

Studies on thermodynamic properties of binary mixture of benzene in DMSO at T = 308.15 K

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ABSTRACT

Density (ρ), ultrasonic speed (u) and excess molar volume (V_m^E) of binary mixtures of benzene in DMSO have been measured over the entire range of composition at 308.15K. From these experimental results, parameters such as isentropic compressibility K_s , interaction parameter, χ_{12} , Flory parameters, coefficients, A_i , standard deviations, $\sigma(Y^E)$, and molar sound velocity, R_m have been estimated. The excess functions have been fitted to the Redlich-Kister polynomial equation. The experimental ultrasonic speeds have been analyzed in terms of Jacobson Free Length Theory (FLT), Schaaff's Collision Factor Theory (CFT), Nomoto's relation, and Van Dael's ideal mixture relation. Intermolecular Free Length, L_f , and available volume, V_a , have been calculated from FLT, CFT, and thermoacoustic approach for binary systems of benzene in DMSO at 308.15K.

Keywords: Ultrasonic speed, excess molar volume, Schaaff's Collision Factor Theory, benzene and DMSO.

INTRODUCTION

The measurement of thermodynamic and acoustic properties contributes to the understanding of the physicochemical behaviour of the binary and multi-component liquid mixtures. Excess properties of liquid systems, such as molar volumes, are required for testing the theories of solutions, development of separation techniques and equipment, and for other industrial applications. Benzene is a versatile organic solvent which finds use in number of industry.

Thus, a study of physical properties data on the binary mixture containing benzene has attracted considerable interest in the literature¹⁻³. Thus, benzene in DMSO mixed solvent would enable us to have a large number of solvents with appropriate physico-chemical properties, which can be used for a particular chemical process. Moreover, literature survey indicates that no ultrasonic study on this binary system has been reported at 308.15K. Therefore, present study was undertaken in order to have deeper understanding of the intermolecular interaction between the

components of the above binary liquid mixture. Thus, a study of thermodynamic properties data on the binary mixture of benzene in DMSO has attracted considerable interest in our present study.

Research workers in the past have shown that NMR^{4,5}, IR⁶⁻⁷ and Raman spectra⁸, have been used to study molecular interactions. The velocity measurement of the propagation of ultrasonic waves⁹⁻¹³ and their absorption^{14, 15} have already been found to be useful in the study of molecular interactions for inorganic, organic and organo-metallic binary systems. Likewise, researchers¹⁶⁻²¹ have also employed ultrasonic measurements to look into the important consequences of ion-solvent interactions for the structure of electrolytic solutions. References^{22, 23} related to the field of medicine, whereas references²⁴⁻²⁷ based on studies on emulsions/microemulsions, polymer surfactants interactions²⁸ and ultrasonic destruction of surfactants²⁹ are only a few cases to suggest versatility of the technique.

EXPERIMENTAL

Benzene was procured from Fluka-Aldrich and DMSO from Fischer Scientific Ltd. and are further purified by the methods given in Vogel text book of practical organic chemistry³⁰. Prior to the experimental measurements, both the organic liquids were stored in dark bottles over 0.4nm molecular sieves to reduce water content and were partially degassed with a vacuum pump under nitrogen atmosphere. The purities of all the samples determined by chromatographic analysis were better than 0.996 on a molar basis. Binary mixtures are prepared by mixing appropriate volumes of the liquid component in the specially designed glass bottles with air tight Teflon coated caps. The required properties are measured on the same day

immediately after preparing each composition. The uncertainty in mole fraction is ± 0.0001 . A multi frequency digital micrometer reading ultrasonic interferometer (M-81, Mittal Enterprises, New Delhi) operating at 1, 2, 3 & 4 MHz was used to measure the ultrasonic velocity of the binary liquid mixtures (with an uncertainty of $\pm 0.3\%$) at a constant temperature of 308.15K by using a digital constant temperature water bath. The temperature stability is maintained within $\pm 0.001\text{K}$ by circulating thermostated water around the cell with a circulating pump. In order to minimize the uncertainty of the measurement, several maxima are allowed to pass and their number (fifty) is counted. All maxima are recorded with the highest swing of the needle on the micrometer scale. The total distance, d (cm) moved by the reflector is given by $d = \frac{n\lambda}{2}$, where λ is the wavelength.

The frequency ν , of the crystal being accurately known (2.0 MHz), the speed of sound, u in ms^{-1} is calculated by using the relation $u = \lambda\nu$. Excess molar volume, V_m^E was calculated by specially designed double limbed glass dilatometer fitted with a microcapillary ($\pm 0.01\text{cm}$) in the centre. The density of solutions was measured by a double arm pycnometer of bulb capacity 10 ml and a capillary of an internal diameter of about 1mm. The mark of the stem was calibrated by double distilled water (conductivity less than $1 \times 10^{-6} \text{ohm}^{-1} \text{cm}^{-1}$) with 0.9970 and 0.9940 g cm^{-3} as its density at 298.15K and 308.15K respectively and benzene with buoyancy corrected. The accuracy of the density results was ± 0.0001 (g cm^{-3}). Before each series of measurements, the instrument was calibrated with triple distilled freshly degassed water. Weight measurement were performed on a

Mettler Toledo AB 135-S/FACT, single pan analytical balance, with a precision of 0.01mg. The densities, and ultrasonic velocities, u of the pure liquids were in good agreement with the values found in the literature and are presented in Table 1.

RESULTS

The excess molar volumes, V_m^E , of the solutions were calculated from the densities of the pure liquids and their mixtures using the following equations³¹:

$$V_m^E = \frac{(x_1 M_1 + x_2 M_2)}{\rho_{mix}} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (1)$$

Where ρ_{mix} is the density of the mixture and x_1, M_1, ρ_1 and x_2, M_2, ρ_2 are the mole fraction, molar mass, and the density of pure component 1 and 2 respectively.

The following relations have been used to correlate the sound velocity, u , of the binary liquid mixtures:

Nomoto Relation³²

$$u = \left(\frac{R_m}{V_{mix}} \right)^3 = \left(\frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \right)^3 \quad (2)$$

Where x_1, x_2, V_1, V_2 and R_1, R_2 are mole fractions, molar volumes, and molar sound velocity of first and second components, respectively.

Van Dael Relation³³

$$\frac{1}{x_1 M_1 + x_2 M_2} \cdot \frac{1}{u_{id,mix}^2} = \frac{x_1}{M_1 u_1^2} + \frac{x_2}{M_2 u_2^2} \quad (3)$$

Where, M_1, M_2 and u_1, u_2 are the molar masses and sound velocities of first and second

components, respectively, and $u_{id,mix}$ is the ultrasonic velocity of the ideal mixture.

Jacobson's Free Length Theory (FLT)³⁴

$$u_{mix} = \frac{K}{L_{f(mix.)} \rho_{mix}^{1/2}} \quad (4)$$

Where K is the Jacobson constant which is temperature dependent only and its value is 642.15 at 313.15K. The $L_{f(mix.)}$ is the intermolecular free length of the binary mixtures, which is given by $L_f = \frac{2V_a}{Y}$. Here

V_a represents the available volume per mole and Y is the surface area per mole and these may be expressed as

$$V_a = (V_T - V_0) \quad (5)$$

$$Y = (36\pi N_A V_0^2)^{1/3} \quad (6)$$

Here N_A is the Avogadro number and V_0 and V_T are the molar volumes at zero Kelvin and at temperature T , respectively. The V_0 can be obtained from the following relation using critical temperature T_C :

$$V_0 = V_T \left(1 - \frac{T}{T_C} \right)^{0.3} \quad (7)$$

The critical temperature, T_C is the mole fraction additive of the values of its pure components and is given by the relation:

$$T_C = x_1 T_{C(1)} + x_2 T_{C(2)} \quad (8)$$

The thermodynamic intermolecular free lengths, L_f , in the binary liquid mixtures have been calculated using the relation:

$$L_f = 2 \left[\frac{V_T - \{x_1 V_{0(1)} + x_2 V_{0(2)}\}}{(x_1 V_1 + x_2 V_2)} \right] \quad (9)$$

The ultrasonic intermolecular free lengths L_f , have also been computed using the Schaaff's relation for available volume (V_a):

$$V_a = V_T \left[1 - \frac{u}{u_\infty} \right] \quad (10)$$

Where, u is the ultrasonic velocity at temperature T and u_∞ is 1600 m.s^{-1} .

Schaaff's Collision Factor Theory (CFT)³⁵⁻³⁶

$$u_{mix} = u_\infty (x_1 s_1 + x_2 s_2) \frac{[x_1 b_1 + x_2 b_2]}{V_{mix}} \quad (11)$$

Where, b and s are the geometric volume and collision factor, respectively. The actual volume of the molecule per mole of the liquid has been computed using the relations

$$b = \frac{4}{3} \pi r^3 N \quad (12)$$

Where, r is the molecular radius which has been computed using the Schaaff's relation³⁶

$$r = \left(\frac{M}{\rho N} \right)^{1/3} \left[\frac{3}{16\pi} \left[1 - \frac{\gamma RT}{Mu^2} \left(\sqrt{1 + \frac{Mu^2}{3\gamma RT}} - 1 \right) \right] \right]^{1/3} \quad (13)$$

$$b' = \left[\frac{M}{\rho} - \frac{\gamma RT}{\rho u^2} \left(\left(1 + \frac{Mu^2}{3\gamma RT} \right)^{1/2} - 1 \right) \right] \quad (14)$$

$$r = \left(\frac{3b'}{16\pi N} \right)^{1/3} \quad (15)$$

Where, b' is the Vander Waals constant and is equal to four times the actual volume of the molecules per mole of the liquid, i.e. $b' = 4b$.

The thermoacoustical method [37-39] has also been employed to obtain the available volume, V_a using the relation

$$V_a = V_T \left(\frac{1}{K' + 1} \right) = V_T \left(\frac{1}{K'' + K' + 1} \right) \quad (16)$$

The K' , K , and K'' are known as isothermal, isobaric and isochoric acoustical parameters, respectively, and can be expressed by the relation

$$K' = K + K'' = \frac{1}{2} \left[3 + \frac{S^* (1 + \alpha T) + X}{\alpha T} \right] \quad (17)$$

$$K'' = 1 + \frac{X}{2\alpha T} \quad (18)$$

$$K = \frac{1}{2} \left[1 + \frac{S^* (1 + \alpha T)}{\alpha T} \right] \quad (19)$$

$$S^* = 1 + \frac{4\alpha T}{3} \quad (20)$$

The X is known as the isobaric temperature coefficient of internal pressure and can be expressed as

$$X = 2 \frac{(1 + 2\alpha T)}{\tilde{V}^{C_1}} \quad (21)$$

Where \tilde{V} represents the reduced molar volume and C_1 is the Moelwyn-Hughes parameter and can be expressed as

$$\tilde{V} = \left[\frac{\alpha T / 3}{1 + \alpha T} + 1 \right]^3 \quad (22)$$

$$C_1 = \frac{13}{3} + \frac{1}{\alpha T} \frac{4\alpha T}{3} \quad (23)$$

The thermal expansion coefficient, α , has been calculated using the equation:

$$\alpha = \left(\frac{1}{\rho} \right) \left(\frac{\partial \rho}{\partial T} \right)_P \quad (24)$$

The isentropic compressibility have been calculated from Newton-Laplace's equation:

$$k_s = \frac{1}{\rho u^2} \quad (25)$$

The excess isentropic compressibility was found out by using the relation,

$$k_s^E = k_s - k_s^{id} \quad (26)$$

Where, k_s^{id} the isentropic compressibility for the ideal mixture, was obtained according to Benson and Kiyohara⁴⁰ and Acree⁴¹:

$$k_s^{id} = \sum_i \phi_i \left[k_{s,i} + \frac{TV_i \alpha_i^2}{C_{p,i}} \right] - T \left(\sum_i x_i V_i \right) \frac{\left(\sum_i \phi_i \alpha_i \right)^2}{\left(\sum_i x_i C_{p,i} \right)} \quad (27)$$

Where, ϕ_i is the volume fraction of component i in the mixture, x_i is the corresponding mole fraction, T is the absolute temperature, and $k_{s,i}$, V , α_i and $C_{p,i}$ are the isentropic compressibility, the molar volume, the cubic expansion coefficient, and the molar heat capacity of pure components respectively. The cubic expansion coefficients were obtained from experimental density measurements performed in our laboratory at different temperatures.

The excess isentropic compressibility of the binary mixtures were fitted with a Redlich-Kister polynomial equation⁴²:

$$k_s^E = x_1 x_2 \sum_{j=0}^n A_j (x_1 - x_2)^j \quad (28)$$

Where, A_j are the adjustable parameters.

Oswal⁴³ extended the Prigogine-Flory-Patterson (PFP) theory to estimate the isentropic compressibilities and speeds of

sound of liquid mixtures. At a given temperature, T , the PFP theory can be used to calculate the molar volumes, V and the molar heat capacities, C_p , of a liquid mixture if the interaction parameter, χ_{12} , is known.

The term $\left(\frac{\partial V}{\partial T} \right)_P$ and $\left(\frac{\partial V}{\partial P} \right)_T$ can also be calculated by means of following equations:

$$\left(\frac{\partial V}{\partial P} \right)_T = \frac{-V^{\frac{7}{3}} + 2V^2 - 2V^{\frac{5}{2}}}{\left(\frac{4}{3} \right) - V^{\frac{1}{3}}} \cdot \frac{V^* T^*}{P^* T} \quad (29)$$

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{V \left(V^{\frac{1}{3}} - 1 \right)}{\left(\frac{4}{3} \right) - V^{\frac{1}{3}}} \cdot \frac{V^*}{T} \quad (30)$$

Where, V^* , P^* and T^* are the characteristic volume, pressure and temperature of the mixture, respectively and V is the corresponding reduced volume. From these quantities the isentropic compressibility,

$$k_s = -V^{-1} \left(\frac{\partial V}{\partial P} \right)_s \quad (31)$$

can be calculated using the following thermodynamic relation:

$$\left(\frac{\partial V}{\partial P} \right)_s = \left(\frac{\partial V}{\partial P} \right)_T + T C_p^{-1} \left(\frac{\partial V}{\partial T} \right)_P^2 \quad (32)$$

and finally the isentropic compressibility is related to the speed of sound u , by the Newton-Laplace equation,

$$k_s = \frac{1}{\rho u^2} \quad (33)$$

Isothermal compressibilities, k_T , were calculated from thermal expansion coefficients, experimental isentropic compressibilities and molar heat capacities.

Inter molecular free length and relative association has been calculated by the following formula:

$$L_f = K (K_s)^{1/2}$$

$$R_A = \frac{\rho}{\rho_0} \left(\frac{u_0}{u} \right)^{1/3}$$

Where ρ_0 and u_0 are the densities and ultrasonic speed of pure solvent, ρ and u are the density and ultrasonic speed of mixture respectively and K is the temperature dependent Jacobson constant (6.0816×10^4 at 35°C).

The deviation parameters of binary liquid mixtures have been evaluated using the general equation:

$$\Delta Y = Y_{\max} - (X_1 Y_1 + X_2 Y_2)$$

Where, Y indicates the parameter such as isentropic compressibility, inter molecular free length and ultra sonic speed: X_1 and X_2 are the mole fraction of component 1 and 2 respectively. ΔY , Y_1 , Y_2 , and Y_{\max} are the deviation parameter, parameters of the component 1 and 2 and observed parameters respectively.

The number of contact sites per segment of a molecule, has been estimated using Bondi's method⁴⁴. Molecular interaction parameter for each binary mixture was obtained by fitting the PFP theory to the

corresponding experimental equimolar H^E values⁴⁵⁻⁴⁶. Once the interaction parameter is obtained, the isentropic compressibility and the speed of sound can be estimated.

Physical properties of pure substance like density, ultrasonic speed at 308.15K are shown in Table 1. Speeds of sound, u , density, isentropic compressibility, k_s , and deviation in speed of sound of binary mixtures of benzene in DMSO over the different composition range at a temperature of 308.15K are reported in Table 2. Values of isentropic compressibilities, ΔK_s , intermolecular free length, L_f , and relative association, R_a , of the binary liquid mixtures of benzene in DMSO at 308.15K are shown in Table 3. Table 4 shows excess molar volumes of the binary liquid of DMSO with benzene at 308.15K. Table 5 shows Intermolecular Free Length, L_f , calculated from free length theory (FLT), Collision Factor Theory (CFT), and Thermoacoustic Approach (TAP) for benzene (1) + DMSO (2) binary mixture at 308.15K. Table 6 shows available volume, V_a , calculated from Free Length Theory (FLT), Collision Factor Theory (CFT), and Thermoacoustic Approach (TAP) for Benzene (1) + DMSO (2) binary mixture at 308.15K.

The values of the coefficients of Redlich-Kister polynomial equation for all the binary mixtures along with values of the standard deviation are represented in Table 7 for benzene in DMSO binary liquid mixtures at 308.15K. Flory parameters^{47, 48} of the pure compounds along with their physical properties are given in Table 8 for benzene in DMSO binary liquid mixtures at 308.15K. Table 9 gives the estimated and experimental equimolar, u and k_s , values along with the

interaction parameter, χ_{12} , for benzene in DMSO binary liquid mixtures at 308.15K. Estimated values for speeds of sound and isentropic compressibility are almost identical to experimental results for benzene mixtures. Table 10 gives theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's and Van Dael and Vangeel's ideal mixing relation and percentage error in calculated values for DMSO + Benzene at 308.15K.

DISCUSSION

All the systems of DMSO with benzene shows negative deviation through ΔK_s isotherms over entire range of mole fraction (Figure 1). A clear minima at the mole fraction around $x_1 = 0.4$, indicates that the maximum interactions are at that this mole fraction range. From Table 2 & 3, it is observed that Δu values are positive while, ΔK_s values are negative, such trends of positive deviation in a speed of sound and negative deviation in isentropic compressibility is quite common⁴⁹⁻⁵².

In pure DMSO, there is dipole-dipole as well as the usual dispersive interaction. The effect of adding a non polar second component is primarily to disrupt the dipolar interaction of the first component, but when the second component is also polar, the dipole-dipole interaction between unlike molecule is most likely which result in contraction of volume and the mixture becomes the less compressible⁵³⁻⁵⁴.

The behavior of binary liquid mixtures can be explained in term of 1) physical forces - dispersion 2) chemical forces - dipole-dipole interaction. The former factor increases the intermolecular free length as described by Jacobson⁵⁴. This is turn, causes negative

deviation in sound speed and positive deviation in compressibility. On the other hand, the latter factor decreases the intermolecular path lengths leading to a positive deviation in sound speed and negative deviation in compressibility and excess molar volume, V_m^E . The actual values depend upon the relative strength of two opposing effects. The observed negative values of ΔK_s and excess molar volume (Table 4) and positive values of Δu for these mixtures imply that the specific interaction dominate over the dispersive interaction between unlike molecules. From Table 5, the negative value of deviation in the molecular free length parameter substantive the above argument undoubtedly and undeniably unveils the fact the specific interaction are being operative between the molecules of solvent and co-solvents in the mixture.

Since, V_m^E is a packing effect and H_m^E is an interactional effect between the A and B constituents of an (A+B) mixture and as V_m^E data of the DMSO + benzene binary mixtures are negative throughout the composition range of DMSO, this suggests that as compared to the dispersion forces, negative value of V_m^E in general, always cause more compact packing of the molecules due to stronger dipole-dipole chemical interaction between the two unlike organic molecules. Their respective contribution to the measured data is a function of the mole fraction of DMSO.

The conclusion is further fortified by the increasing value of relative association, R_A included in Table 3. All the trends of the above parameters indicate that the mixtures are less compressible than their corresponding ideal mixtures. Generally, the deviation parameter is

considered to be the reflecting agents of the magnitude of polarity at the site of interaction in the molecules⁵⁵.

The intermolecular free length, L_f , can be related to the space filling ability assuming that the molecules are incompressible hard spheres having uniform radius. The intermolecular free length, L_f , obtained using free length theory (FLT) for the (DMSO + benzene) decreases with the increase in mole fraction of DMSO (Table 5). However, the L_f value obtained from Schaaf's collision factor theory (CFT) increases with the increase in the mole fraction of DMSO. The change in the slope of the isotherms of L_f as a function of mole fraction in the higher mole fraction region predicted by FLT and CFT shows that the entropy effect related to the structural rearrangement of solvent molecules due to disruption of dipole-dipole interactions between like polar molecules. However, the thermoacoustic approach (TAP) predicts that the L_f values in these binary mixtures decrease with increase in the mole fraction of DMSO. The L_f values for these binary mixtures obtained from the ultrasonic methods are higher than those obtained from the free length theory and the thermoacoustical approach.

The available volume, V_a , obtained using Free Length Theory (FLT) for the (DMSO + benzene) decreases with the increase in mole fraction of DMSO (Table 6). However, the V_a value obtained from Schaaf's Collision

Factor Theory (CFT) increases with the increase in the mole fraction of DMSO. The change in the slope of the isotherms of available volume as a function of mole fraction in the higher mole fraction region predicted by FLT and CFT shows that the entropy effect related to the structural rearrangement of solvent molecules due to stronger dipole-dipole interactions between unlike molecules of benzene in DMSO. However, the thermoacoustic approach (TAP) predicts that the V_a values in these binary mixtures decrease with increase in the mole fraction of DMSO.

The study of standard deviations, $\sigma^{(k, \epsilon)}$, presented in Table 7, reveals that the results of ultrasonic velocity for DMSO with benzene systems can be satisfactorily explained by Van Deal Ideal Mixture relation (minimum < 0.1). However, the prediction of these results is better for the DMSO with benzene system by the CFT formulation.

Stronger dipolar interaction between unlike molecules is also justified by the values of interaction parameters (Table 9). Values of interaction parameters are low for Benzene in DMSO which suggest dipole-induced dipole interaction between the DMSO and Benzene. Theoretical values of ultrasonic speed calculated from FLT theory shows large percentage error in DMSO with benzene binary liquid mixtures at 308.15K (Table 10). Theoretical values of ultrasonic speed calculated from Nomoto's and Van Dael and Vangeel's ideal mixing relations are almost identical. These relations show minimum percentage error in theoretical ultrasonic speed.

Table 1. Comparison of experimental densities, ρ of pure liquids with literature values at 298.15K, ultrasonic speed, u and molar volume, V^0 at 308.15K.

Components	ρ (g cm ⁻³)		u (m s ⁻¹)		V^0 (cm ³ mol ⁻¹) at 308.15K [58]
	Expt.	Lit.	Expt.	Lit.	
Benzene	0.8791	0.8762[56]	1292	1290	120.9
DMSO	1.092	1.090 [57]	1487#	1483# [57]	66.5

value at 298.15K

Table 2. Values of density, ρ speed of sound and derivation in speed, Δu of sound of binary liquid mixtures at 308.15K.

Mole Fraction (x_1)	ρ (g cm ⁻³)	u (m s ⁻¹)	Δu (m s ⁻¹)
Benzene (2) + DMSO (1)			
0.0000	0.8791	1487.00	0.000
0.0481	0.8123	1169.00	09.59
0.1223	0.8333	1191.00	14.84
0.1867	0.8631	1222.00	21.50
0.2863	0.8869	1250.00	26.18
0.3854	0.9181	1298.00	31.23
0.4647	0.9338	1318.00	31.74
0.5785	0.9559	1341.00	28.13
0.6821	0.9768	1380.00	21.35
0.7895	0.9918	1405.00	16.18
1.0000	1.0920	1487.00	0.000

Table 3. Values of deviation in isentropic compressibility ΔK_s , intermolecular free length, ΔL_f and relative association (R_A) of sound of binary liquid mixture at 308.15K.

Mole Fraction (x_1)	$-\Delta K_s$ (10^{-11} Pa $^{-1}$)	$-\Delta L_f$ (10^{-11} m)	(R_A)
Benzene (2) + DMSO (1)			
0.0000	00.00	0.0000	-
0.0582	04.46	1.4311	1.0270
0.1109	07.28	2.2679	1.0473
0.1957	10.13	3.2024	1.0752
0.2736	11.60	3.7180	1.0964
0.3939	12.34	4.0415	1.1230
0.4591	12.04	3.9785	1.1352
0.5681	10.59	3.5272	1.1534
0.6945	08.11	2.7205	1.1713
0.7954	05.79	1.9350	1.1827
1.0000	00.00	0.0000	-

Table 4. Excess molar volumes, V_m^E of the binary liquid mixtures at 308.15 K.

x_1	$-V_m^E$ (cm 3 mol $^{-1}$)	x_1	$-V_m^E$ (cm 3 mol $^{-1}$)
Benzene (1) + DMSO (2)			
0.0992	0.075	0.6012	0.110
0.2001	0.120	0.6656	0.095
0.2302	0.130	0.7304	0.075
0.3102	0.145	0.8054	0.055
0.3912	0.146	0.8659	0.040
0.4509	0.140	0.9112	0.025
0.5358	0.125		

Table 5. Intermolecular Free Length ($-L_f$), calculated from Free Length Theory (FLT), Collision Factor Theory (CFT), and Thermoacoustic Approach (TAP) for binary mixtures at 308.15K.

x_1	$-L_f(FLT)/nm$	$-L_f(CFT)/nm$	$-L_f(TAP)$
DMSO (1) + Benzene (2)			
0.0502	0.0552	0.0615	0.0610
0.0999	0.0552	0.0654	0.0608
0.1953	0.0551	0.0680	0.0608
0.2899	0.0551	0.0731	0.0606
0.3996	0.0550	0.0791	0.0602
0.5017	0.0550	0.0833	0.0600
0.6007	0.0548	0.0903	0.0594
0.6990	0.0547	0.0922	0.0592
0.7956	0.0544	0.0971	0.0585
0.8994	0.0541	0.1001	0.0579
0.9446	0.0537	0.1021	0.0572

Table 6. Available Volume, V_a , calculated from Free Length Theory (FLT), Collision Factor Theory (CFT), and Thermoacoustic Approach (TAP) for binary mixtures at 308.15K.

x_1	$V_a \cdot 10^6(FLT)/(m^3 \cdot mol^{-1})$	$V_a \cdot 10^6(CFT)/(m^3 \cdot mol^{-1})$	$V_a \cdot 10^6(TAP)/(m^3 \cdot mol^{-1})$
DMSO (1) + Benzene (2)			
0.0682	24.4432	28.9804	26.9430
0.1276	24.2861	29.9410	26.7320
0.2056	23.9473	31.7431	26.2814
0.2686	23.4721	33.7101	25.6754
0.3892	23.0940	35.0104	25.1804
0.4277	22.3420	36.8421	24.2196
0.5444	22.0911	37.2440	23.8980
0.6405	21.3423	38.0840	22.9370
0.7326	20.7030	38.2613	22.1306
0.8519	20.0731	38.0721	21.3434
0.9273	19.2309	37.2609	20.3014

Table 7. Values of Parameters A_j of the Redlich-Kister equation and corresponding standard deviations, $\sigma(k_s^E)$ for the binary systems at 308.15K.

A_0	A_1	A_2	A_3	$\sigma(k_s^E) (T Pa^{-1})$
DMSO (1) + Benzene (2)				
77.5	-38.20	9.20	-13.90	0.10

Table 8. Physical properties reduced molar volume \tilde{V} , critical pressure P^* and Flory parameters isothermal compressibility, k_T collision factor, s of the pure compounds at 308.15K.

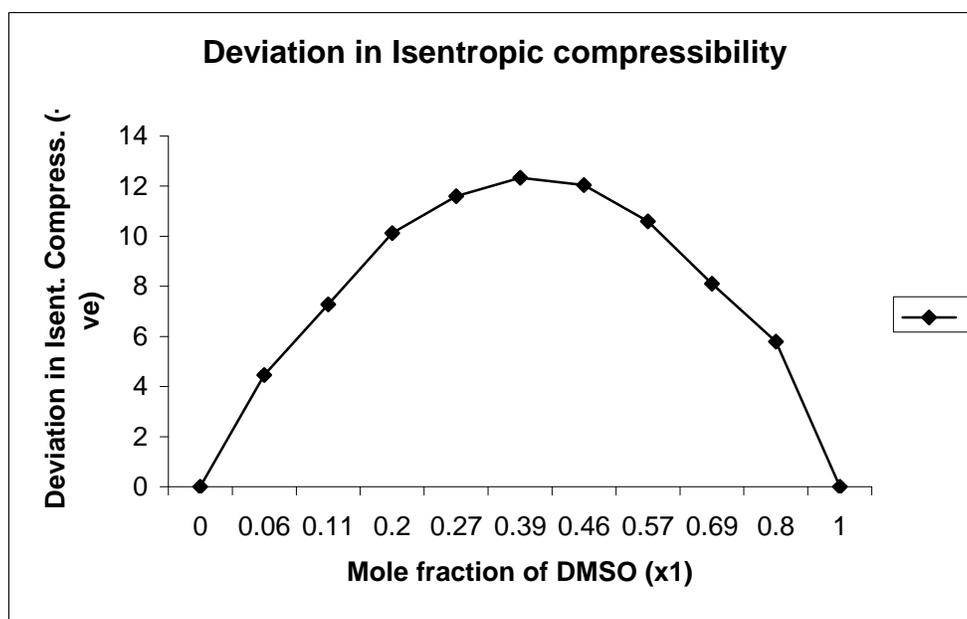
Compound	$k_T (T Pa^{-1})$	\tilde{V}	$P^* (J cm^{-3})$	$s (A^{\circ-1})$
DMSO	743.1	1.27	697.9	1.25
Benzene	1126.5	1.29	533.8	1.25

Table 9. Interaction Parameters, χ_{12} , calculated and experimental equimolar speed of sound, and isentropic compressibilities, k_s , of the binary systems at 308.15K.

$\chi_{12} (J cm^{-3})$	$u_{cal} (m s^{-1})$	$u_{expt} (m s^{-1})$	$k_s (T Pa^{-1})$	$k_{s,exp} (T Pa^{-1})$
DMSO + benzene				
81.1	1279.00	1255.20	14.37	14.46

Table 10. Theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's (NOM) and Van Dael and Vangeel's ideal mixing relation (VD) and percentage error in calculated values for DMSO (2) + benzene (1) at 308.15K.

x_1	u ($m s^{-1}$)				% error			
	FLT	CFT	NOM	VD	FLT	CFT	NOM	VD
0.0000	1146.0	1146.0	1146.0	1146.0	0.00	0.00	0.00	0.00
0.1150	1171.6	1173.9	1173.0	1173.2	2.28	0.48	0.12	0.09
0.2262	1190.3	1193.3	1194.1	1194.4	4.18	0.82	0.10	0.05
0.3338	1220.8	1225.4	1226.1	1226.0	5.30	0.93	0.06	0.00
0.4380	1249.6	1254.9	1254.0	1254.2	5.76	0.86	0.00	0.08
0.5390	1288.8	1294.3	1295.2	1294.0	6.04	0.80	0.10	0.18
0.6368	1310.3	1313.4	1315.3	1315.6	5.91	0.71	0.15	0.22
0.7317	1340.8	1344.9	1344.4	1344.5	4.86	0.42	0.19	0.25
0.8238	1371.1	1375.8	1375.4	1375.6	3.79	0.28	0.18	0.23
0.9132	1403.3	1401.4	1401.3	1401.4	2.57	0.19	0.17	0.19
1.0000	1445.0	1445.0	1445.0	1445.0	0.00	0.00	0.00	0.00

**Figure 1. Deviation in isentropic compressibility ($-\Delta K_s$) with the mole fraction of DMSO.**

CONCLUSION

Density (ρ), ultrasonic velocity (u) and excess molar volume (V_m^E) of binary mixtures of benzene in DMSO have been measured over the entire range of composition and at 308.15K. From these experimental results, parameters such as deviation in isentropic compressibility ΔK_s , interaction parameter χ_{12} , Flory parameters, Coefficients A_i , standard deviations $\sigma(Y^E)$ and molar sound velocity R_m have been estimated. The excess functions have been fitted to the Redlich-Kister polynomial equations. The experimental ultrasonic velocities have been analyzed in terms of Nomoto's relation, Van Dael's ideal mixture relation, Jacobson free length theory and Schaaff's collision factor theory. Intermolecular free length, L_f , and available volume, V_a , have been calculated from Jacobson free length theory, Schaaff's collision factor theory, and thermoacoustic approach for binary systems of benzene in DMSO at 308.15K. The observed negative values of ΔK_s and excess molar volume V_m^E and positive values of Δu for these mixtures imply that the specific chemical dipole-induced dipole interactions dominate over the physical dispersive interaction between unlike molecules.

ACKNOWLEDGEMENTS

Authors are grateful to the Ch. Devi Lal University, Sirsa authorities for providing the necessary infrastructural facilities to carry out the research work.

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