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Molecular Interactions of Binary Liquid Mixtures of Dimethylsulfoxide by Evaluation of Excess Acoustical Parameters at Different Temperatures Dr. SUNIL DAHIRE Dada Ramchand Bakharu Sindhu Mahavidyalya, Nagpur-440017. Email: drsunildahire@gmail.com 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 (Lf), acoustic impedance (Z) and molar volume (Vm). Excess values of above parameters have been also evaluated, excess molar volume (VmE), excess intermolecular free length (LfE), excess adiabatic compressibility (βE) and excess acoustic impedance (ZE) at each temperature. These values are useful to understand molecular interactions of binary liquid mixtures. Positive deviations of LfE, VmE, ZE and βE 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 DMSO+ANS show the large value of standard deviations of excess parameters βE, LfE ZE, VmE. These results suggest that ANS has strong molecular interactions with DMSO than ETB and TOL. The strong molecular interaction of DMSO with ANS than ETB and TOL may attribute due to strong dipole-dipole interactions between these molecules. The greater interaction of ANS may be due to more +I effect of OCH3 group. It has been found that, molecular interactions in the binary systems of DMSO 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]. In present work acoustical parameters of binary liquid mixtures of Dimethylsulfoxide 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[3]. Recently various theories[4-6] 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. 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 Adiabatic compressibility (β) = 1/U2. ρ ..... (1) Intermolecular Free

length (Lf) = K. β ½ 1..... (2) Where K is temperature dependant constant, value of K is 642 X 10-6 at 313 k. Acoustic impedance (Z) = Uρ . ..... (3) Molar Volume (V) = (Meff . U / K.η)3/2 ..... (4) Where M is mean molecular weight. 7It is calculated as M = X1M1 + X2M2 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 YE = Yexp.- (X1Y1 + X2Y2) ..... (5) Where, Yexp. 1= 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: 2The 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 βE Vs. X1for DMSO+ANS Fig.2.Plots of LfE Vs. X1for DMSO+ANS Fig.3.Plots of ZE Vs. X1for DMSO+ANS Fig.4.Plots of VmE Vs. X1for DMSO+ANS Fig.5.Plots of βE Vs. X1for DMSO+TOL Fig.6.Plots of LfE Vs. X1for DMSO+ TOL Fig.7.Plots of ZE Vs. X1for DMSO+ TOL Fig.8.Plots of VmE Vs. X1for DMSO+ TOL Fig.9.Plots of βE Vs. X1for DMSO+ETB Fig.10.Plots of LfE Vs. X1for DMSO+ ETB Fig.11.Plots of ZE Vs. X1for DMSO+ ETB Fig.12.Plots of VmE Vs. X1for DMSO+ ETB 2Results and Discussion The excess values of intermolecular free length(LfE), adiabatic compressibility (βE), acoustic impedance (ZE) and molar volume (VmE) plotted against mole fraction of DMSO binary mixtures at 293–313K. For ideal solutions 1the 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. 3The 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]. Positive deviations of LfE, VmE, ZE, and βE 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[13]. Sign and magnitude of excess adiabatic compressibility (βE) 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[14-15]. Fig.1, 5 and 9 shows βEvalues for all the binary mixtures of DMSO. The values of βEfor DMSO + ANS, DMSO + TOL and DMSO + EBT are negative. The observed facts are attributed mainly to strong dipole-dipole and dipole-induced dipole interactions of binary liquid mixtures of DMSO[16]. 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 (LfE). S. Azhagiri[17] 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 and 10 show LfEvalues for all the binary mixtures of DMSO. The values of LfE 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. Molar excess volumes (VmE) 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[18-20]. A qualitative explanation is given for the change in VmE with composition and temperature. Thus, it is interesting to note that the results obtained so far suggest that the values of VmE, for the present systems, are essentially influenced by different factors as given in the literature[21]. Structure making dipole-dipole or dipole-induced dipole (π ...π) 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 VmE positive. The observed negative VmE values suggest that the combined effect due to (i) and (ii) dominates over that of (iii). The sign of VmE of a system depends upon the relative magnitude of expansion and contraction of the two liquids due to mixing[22]. If the factors causing expansion dominate the contraction factors, the VmE becomes positive. On the other hand if the contraction factors dominate the expansion factors, then VmE 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 VmE 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 VmE 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[23-27]. VmE values are negative for all binary mixtures of DMSO with ANS, TOL and EBT. The negative VmE 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 VmE show negative deviation for the mixture of DMSO with ANS / ETB / TOL and follows the

sequence: Anisole> Ethylenebenzene >Toluene. ZE values are negative for all DMSO + ANS, DMSO + TOL, DMSO + EBT. Positive values of ZE attributed to strong intermolecular interactions and negative values may be due to weak interactions[28].

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