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Ultrasonic Study of Molecular Interactions in Binary Liquid Mixtures and Acoustic Parameters of Dimethylsulphoxide with Ethanol at 303K

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ABSTRACT

The Ultrasonic velocity (U), density (ρ) and viscosity (η) of binary liquid mixtures of Dimethylsulphoxide and ethanol have been measured using Ultrasonic Interferometer at frequency 2MHz and at constant temperature 303K for entire composition. From the measured data of ultrasonic velocity, density and viscosity, acoustical parameters such as adiabatic compressibility (β), intermolecular free length (L_f), free volume (V_f), acoustic impedance (Z), internal pressure (πi), Gibb's free energy (ΔG) and Rao's constant (R) have been calculated using standard relations. The variation of adiabatic compressibility (β), intermolecular free length (Lf), free volume (Vf), acoustic impedance (Z), internal pressure (πi), Gibb's free energy (ΔG), Rao's constant with mole fraction at constant temperature have been studied. Acoustic parameters provide valuable information in understanding the molecular interaction in binary liquid mixtures.

Keywords: ultrasonic velocity, acoustical parameters, Hydrogen bonding;

INTRODUCTION

The ultrasonic study of liquid and liquid mixture is important in understanding the nature of molecular interactions. The biological activity of drug molecules and the activation energy of the metabolic process basically depend on the type and strength of the intermolecular interactions. The thermo-acoustic properties of liquid mixtures have been extensively used to study the departure of a real liquid mixture behavior from ideality. The nature and degree of molecular interactions in different solutions depends upon the nature of solvent, the structure of solute molecule and extent of solutes taking place in the solution [1]. Ultrasonic investigation of liquid mixture is of considerable importance in understanding intermolecular interaction between the molecules which finds application in industrial and technological processes. Ultrasonic velocity and the derived acoustical parameters provide valuable information about the molecular interactions. This has been studied for various binary mixtures with respect to variation in concentration of the liquids [2-3]. The acoustical and thermodynamic parameter have been used to study different kinds of association, molecular motion and various types of interaction and their strength influenced by the size of pure component and the mixtures [4]. The accurate thermodynamic and acoustic properties of alcohols, in particularly 1-propanol are of interest for different branches of science and engineering.1-propanol is an important industrial chemical fluid. 1-propanol is used as a solvent in the pharmaceutical industry. Hydrogen bonding is one of the most important types of intermolecular interactions play an important role in various physicochemical, biological and industrial processes [5-6].

In the present paper, variations of some acoustic parameters of binary mixture of DMSO and 1-propanol with different concentration have been studied for a constant temperature at 303K..

METHODOLOGY

The ultrasonic velocities were measured by using a single crystal Ultrasonic Interferometer (Mittal Enterprises, Model No. M-81S). The measurement of velocities was made at a fixed frequency of 2MHz. The temperature was controlled by circulating water around the cell from thermostatically controlled constant temperature water bath. The densities of pure liquid and liquid mixtures were measured by using 25ml specific gravity bottle with an accuracy of ± 0.5% and weight was measured with an electronic balance (Citizen, Model- CY-220, India) capable of measuring up to 1mg. The viscosity of liquid mixtures was measured by Ostwald's viscometer and distilled water has been used as a standard liquid. The liquid mixtures of various concentrations in mole fraction were prepared by taking AR grade chemicals (Merck, Germany- 99%) DMSO and 1- Propanol. From experimental data, various acoustic parameters were calculated [7].

Adiabatic Compressibility $\beta = 1/(U^2 \times \rho)$ (1)

Intermolecular free Length

$L_f = K_T \times \beta^{1/2}$ where K_T is Jacobson constant (2)

Free Volume $V_f = [M_{eff}\,U/K\eta]^{3/2}$ (3)

Acoustic Impedance $Z = \rho \times U$ (4)

Internal Pressure $\pi_i = bRT\,[(k\eta/U)^{1/2}(\rho^{2/3}/M^{7/6})]$ (5)

Gibbs Free Energy $\Delta G = K_BT\,\ln(K_B T \tau / h)$ (6)

Rao's constant $R = U^{1/3}M_{eff}/\rho$ (7)

RESULT AND DISCUSSION

The Experimentally measured value of ultrasonic velocity, density and viscosity for the binary mixtures of DMSO and 1-Propanol in different mole fractions at temperature 303K is given in **table 1.** The values of acoustical parameters such as adiabatic compressibility, free length, free volume, available volume, acoustic impedance, relaxation time, internal pressure, Gibb's free energy, Rao's constant and absorption coefficient at constant temperature 303K has been given in **table 2.**

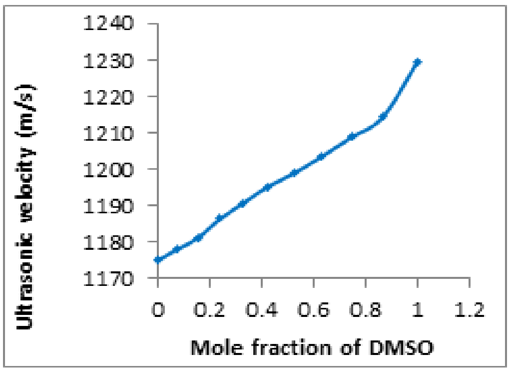
Figure 1 shows that the ultrasonic velocity increases with increase in mole fraction of DMSO, which indicates the presence of molecular association between solute and solvent. The variation of ultrasonic velocity in a mixture depends upon the increase or decrease of intermolecular free length, on the basis of a model for propagation proposed by Eyring and Kincaid [8]. The increase in velocity may be due to the structural changes of molecules in the mixture take place due to the existence of electrostatic field between the interacting molecules. From **Figure 2** it can be seen that the density of mixture increases with concentration due to the presence of large number of molecules in the mixture, while viscosity (**Figure 3**) decreases with increase in concentration. The decrease in viscosity indicates the weak intermolecular forces between the molecules.

Table -1 Values of Ultrasonic Velocity (U), Density (ρ) and Viscosity (η) of DMSO + ethanol at 303^0K

Mole Fraction of DMSO	Mole Fraction of 1-Propanol	Ultrasonic Velocity $U(ms^{-1})$	Density (kg m^{-3})	Viscosity $x10^{-3}$ $(Nm^{-2}s)$
0.0000	1.0000	1175.16	789.02	0.1398
0.0756	0.9399	1180.21	808.90	0.1362
0.1554	0.8711	1181.37	818.30	0.1297
0.2398	0.7930	1191.47	873.20	0.1262
0.3292	0.7053	1192.80	910.20	0.1088
0.4240	0.6075	1195.3	933.70	0.0836
0.5248	0.5002	1197	963.40	0.0788
0.6320	0.3839	1203.57	993.50	0.0744
0.7465	0.2602	1208.84	1017.90	0.0684
0.8689	0.1313	1214.4	1030.50	0.0652
1.0000	0.0000	1229.26	1087.80	0.0631

Table -2 Values of adiabatic compressibility (β), acoustic impedance (Z), free length (L_f), (free volume (V_f), (internal pressure (π_i), Gibbs free energy (ΔG), Rao's constant (R) of DMSO +ethanol at 303^0K

□ $\times10^{-10}$ ms^2 kg^{-1}	$Z\times10^6$ kg $m^{-2}s^{-1}$	L_f $\times10^{-9}$m	V_f $\times10^{-6}$ (ml)	π_i ($\times10^3$ Nm^{-2})	□G $\times10^{-21}$ $Jmol^{-1}$	Rao's Const. 'R'
9.177	0.927	0.634	5.5523	6.500	8.843	991.32
8.875	0.955	0.624	5.9717	6.372	8.828	986.10
8.756	0.967	0.620	6.6199	6.127	8.812	993.61
8.067	1.040	0.595	7.1723	6.157	8.784	950.33
7.722	1.086	0.582	9.1791	5.772	8.735	925.82
7.496	1.116	0.573	13.9066	5.073	8.660	913.50
7.244	1.153	0.564	15.3880	4.985	8.636	891.92
6.948	1.196	0.552	16.9530	4.921	8.610	867.90
6.723	1.230	0.543	19.2268	4.811	8.580	844.48
6.580	1.251	0.537	20.4369	4.790	8.563	825.62
6.084	1.337	0.517	21.1997	4.973	8.534	769.40



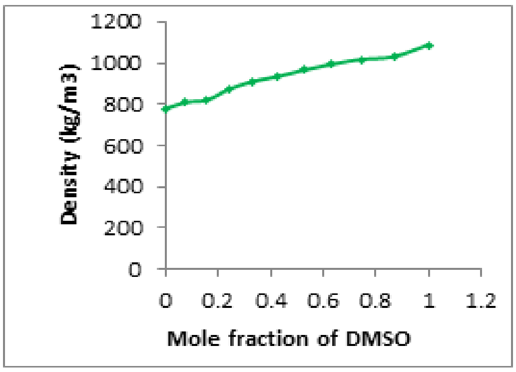


Figure 1: Variation of Ultrasonic velocity

Figure 2: Variation of density
versus mole fraction at temperature 303K versus mole fraction at temperature 303K

Figure 1

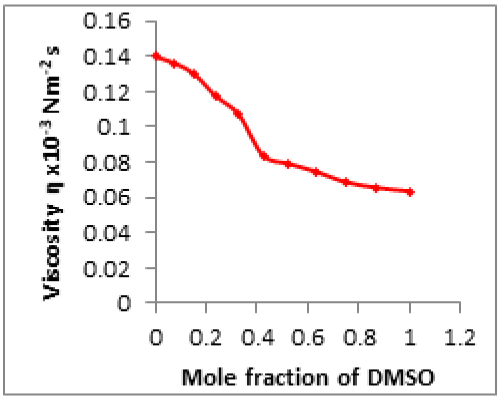


Figure 3:

Figure 2

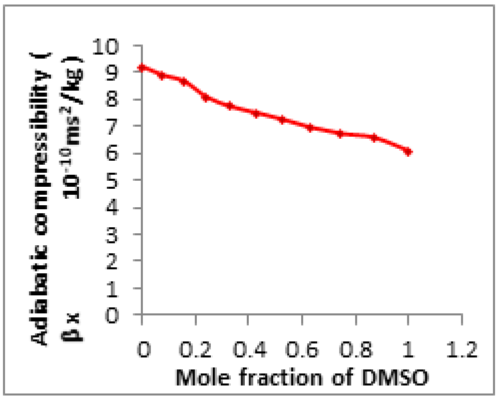
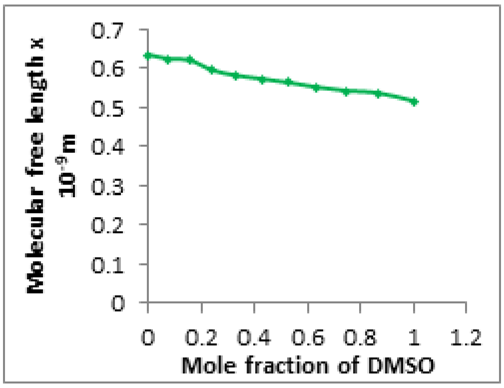


Figure 4:

Figure 3: Variation of viscosity versus mole fraction at temperature 303K

Figure 4: Variation of adiabatic compressibility versus mole fraction at temperature 303K



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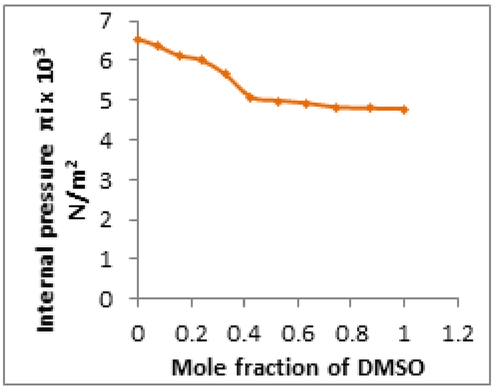

Figure 6:

Figure 5: Variation of molecular free length versus mole fraction at temperature 303K

Figure 6: Variation of internal pressure versus mole fraction at temperature 303K

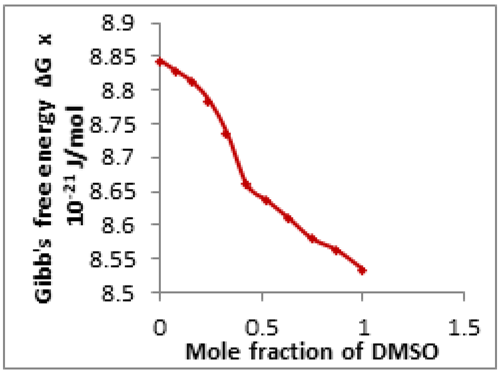

Figure 7:

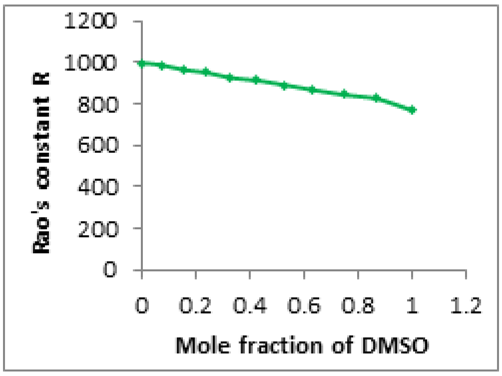

Figure 8:

Figure 7: Variation of Gibb's free energy versus mole fraction at temperature 303K

Figure 8: Variation of Rao's constant versus mole fraction at temperature 303K

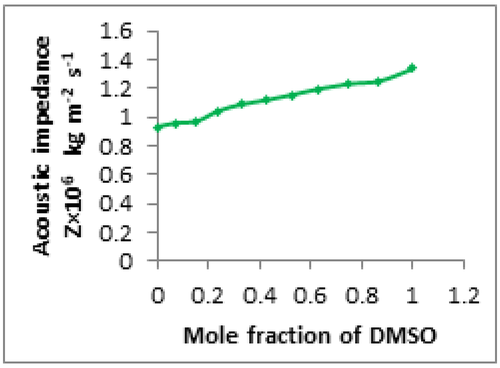

Figure 9:

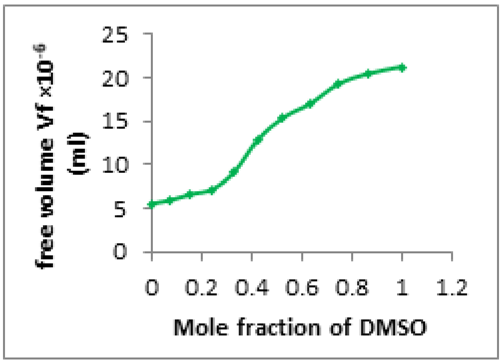

Figure 10:

Figure 9: Variation of acoustic impedance versus mole fraction at temperature 303K

Figure 10: Variation of free volume versus mole fraction at temperature 303K

The adiabatic compressibility decreases with increasing concentration which shows that there is strong interaction between the molecules of liquid mixture shown in **Figure 4**. **Figure 5** depicts the variation in intermolecular free length with mole fraction. This decrease in free length is due to the decreased adiabatic compressibility which brings the molecules to a closer packing.

Figure 6 gives variation in internal pressure with concentration of DMSO. Due to decrease in internal pressure of the mixture there is an increase in the values of free volume which indicates that the strength of interaction between the molecules decreases gradually with increase in concentration and hence weak interaction between the molecules is found.

Figure 7 shows variation in Gibb's free energy with concentration of DMSO. Gibb's free energy decreases with increase in concentration which confirms the hydrogen bonding formation in binary liquid mixtures [9]. Rao's constant decreases with increase in concentration as shown in **Figure 8,** which predicts that there is presence of small complex formation in the mixture.

Acoustic impedance increases with increase in concentration of DMSO (**Figure 9**). Acoustic impedance shows opposite behavior as that of adiabatic compressibility and intermolecular free length. **Figure 10** shows that free volume increases with increase in concentration which suggests that there is weak interaction among the solute and solvent molecules.

CONCLUSION

In the present investigation, the various acoustical parameters such as adiabatic compressibility, intermolecular free length, internal pressure, Gibb's free energy, Rao's constant, acoustic impedance and free volume have been evaluated from ultrasonic velocity, density and viscosity for the binary liquid mixtures of DMSO with ethanol at 303K. From the above studies it is concluded that ultrasonic velocity increases as intermolecular free length decreases. The decrease in viscosity indicates the weak intermolecular forces between the molecules. The decrease in adiabatic compressibility shows that there is strong interaction between the molecules of liquid mixture. Decrease in Gibb's free energy confirms formation of hydrogen bonding in the liquid mixtures.

Conflicts of interest: The authors stated that no conflicts of interest.

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