



Acoustical studies on binary liquid mixtures of some aromatic hydrocarbons with dimethylsulphoxide (DMSO) at 303.15 K

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ABSTRACT

The ultrasonic velocity, density and viscosity have been measured for the binary mixtures of some of the aromatic hydrocarbons such as toluene, benzene, and chlorobenzene with dimethylsulphoxide (DMSO) at 303.15K. The experimental data have been used to calculate the acoustical parameters namely adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), and acoustic impedance (Z). The excess values of some the above parameters are also evaluated and discussed in the light of molecular interaction in the mixtures. It is eventually concluded that a weak molecular interaction is noticed. Such interactions are primarily due to weak dipole-dipole or dipole-induced dipolar forces. Among the three liquid systems studied, the molecular interactions are more pronounced in System-II and less pronounced in System-III.

Key Words: *adiabatic compressibility, intermolecular free length, dipole-dipole induced interactions, dispersive forces, internal pressure*

INTRODUCTION

Investigations on being binary and ternary mixtures of non-electrolytes by calculating excess thermodynamic parameters are found to be highly useful in understanding the solute-solvent interactions in these mixtures. Ultrasonic wave propagation affects the physical properties of the medium and hence, can furnish information on the physics of the liquid and liquid mixtures. The measured ultrasonic parameters are being extensively useful to study intermolecular processes in liquid systems.[1-3] The sign and magnitude of the non-linear deviations from ideal values of velocities and adiabatic compressibilities of liquid mixtures with composition are attributed to the difference in molecular size and strength of interaction between unlike molecules.[4] The present investigation related on thermodynamic properties of binary liquid mixtures of containing dimethylsulphoxide (DMSO), which is aprotic, strongly associated due to highly polar S=O group molecule and large dipole moment and dielectric constant ($\mu = 3.96$ & $\epsilon = 46.68$ at 298 K) [5]

The study of DMSO is important because of its utilization in a broad range of applications in medicine.[6] It easily penetrates biological membranes, facilitates chemical transport into biological tissue and it is well known for its cryoprotective effects on biological systems.[7-8] Also, well established is the use of DMSO as an anti-inflammatory agent which commonly has been used for arthritic conditions. DMSO has also been utilized as a free radical scavenger for various cancer treatments. The unique properties of DMSO also give rise to its wide use as a solvent. In view of the importance mentioned, an attempt has been made to elucidate the molecular interactions in the mixtures of DMSO + toluene, benzene and chloronenzene at 303.15K. Further, acoustical and thermodynamical parameters namely adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), and acoustic impedance (Z) haven been evaluated. Also, the excess values of some of the acoustical parameters have been calculated from the measurements of ultrasonic velocity, density and viscosity of the mixtures

The binary liquid systems taken up for present study at 303.15K are

- System-I** Dimethylsulphoxide (DMSO) + Toluene
System II Dimethylsulphoxide (DMSO) + Benzene
System- III Dimethylsulphoxide(DMSO) + Chlorobenzene

MATERIALS AND METHODS

The liquid mixtures of various concentrations in mole fraction were prepared by taking AR grade Chemicals, which were purified by standard methods [9]. In all systems, the mole fractions were varied from 0.0 to 0.9 so as to have the mixtures of different compositions. Analytical reagent grade (AR) and spectroscopic reagent (SR) with minimum assay of 99.9% of L.valine, L-lysine and L-histidine obtained from E-Merk, Germany and Sd fine Chemicals, India, which are used as such without further purification. Water used in the experiments was deionised, distilled and degassed prior to making solutions. Liquid mixtures of different mole fractions were prepared on the concentration scale with a precision of 0.0001g using an electronic digital balance [Model: SHIMADZU AX-200].The density of liquid mixtures was determined using a specific gravity bottle by relative displacement method with an accuracy of $\pm 0.01\text{kgm}^{-3}$. An Ostwald's Viscometer (10ml capacity) was used for the viscosity measurements with efflux time was determined using a digital chronometer to within $\pm 0.01\text{s}$. An ultrasonic interferometer having the frequency of 2 MHz (Mittal Enterprises, New Delhi, Model-F-81) with overall accuracy of 3ms^{-1} has been used for velocity measurements. An electronically digital operated constant temperature bath (RAGAA Industries, Chennai) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is $\pm 0.1\text{K}$.

RESULTS AND DISCUSSION

The experimentally determined values of density (ρ), viscosity (η) and ultrasonic velocity (U) of all the three liquid systems at 303.15K are presented in Table 1. The values of adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i) and acoustic impedance (Z) for the three liquid systems at 303.15K are reported in Table 2, whereas, the Tables 3 & 4 summarise some of the evaluated excess values of the above parameters. It is evident from the Table 1 that the density (ρ), viscosity (η) and ultrasonic velocity (U) increases with increasing molar concentration of DMSO in all the three liquid

systems. The pronounced increase or decrease in these parameters with composition of mixtures indicates the presence of interactions between the component molecules in the ternary mixtures.

DMSO itself being a polar molecule, when it is associated with benzene, and chlorobenzene and the mixtures formed by these combinations have not only dipolar-dipolar interaction between DMSO molecules, but also the interaction of dipolar-induced dipolar between DMSO molecules and the substituted benzene molecules. The interaction between unlike molecules seems to be stronger than the intra-molecular interactions and it leads to decrease of interaction of molecule. In addition, the relatively small size of DMSO as well as its linear aliphatic configuration may be another factor contributing to the volume contraction of the mixtures.

When DMSO is in association with benzene, being a polar one where both benzene and the toluene are non-polar. Mixing of benzene/toluene with DMSO tends to break DMSO-DMSO dipolar association releasing several DMSO dipoles. Consequently, the free dipoles of DMSO would induce moments in the neighboring molecules (toluene/benzene), resulting in dipolar-induced dipole interaction leading to contraction in volume. This leads to subsequent decrease in adiabatic compressibility (β), and as well as in intermolecular free length (L_f) is observed in all the three liquid systems, with the increasing molar concentration of DMSO, which is evident from the Table 2.

Also, in particular, in the DMSO + chlorobenzene system, the chlorobenzene molecules which are quite polar ($\mu = 1.54$ D) [10] The chlorine atom being an electron withdrawing atom, attracts the π -electrons of the benzene ring in C_6H_5Cl molecules and thus decrease of electron density of the ring. This makes the benzene ring a relatively poor electron donor towards the DMSO molecules, resulting a weak interaction between chlorobenzene and DMSO is expected. On the other hand, a dipole-dipole interaction between DMSO and chlorobenzene seems to be significant, which suggest that dipole-dipole interaction between them predominates in these systems. Similar observations were noticed by earlier workers supports the present study.[11] Further, a decrease in free volume and an increase in internal pressure with increase in concentrations of DMSO is observed, which may be attributed to increasing magnitude of interactions [12] which are evident from the Table 2.

Further, in all three liquid systems, the values of acoustic impedance (Z) is found to be increased, which are listed in Table 2. when an acoustic wave travels in a medium, there is a variation of pressure from particle to particle. The ratio of the instantaneous pressure excess at any particle of the medium to the instantaneous velocity of that particle is known as 'specific acoustic impedance' of the medium. This factor is governed by the inertial and elastic properties of the medium. It is important to examine specific acoustic impedance in relation to concentration and temperature. When a plane ultrasonic wave is set up in a liquid, the pressure and hence density and refractive index show specific variations with distance from the source along the direction of propagation. In the present investigation, it is observed that these acoustic impedance (Z) values increase with increasing concentration of DMSO. Such an increasing values of acoustic impedance (Z), further supports the possibility of molecular interactions between the unlike molecules.

In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in term of excess parameter rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behaviour with respect to concentration and these have been interpreted as arising from the

presence of strong or weak interactions. The extent of deviation depends upon the nature of the constituents and composition of the mixtures.

Table 3 showing the values of excess adiabatic compressibility (β^E) for all the three liquid systems. The negative values of β^E is associated with a structure-forming tendency, while positive values are an indication of structure-breaking tendency due to hetero-molecular interaction between the component molecules of the mixtures. The positive values of β^E for binary mixtures indicate the formation of H-bonds (between the $-\text{O}=\text{S}-$ group of $(\text{CH}_3)_2\text{SO}$ and the substituted benzenes such as toluene, benzene and chlorobenzene. The positive values of excess adiabatic compressibility which indicates the loosely packed molecules in the mixtures resulting due to shape and size. In the present investigation, the system-III which exhibit positive values has been attributed to dispersive forces that show weak molecular interactions and the systems I & II which exhibit negative excess values of adiabatic compressibility suggesting the greater molecular interactions.

The perusal of Table 3 shows the values of excess free length (L_f^E) for all the three binary liquid systems. It was noticed that the L_f^E values are negative in system-II and positive in the systems I & III over the entire range of molar concentrations. According to Kannappan *et.al.*, [13], the negative values of L_f^E indicate that sound waves cover long distances due to decrease in intermolecular free length describing the dominant nature of hydrogen bond interaction between unlike molecules. Fort & Moore [14] indicated that the positive excess values of free length should be attributed to the dispersive forces and negative excess values of should be due to charge transfer and hydrogen bond formation. In the present study, the negative excess values of free length reported in system-II predict the existence of much more influenced molecular interactions. Spencer *et.al.*, [15] have also reported a similar observation on the basis of excess values of free length.

The perusal of Table 3 provides a qualitative picture of excess free volume (V_f^E) values for all the three binary liquid systems. This indicates the extent of deviation from ideal with the mole fraction of the mixtures. The excess values for all the three liquid systems found to be negative. The values found to be increased on increasing the molar concentration of DMSO in system-II and however, the other two systems show a non-linear trend. The results can be explained in terms of molecular interaction, structural effect and interstitial accommodation along with the changes in free volume. The sign of the V_f^E depends on the relative strength between the contractive forces and expansive forces. The factors responsible for volume contraction are (i) specific interactions between the component molecules and (ii) weak physical forces, such as dipole-dipole or dipole-induced dipole interactions or Vanderwaal's forces. The factors that cause expansion in volume are dispersive forces, steric hindrance of component molecules, unfavorable geometric fitting and electrostatic repulsion.

The negative values of excess free volume in all the systems assert that the combined effect of the factors responsible for volume contraction and vice-versa [16]. Adgaonkar *et.al.*, [17] showed positive values of V_f^E indicating the existence of weak molecular interactions in the liquid mixtures and the negative values of excess free volume suggesting the specific interactions among unlike molecules.

In the study of liquid mixtures the variation of internal pressure may give some suitable information regarding the nature and strength of the forces existing between the molecules. In fact, the internal pressure is a broader concept and it is a measure of the totality of forces of the dispersion, ionic and dipolar interaction that contribute to be overall cohesion of the liquid

systems. The excess internal pressure values (π_i^E) are negative in all the three liquid systems in the present study. Such negative values of π_i^E indicate that only dipolar forces are operating between the unlike molecules. Further, the observed behavior of excess internal pressure values reveals that the strengthening of cohesive forces resulting perhaps due to making up of the structure of the solvent.

One should observe from the Table 4 the variation of excess Gibbs energy ΔG^E for the three binary liquid systems. The values of ΔG^E are positive in system-II and exhibit negative values in systems I & III. According to Read et.al., [18], the positive values of excess Gibbs energy values may be attributed to specific interactions like hydrogen bonding and charge transfer, while negative ΔG^E values may be ascribed to the dominance of dispersion forces.[19] In the present study, the existence of molecular interaction prevails more in System-II between the components of unlike molecules than the other two liquid systems.

From the Table 4, which exhibits the excess molar volume (V_m^E) values. According to Thirumaran *et.al.*, [20] the excess molar volume (V_m^E) are influenced by

- (1) the loss of dipolar associations and differences in size and shape and
- (2) dipole-dipole, dipole-induced dipole interactions or charge transfer complexation between the unlike molecules

Table -1 Values of density, viscosity and ultrasonic velocity of three binary liquid systems at 303.15K

Mole Fraction		DENSITY $\rho/(\text{kg/m}^3)$	VISCOSITY $\eta/(\times 10^{-3} \text{ NSm}^{-2})$	VELOCITY U/(m/s)
X_1	X_3	Temperature (K) at 303.15K		
System-I				
0.0998	0.9001	867.5	0.6553	1287.0
0.2999	0.7000	906.6	0.7960	1320.7
0.5000	0.5000	950.6	0.9170	1354.4
0.7000	0.2999	998.1	1.1354	1396.3
0.9001	0.0998	1049.4	1.6331	1434.6
System-II				
0.0998	0.9001	881.98	0.7063	1290.5
0.3000	0.6999	922.44	0.8562	1328.2
0.5000	0.4999	965.10	1.0363	1362.3
0.7000	0.2999	1009.58	1.3505	1399.2
0.9001	0.0998	1058.37	1.6277	1438.8
System-III				
0.0998	0.9001	1086.02	0.7906	1256.7
0.2999	0.7000	1086.71	0.9197	1292.6
0.5000	0.5000	1087.12	1.0981	1330.0
0.7000	0.2999	1087.63	1.3065	1375.4
0.9001	0.0999	1088.32	1.6319	1420.3

The former effect leads to expansion in volume and the latter contributes to contraction in volume. The actual V_m^E depends upon the balance between these two opposing considerations. The negative excess values of molar volume (V_m^E) is further may be interpreted as that formation of a hydrogen bond of type X...S-O between DMSO and the substituted benzenes changes free volume, interstitial accommodation and confirmation changes in DMSO and substituted benzenes appear to occur in these mixtures. Also, the negative value of V_m^E is further attributed to the formation of charge complexes between the π -electrons of DMSO and substituted benzenes.

The experimental data in the present study suggest that the factors which are favourable for latter effect, which account for the existence of dipole-dipole interactions present in the liquid mixtures. The negative values of V_m^E in all the three liquid systems clearly supporting this prediction.

Table -2 Values of adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), and acoustic impedance (z) for the three binary liquid systems at 303.15K

Mole Fraction		Adiabatic compressibility $\beta/(\times 10^{-10} \text{ m}^2 \text{ N}^{-1})$	Free length $L_f/(\times 10^{-10} \text{ m})$	Free volume $V_f/(\times 10^{-7} \text{ m}^3 \text{ mol}^{-1})$	Internal pressure $\pi_i/(\times 10^6 \text{ Nm}^{-2})$	Acoustic impedance $Z/(\times 10^6 \text{ kg m}^2 \text{ s}^{-1})$
X_1	X_3	Temperature (K) at 303.15K				
System-I						
0.0998	0.9001	6.9594	0.5263	2.6866	110.02	1.1664
0.2999	0.7000	6.3237	0.5017	1.9900	129.03	1.1973
0.5000	0.5000	5.7346	0.4778	1.5924	146.74	1.2874
0.7000	0.2999	5.1388	0.4523	1.1504	172.57	1.3936
0.9001	0.0998	4.6301	0.4293	0.6593	220.18	1.5054
System-II						
0.0998	0.9000	6.8080	0.5206	1.9252	138.86	1.1381
0.3000	0.6999	6.1451	0.4946	1.5062	155.27	1.2251
0.5000	0.4999	5.5831	0.4714	1.1751	173.82	1.3147
0.7000	0.2999	5.0594	0.4488	0.8222	201.75	1.4126
0.9001	0.0998	4.5641	0.4262	0.6480	225.38	1.5227
System-III						
0.0998	0.9001	5.8304	0.4817	2.5796	115.79	1.3648
0.2999	0.7000	5.5075	0.4682	1.9448	132.74	1.4046
0.5000	0.5000	5.2001	0.4550	1.4015	155.24	1.4458
0.7000	0.2999	4.8602	0.4398	1.0147	181.74	1.4959
0.9000	0.0999	4.5549	0.4258	0.6754	219.97	1.5457

Table -3 Excess Values of adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E) and internal pressure (π_i^E), for the three binary liquid systems at 303.15K

Mole Fraction		Excess adiabatic compressibility $\beta^E/(\times 10^{-10} \text{ m}^2 \text{ N}^{-1})$	Excess free length $L_f^E/(\times 10^{-10} \text{ m})$	Excess free volume $V_f^E/(\times 10^{-7} \text{ m}^3 \text{ mol}^{-1})$	Excess internal pressure $\pi_i^E/(\times 10^6 \text{ Nm}^{-2})$
X_1	X_3	Temperature (K) at 303.15K			
System-I					
0.0998	0.9001	0.0108	0.0018	-0.2482	-5.7838
0.2999	0.7000	-0.0437	0.0015	-0.4063	-16.5946
0.5000	0.5000	-0.0523	0.0017	-0.2659	-27.9209
0.7000	0.2999	-0.0664	0.0014	-0.1693	-31.0928
0.9001	0.0998	0.0061	0.0019	-0.1219	-12.4981
System-II					
0.0998	0.9001	-0.3972	-0.0133	-0.5406	7.1250
0.3000	0.6999	-0.4218	-0.0130	-0.5253	-2.1316
0.5000	0.4999	-0.3457	-0.0098	-0.4224	-9.2317
0.7000	0.2999	-0.2314	-0.0060	-0.3413	-6.9498
0.9001	0.0998	-0.0884	-0.0023	-0.0812	-8.9755
System-III					
0.0998	0.9001	0.0477	0.0025	-0.1307	-6.9224
0.2999	0.7000	0.0463	0.0033	-0.2769	-17.3037
0.5000	0.5000	0.0608	0.0041	-0.3321	-22.6465
0.7000	0.2999	0.0434	0.0033	-0.2302	-23.8522
0.9000	0.0999	0.0599	0.0035	-0.0812	-13.3414

Table -4 Excess Values of Gibb's free energy (ΔG^E) and molar volume (V_m^E) for the three binary liquid systems at 303.15K

Mole Fraction		Excess Gibb's free energy $\Delta G^E/(\times 10^{-3} \text{ m}^3 \text{ mol}^{-1})$	Excess molar volume $V_m^E/(\times 10^{-7} \text{ m}^3 \text{ mol}^{-1})$
X_1	X_3	Temperature (K) at 303.15K	
System-I			
0.0998	0.9001	0.0007	-0.0003
0.2999	0.7000	-0.0050	-0.0007
0.5000	0.5000	-0.0228	-0.0008
0.7000	0.2999	-0.0255	-0.0005
0.9001	0.0998	-0.0061	0.0001
System-II			
0.0998	0.9001	0.0127	-0.0036
0.3000	0.6999	0.0039	-0.0031
0.5000	0.4999	-0.0040	-0.0023
0.7000	0.2999	0.0010	-0.0014
0.9001	0.0998	0.0090	-0.0004
System-III			
0.0998	0.9001	-0.0028	-0.0002
0.2999	0.7000	-0.0101	-0.0004
0.5000	0.5000	-0.0108	-0.0002
0.7000	0.2999	-0.0149	-0.0002
0.9000	0.0999	-0.0098	-0.0007

CONCLUSION

From the observed experimental values of ultrasonic velocity, density and viscosity, related acoustical parameters and some of their excess values for the binary liquid mixtures of toluene, benzene and chlorobenzene with dimethylsulphoxide (DMSO) at 303.15K, it is very obvious that there exists a molecular association between the components of the liquid mixtures. In specific, a weak molecular interaction is noticed in the present systems of liquid mixtures. When DMSO is associated with substituted benzenes such as toluene and chlorobenzene and the mixtures formed by these combinations have not only dipolar-dipolar interaction between the DMSO molecules, but also the interaction of dipolar-induced dipolar between the DMSO molecules and the substituted benzenes. Such an interaction between unlike molecules seem to stronger than the intra-molecular interactions which will lead to decrease of interaction. Hence, it is very obvious that weak dipole –dipole and dipole-induced dipole forces dominate resulting in existence of weak interactions in the present study. Dispersive forces are also found to exist between the component molecules of the mixture. Among the liquid systems taken up for present study, the strength of the molecular interactions are more pronounced in System-II (DMSO + benzene) and less pronounced in System-III (DMSO + chlorobenzene)

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