $X_1$for DMSO+ TOL

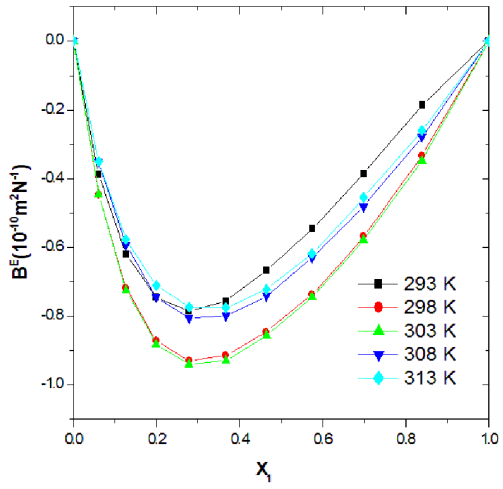

Fig.9. Plots of β^E Vs. $X_1$for DMSO+ETB

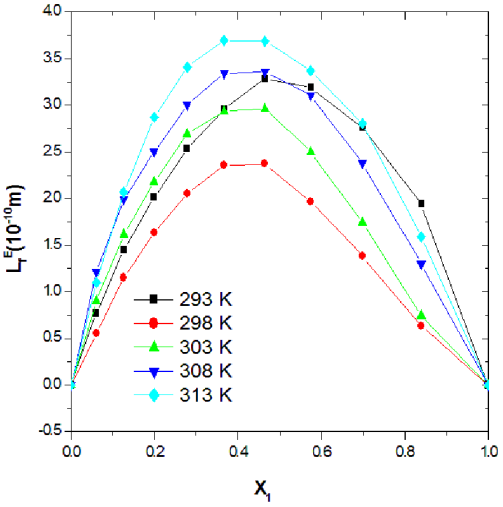

Fig.10. Plots of L_f^E Vs. $X_1$for DMSO+ ETB

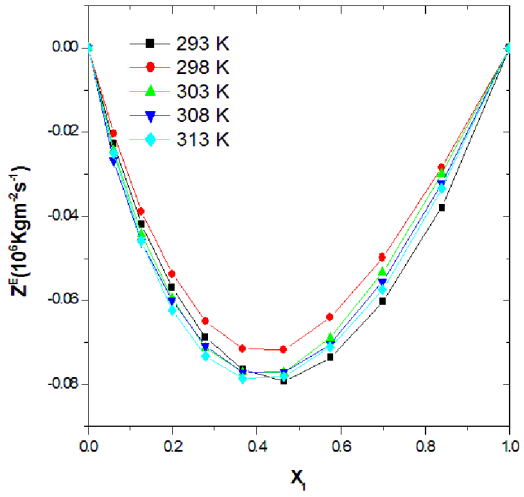

Fig.11. Plots of Z^E Vs. $X_1$for DMSO+ ETB

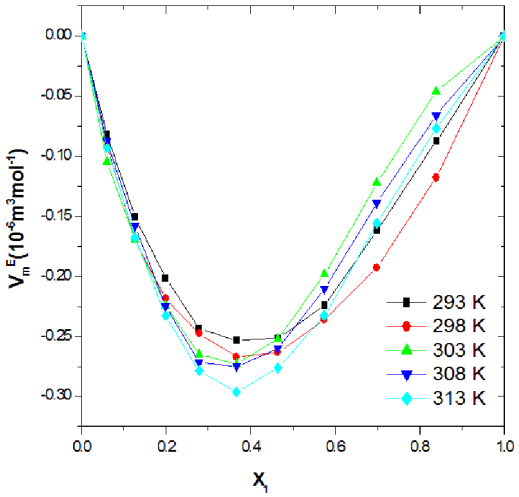

Fig.12. Plots of V_m^E Vs. $X_1$for DMSO+ ETB

Conclusion:

It observed that, molecular interactions in the binary systems of Dimethylsulfoxide with Anisole, Ethylbenzene and Toluene follow the order of Anisole> Ethylbenzene> Toluene. The strong molecular interaction of Dimethylsulfoxide with Anisole may be due to more positive Inductive effect of OCH_3 group which results in strong dipole-dipole interactions between these molecules.

Conflict of Interest:

The authors declared that they have no conflict of interest.

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