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Ultrasonic Study on Binary Mixtures Containing DMSO with Chlorobenzene, Bromobenzene and Nitrobenzene over the Entire Miscibility Range ($0 < X_1 < 1$) at Temperature 313K.

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Abstract : This paper presents experimental data for densities (ρ), viscosities (η) and ultrasonic speeds (U) of pure Dimethylsulphoxide (DMSO), Chlorobenzene (CB), Nitrobenzene (NB) and Bromobenzene (BB) and of their binary liquid mixtures over the entire composition range ($0 < X_1 < 1$) at temperature 313 K. These parameters were used to determine the adiabatic compressibility (β), intermolecular free length (L_f), molar volume (V_m) and acoustic impedance (Z) and their excess values. The derived functions namely V_m^E , L_f^E , Z^E and β^E were used to have a better understanding of intermolecular interactions between the component molecules of the present liquid mixtures. The variations of these parameters with composition of mixture indicate the nature and extent of interaction between unlike molecules & suggest that the interactions occurring between DMSO, chlorobenzene, nitrobenzene and bromobenzene molecules follow the sequence: (Bromobenzene > Chlorobenzene > Nitrobenzene). The excess and deviation functions were fitted to Redlich-Kister type polynomial equation. The results provide information on the molecules in the pure liquids as well as in the binary mixtures. The deviations from ideality of these functions suggest that the effect of interactions between like and unlike molecules balance each other to varying degrees in mixtures.

Keywords: Density, Viscosity, Ultrasonic speed, Molar volume, Binary mixtures.

I. Introduction

Ultrasonic wave propagation affects the physical properties of the medium and hence can furnish information about molecular interactions of the liquid and liquid mixtures. The measured ultrasonic parameters are being extensively useful to study intermolecular processes in liquid systems. The sign and magnitude of the non-linear deviations from ideal values of velocities and adiabatic compressibility's of liquid mixtures with composition are attributed to the difference in molecular size and strength of interaction between unlike molecules.

Studies of thermodynamic properties of binary mixtures are of considerable interest in the fundamental understanding of the nature of interactions between the unlike molecules. In recent years, the theoretical and experimental investigations of excess and deviation functions are taken as interaction parameters to improve the results [1-4]. Our research 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 [5]. The present work is a continuation of our earlier studies [6-8] and deals with the qualitative and quantitative study on the binary mixtures of Dimethylsulphoxide (DMSO) with chlorobenzene (CB), nitrobenzene (NB) and bromobenzene (BB). The present investigation related on acoustical 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). The study of DMSO is important because of its utilization in a broad range of applications in medicines. 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 [12-16]. Chlorine atom in chlorobenzene is an electron- withdrawing atom, tends to attract to π electrons of the benzene ring thereby and decreases the electron density of the benzene ring. As a result, the benzene ring in chlorobenzene becomes relatively poor electron-donor towards the electron seeking proton of any groups. Chlorobenzene is more reactive because chlorine atom is bonded with sp^3 hybridized carbon atom and consequently can be removed easily. Bromobenzene and Nitrobenzene are occasionally used as a solvent for electrophilic substitution reactions. Therefore, a better understanding of the physicochemical properties of mixed solvent System I (DMSO & CB), System II (DMSO & NB) and System III (DMSO & BB) may help in the study of chemicals and biological processes in these media.

In view of their industrial importance, the present study reports the experimental values of densities (ρ), viscosities (η) and ultrasonic speeds (u) of pure DMSO, CB, NB, BB and those of their binary mixtures over the entire

composition range and at 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 313K temperature. All of these excess and deviation quantities have been fitted to Redlich-Kister type polynomial equation (6). The study of molecular interactions in the liquid mixtures is therefore important in elucidation of the structural properties of the molecules.

II. Experimental

Dimethylsulphoxide (Acros Organics, USA) of AR grade 99%, chlorobenzene, nitrobenzene and bromobenzene (S.D Fine Chem. Ltd. India) also of A.R grade 99.5% were further purified by the method given in the literature [11]. All the chemicals were stored over 0.4 nm molecular sieves to remove the traces of water, if any, and degassed just before use.

In all systems, the various concentrations of the binary liquid mixtures were prepared in terms of mole fraction. The mole fractions of the first and second component (X_1 and X_2) were varied from 0 to 1. Purities of these chemicals were checked by density determination at the temperature 313 K which showed an accuracy of $0.0001 \text{ gm cm}^{-3}$ as compared to reported values. The density, viscosity and velocity were measured as a function of composition of binary liquid mixture at the temperature 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 the temperature 313 K. An ultrasonic interferometer (Model: F81) working at a frequency 3MHz with an overall accuracy of $\pm 2 \text{ ms}^{-1}$ has been used for velocity measurement. An electronically digital constant temperature bath has been used to circulate water through the double walled measuring cell made up of steel containing experimental mixtures at the desired temperature. The accuracy in the temperature measurement is $\pm 0.1\text{K}$. Reliability of the experimental data and the purity of the solvents were ascertained by calculating their densities, ultrasonic speeds and viscosities at the temperature 313K with the values reported in Table 1.

III. Results and discussion

The experimental densities (ρ), ultrasonic speeds (U) and viscosities (η) of pure DMSO, chlorobenzene, nitrobenzene, bromobenzene and their binary mixtures are used to calculate excess thermodynamic properties of mixtures which correspond to the difference between the actual property and the property if the system behaves ideally and thus are useful in the study of molecular interactions and arrangements in the mixtures. In particular, they reflect the interactions that take place between solute-solute, solute-solvent and solvent-solvent species. The effects which are expected to operate between the component molecules under study are (i) structural effect which is due to the differences in shape and size of the component molecules (ii) reorientation effect between component molecules and (iii) energetic effect, i.e., molecular interaction that can be weakened or destroyed or established during the mixing process [17]. Thus, in the present study various acoustical parameters were calculated from measured data by using following equations

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

$$\text{Intermolecular Free length } (L_f) = K \sqrt{\beta} \quad (2)$$

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

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

$$\text{Molar Volume } (V_m) = M/\rho \quad (4)$$

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. The values of excess molar volumes (V_m^E), excess intermolecular free length (L_f^E), excess acoustic impedance, (Z^E) and excess adiabatic compressibility (β^E) were calculated with the help of the following standard relations:

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

Where,

$Y_{\text{exp.}}$ = 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(CB or NB or BB) and liquid 2 (DMSO).

The values of excess adiabatic compressibility (β^E), free length (L_f^E), acoustic impedance (Z^E) and molar volume (V_m^E) for each mixture have been least-squares fitted to Redlich-Kister type polynomial equation given in literature [10] by taking the limits $n=0$ to i .

$$F(X) = X_1 \cdot (1-X_1) \sum A_i \cdot (1-2 \cdot X_1)^i, \quad (6)$$

Where $F(x)$ refers to V_m^E or L_f^E . The coefficient A_i is the polynomial coefficient tabulated by using the least square method computed by the MAPLE software has been used. The values of the standard deviation (σ) were obtained from the expression

$$\sigma = \left\{ \sum (F(x)_{\text{exp}} - F(x)_{\text{cal}})^2 / (k/n) \right\}^{1/2} \quad (7)$$

Where k is the number of experimental points excluding the end points and n is order of polynomial equation. The values of $F(X)_{\text{cal}}$ are obtained from Eq. (6) by using the best fit values of A_i coefficients. The coefficients A_0 , A_1 , A_2 , A_3 and A_4 along with standard deviations σ of fit for all the mixtures are listed in Table 4 and it has been observed that standard deviations are very low.

Values of density (ρ), viscosity (η), ultrasonic velocity (U), adiabatic compressibility (β), free length (L_f), acoustic impedance (Z) and molar volume (V_m) of pure liquids at 313 K are listed in Table [1]. Values of binary liquid mixtures of DMSO with chlorobenzene, nitrobenzene and bromobenzene for different compositions at 313 K are presented in Table [2]. Respective values of excess parameters have been evaluated and listed in Table [3].

It has been seen from Table [2] that the ultrasonic velocity & viscosity decreases and density increases with decrease in concentration of DMSO in case of all the three systems. Adiabatic compressibility & free length increase in system I & III but decreases in system II, molar volume increases in all the three systems and acoustic impedance decreases in system I & III but increases in system II with increasing mole fraction of DMSO.

Fig.1 (a), Fig. 1(b) and Fig. 1(c) show the plots of excess molar volume (V_m^E) vs. mole fraction of first component (X_1) for all the three systems. In the system I, V_m^E is less negative. In system II, V_m^E is positive but for system III, V_m^E is more negative over the entire composition and temperature range. The positive and negative variations of the excess values with concentration and temperature of the same acoustic parameters supported the presence of interaction between unlike molecules [10].

In nitrobenzene, $-\text{NO}_2$ group has an electron withdrawing inductive effect, which tends to intensify the positive charge of the nearest carbon atom of the benzene ring. The highly polar DMSO molecule induces a moment in the highly polarizable nitrobenzene molecule and increases the dipole moment of the binary liquid mixture of DMSO & nitrobenzene, showing large values of ultrasonic velocity for the binary liquid mixture of DMSO & nitrobenzene [9].

IV. Conclusions

In the present work, experimental densities, viscosities and ultrasonic velocities of binary mixtures of DMSO with chlorobenzene, bromobenzene and nitrobenzene determined as a function of composition at 313 K temperature. Using these data, values of acoustical parameters and excess parameters were evaluated with the help of standard relations. The variation of these parameters with the composition indicates that the weak molecular interaction exist in the mixtures which are in the order (Bromobenzene > Chlorobenzene > Nitrobenzene).

Among five theories taken up for the prediction of ultrasonic velocity, Free Length Theory (FLT) is found to yield excellent in comparison with experimental values, while Nomoto Relation (NR) shows greatest deviation for the systems investigated. It has been found the existence of molecular association between the components of the mixtures. There is a weak molecular interaction prevailing in the present systems of the mixtures. Such interactions are due to weak dipole-dipole and dipole- induced dipole forces. Dispersive forces are also found to exist between the components of the mixtures. The values of standard deviations are presented in Table (4) and it has been observed that standard deviations are very low.

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Table 1: Values of density (ρ), viscosity (η), ultrasonic velocity (U), adiabatic compressibility (β), free length (L_f), acoustic impedance (Z) and molar volume (V_m) of pure liquids at 313 K.

Liquids	ρ / Kg m ³	η / 10 ³ Nsm ²	U / ms ⁻¹	β / 10 ¹⁰ m ² N ⁻¹	L_f / 10 ¹⁰ m	$Z/10^6$ Kg m ⁻² s ⁻¹	$V_m/10^6$ m ³ mol ⁻¹
DMSO	1079.20	1.6927	1437.73	4.4827	135.93	1.5516	72.40
CB	1084.80	0.6341	1208.93	6.3073	161.23	1.3115	103.76
BB	1466.50	0.8736	1044.80	6.2467	160.46	1.5322	107.07
NB	1182.70	1.3164	1398.93	4.3205	133.44	1.6545	104.09

Table 2: Values of density (ρ), viscosity (η), ultrasonic velocity (U), adiabatic compressibility (β), free length (L_f), acoustic impedance (Z) and molar volume (V_m) at 313 K for all the three binary liquid mixtures.

Liquid Mix. T/K	Mole fraction X_1	ρ / Kg m ³	$10^3\eta$ / Nsm ²	U /ms ⁻¹	$10^{10}\beta$ / m ² N ⁻¹	$10^{10}L_f$ / m	$10^{-6}Z$ /Kg m ⁻² s ⁻¹	10^6V_m / m ³ mol ⁻¹
MSO+CB								
313K	0.0000	1079.20	1.6927	1437.73	4.4827	135.93	1.5516	72.40
	0.1486	1080.62	1.3419	1383.07	4.8377	141.21	1.4946	77.03
	0.3175	1081.97	1.0788	1332.93	5.2020	146.43	1.4422	82.32
	0.5114	1083.12	0.8846	1291.13	5.5384	151.09	1.3985	88.39
	0.7363	1084.04	0.7448	1249.47	5.9089	156.06	1.3545	95.46
	1.0000	1084.80	0.6341	1208.93	6.3073	161.23	1.3115	103.76
DMSO+NB								
313K	0.0000	1079.20	1.6927	1437.73	4.4827	135.93	1.5516	72.40
	0.1478	1106.31	1.5213	1421.14	4.4756	135.82	1.5722	76.63
	0.3162	1132.91	1.4219	1406.43	4.4624	135.62	1.5934	81.52
	0.5099	1147.76	1.3576	1402.93	4.4266	135.07	1.6102	88.05
	0.7350	1164.10	1.3324	1400.22	4.3814	134.38	1.6300	95.52
	1.0000	1182.70	1.3164	1398.93	4.3205	133.44	1.6545	104.09
DMSO+BB								
313K	0.0000	1079.20	1.6927	1437.73	4.4827	135.93	1.5516	72.40
	0.1446	1155.28	1.4659	1343.27	4.7972	140.61	1.5518	77.51
	0.3108	1231.79	1.2614	1258.48	5.1259	145.35	1.5502	83.33
	0.5036	1308.94	1.1102	1182.97	5.4593	150.00	1.5484	90.04
	0.7301	1387.55	0.9847	1114.67	5.8004	154.62	1.5467	97.82
	1.0000	1466.50	0.8736	1044.80	6.2467	160.46	1.5322	107.07

Table 3: Values of excess adiabatic compressibility (β^E), free length (L_f^E), acoustic impedance (Z^E) and molar volume (V_m^E) at 313 K.

Liquid Mix.	Mole fraction(X_1)	β^E x 10 ¹⁰ m ² N ⁻¹	L_f^E x 10 ¹⁰ m	Z^E x10 ⁻⁶ Kg m ⁻² s ⁻¹	V_m^E x10 ⁶ m ³ mol ⁻¹
DMSO+CB					
313K	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0720	-0.2069	0.8591	-0.0122	-0.0104
	0.1486	-0.3311	1.5201	-0.0214	-0.0214
	0.2302	-0.3893	2.0976	-0.0287	-0.0324
	0.3175	-0.4055	2.4633	-0.0332	-0.0403
	0.4110	-0.4056	2.3974	-0.0326	-0.0472
	0.5114	-0.3737	2.2161	-0.0303	-0.0457
	0.6195	-0.3154	1.8911	-0.0260	-0.0407
	0.7363	-0.2270	1.4987	-0.0203	-0.0317
	0.8627	-0.1271	0.8014	-0.0111	-0.0174
	1.0000	0.0000	0.0000	0.0000	0.0000

DMSO+NB

313K	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0715	0.0171	0.1401	0.0022	-0.1679
	0.1478	0.0312	0.2586	0.0054	-0.4499
	0.2291	0.0423	0.3580	0.0067	-0.5700
	0.3162	0.0529	0.4761	0.0092	-0.9006
	0.4095	0.0538	0.4717	0.0071	-0.6550
	0.5099	0.0493	0.4130	0.0062	-0.5039
	0.6181	0.0432	0.3578	0.0053	-0.4168
	0.7350	0.0337	0.2805	0.0027	-0.1765
	0.8619	0.0176	0.1345	0.0013	-0.0337
	1.0000	0.0000	0.0000	0.0000	0.0000

DMSO+BB

313K	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0699	-0.3325	0.5938	0.0020	0.0565
	0.1446	-0.4989	1.1389	0.0031	0.0941
	0.2247	-0.5710	1.5502	0.0038	0.1305
	0.3108	-0.5833	1.8007	0.0046	0.1598
	0.4035	-0.5548	1.8777	0.0054	0.1808
	0.5036	-0.4999	1.7225	0.0066	0.1838
	0.6121	-0.4247	1.3298	0.0082	0.1634
	0.7301	-0.3262	0.7820	0.0092	0.1067
	0.8589	-0.1911	0.2624	0.0073	0.0490
	1.0000	0.0000	0.0000	0.0000	0.0000

Table (4). Redlich-Kister constants for the deviations of Excess parameters of intermolecular free length, acoustic impedance, adiabatic compressibility and molar volume of different binary mixtures of styrene at temperature 313K

Property	T/K	a0	a1	a2	a3	a4	$\sigma (Y^E)$
DMSO+CB							
$10^{10}L_f^E/(m)$	313K	9.0134	4.7467	3.8075	-1.7864	-4.9506	0.071307
$10^6V_m^E/m^3mol^{-1}$		-0.1858	-0.0365	0.0601	0.0444	-0.0146	0.001101
$10^{-6}Z^E/Kgm^{-2}S^{-1}$		-0.1231	-0.0619	-0.0458	0.0144	0.0469	0.000690
$10^{10}\beta^E/m^2N^{-1}$		-1.4256	-1.1145	-2.4449	0.8085	4.5140	0.102743
DMSO+NB							
$10^{10}L_f^E/(m)$	313K	5.2268	3.8371	0.7986	-4.0682	-0.7044	0.047702
$10^6V_m^E/m^3mol^{-1}$		0.8161	0.1072	-0.0463	0.0032	0.3574	0.003933
$10^{-6}Z^E/Kgm^{-2}S^{-1}$		-0.0430	-0.0392	-0.0078	0.0478	0.0039	0.000566
$10^{10}\beta^E/m^2N^{-1}$		0.4331	0.2820	0.0598	-0.2673	-0.0481	0.003164
DMSO+BB							
$10^{10}L_f^E/(m)$	313K	6.9061	5.2375	-2.8961	-0.7113	0.8648	0.012617
$10^6V_m^E/m^3mol^{-1}$		0.7416	0.1643	-0.5546	0.1895	0.4927	0.002977
$10^{-6}Z^E/Kgm^{-2}S^{-1}$		0.0264	-0.0291	0.0371	0.0093	-0.0095	0.000135
$10^{10}\beta^E/m^2N^{-1}$		-2.0155	-1.2007	-1.1599	-1.0682	-0.8643	0.004488

Graphs:

