

## A Study of Some Excess Thermodynamic Properties in Binary Mixtures of Non-Aqueous Solvents at Variable Temperatures

V. Pathania<sup>a</sup>, S. Sharma<sup>a,\*</sup>, B.K. Vermani<sup>a</sup> and D.S. Gill<sup>b</sup>

<sup>a</sup>Department of Chemistry, D.A.V. College, Chandigarh-160011, India

<sup>b</sup>Department of Chemistry, Panjab University, Chandigarh-160014, India

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Excess thermodynamic properties, such as viscosity deviation ( $\ln\Delta\eta$ ), excess isentropic compressibility ( $K_s^E$ ), excess molar volume ( $V_m^E$ ), excess intermolecular free length ( $L_f^E$ ), excess free volume ( $V_f^E$ ), excess acoustic impedance ( $Z^E$ ), and excess internal pressure ( $\Pi_i^E$ ), were calculated from the experimentally measured values of density ( $\rho$ ), ultrasonic velocity ( $u$ ), and viscosity ( $\eta$ ) for the binary mixtures of acetonitrile (AN) with dimethyl sulfoxide (DMSO) and N, N-dimethylacetamide (DMA) as a function of mole fraction at temperatures 298 K, 308 K, 318 K, and 328 K. The excess values were further fitted to Redlich-Kister polynomial equation to ascertain the fitting parameters and standard deviations. The variations of excess parameters with composition and temperature were further discussed with regard to the nature and extent of molecular interactions among the dissimilar component molecules of the investigated solvent systems. The analysis of these excess parameters revealed the presence of strong interactions between the components of the investigated binary mixtures. Overall, the positive deviation in  $Z^E$  values and negative deviations in  $L_f^E$ ,  $V_f^E$ , and  $K_s^E$  values over the entire solvent composition range suggested the existence of strong molecular interactions between dissimilar molecules of the components. Compared to AN-DMSO solvent system, the AN-DMA solvent system exhibited more deviation towards a stronger interaction mode.

**Keywords:** Intermolecular free length, Impedance, Molar volume, Free volume, Viscosity

### INTRODUCTION

The transport and thermodynamic properties of non-aqueous binary solvent mixtures have gained a lot of attention due to their potential engineering, industrial, and theoretical applications. Numerous engineering applications demand detailed experimental measurements on density, ultrasonic velocity and viscosity of binary solvent mixtures [1]. They also provide some facts regarding the nature of various intermolecular interactions occurring among unlike components of binary liquid mixtures. The binary mixtures of solvents are preferable to the pure solvents and have many industrial applications because mixing different solvents sets out some flexibility in the solution by changing the composition of solvents, thereby enhancing the

properties of binary solvent mixtures [2]. Also, by mixing different solvents, some degree of freedom is introduced in the solution that leads to different processes, such as complex formation, association, dissociation, *etc.* Mixed solvent systems are generally utilized to alter molecular environments so as to acclimate processes such as solvent extraction, protein folding, chromatographic separation, reaction kinetics, ion-extraction systems, gas adsorption solvents, mass transfer phenomenon, and organic synthesis. A survey of the literature indicated that the excess thermo-acoustical parameters, which play a very important role in elucidating the nature and type of various molecular interactions prevailing in the liquid mixtures, had been studied by a number of researchers [3-10]. The excess thermo-acoustical parameters are defined as the difference between the experimental values and ideal mixture values. They are the measures of non-ideality of the system arising

\*Corresponding author. E-mail: shrutilasharma@gmail.com

from associative or other interactions. Although a significant number of recent studies on excess parameters in various liquid mixtures with variation in composition and temperature are available [11-16], a lot more remains to be explored. The solvents chosen in the present work included AN, DMSO and DMA, where AN is primary or the main solvent and DMSO and DMA are co-solvents. AN is an excellent polar aprotic solvent [17] with high dipole moment ( $D_{AN} = 3.4$ ) and dielectric constant ( $\epsilon_{AN} = 36.0$ ) [18]. DMSO, in comparison, is a superior dipolar aprotic solvent with a higher dielectric constant and dipole moment ( $\epsilon_{DMSO} = 46.7$ ,  $D_{DMSO} = 3.9$ ) [18]. Due to its low toxicity [19] and excellent solvating ability for a vast array of compounds, DMSO would be of great interest to extend the investigation to the binary mixtures of AN and DMSO. Even though AN and DMSO have drawn much attention as solvents in solvation studies, still more studies on various types of molecular interactions in their binary mixtures are needed. DMA is an excellent ionizing solvent with more favorable steric and donor properties. Its dielectric constant is also high ( $\epsilon_{DMA} = 37.8$ ) [20]. Therefore, the binary mixtures of AN and DMA can help us gain a deeper understanding of the molecular interactions taking place in them. For this purpose, this study aimed to investigate the mutual and specific interactions in the binary mixtures of AN+DMSO and AN+DMA solvent mixtures. The main focus of this study was to evaluate the effects of the introduction of DMSO and DMA to AN to form the binary mixtures of AN+DMSO and AN+DMA, respectively, on both the sign and magnitude of the derived excess/deviation parameters.

## EXPERIMENTAL

The mass fraction purity of the liquids obtained from E. Merck (gas chromatography) was as follows: Acetonitrile (0.999), dimethylsulfoxide (0.999), and N, N-dimethylacetamide (0.999). The water content in the investigated solvents, including AN, DMSO, and DMA, was assessed by Karl Fischer titrations and found to be 0.00030, 0.00020, and 0.00009, respectively. The purification of solvents was done by the standard methods described in previous studies [21-24]. After purification, the solvents AN and DMSO were kept for drying for around 72 h over 4 Å molecular

sieves while 3 Å molecular sieves were used for drying DMA. Before taking experimental measurements, all the purified solvents were partially degassed with a vacuum pump. Ultrasonic velocity and densities were measured with the help of vibrating U-tube Anton Paar digital density and sound velocity meter (Model DSA 5000M) with an inbuilt Peltier type thermostat. Viscosities were measured with an Ubbelohde suspended level viscometer. Before the start of each series of measurements, the DSA cell and the Ubbelohde viscometer were cleaned and calibrated. The specification and calibration of both instruments used have already been reported in our previous studies [20,25-26]. Each studied binary mixture was prepared by mixing the suitable volumes of liquids. To avoid absorption of atmospheric moisture, the solutions were kept in airtight stoppered glass bottles and weighed using an ACZET-602CY balance with a precision of 0.1 mg. In order to prevent the formation of gas bubbles in the densimeter capillary at higher temperatures, the samples were degassed for 30 min. A thermostatic water bath (Narang Scientific works, New Delhi, India) was used for maintaining the desired temperature ( $\pm 0.01$ ) K in viscosity measurements.

## RESULTS AND DISCUSSION

The experimentally measured density ( $\rho$ ), ultrasonic velocity ( $u$ ), and viscosity ( $\eta$ ) for pure AN, DMSO, DMA, and their binary mixtures containing a mole fraction of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 of DMSO and DMA in AN+DMSO and AN+DMA solvent systems, respectively, at 298 K, 308 K, 318 K, and 328 K are reported in Tables S1-S2. The derived parameters, such as isentropic compressibility ( $K_s$ ), molar volume ( $V_m$ ), intermolecular free length ( $L_f$ ), free volume ( $V_f$ ), acoustic impedance ( $Z$ ), and internal pressure ( $\Pi_i$ ) were evaluated using the following equations [26] (Tables S1-S2).

Isentropic compressibility is the fractional decrease of volume per unit rise of pressure when there is no transfer of heat in or out of the system. These changes can be coupled to the compressibility of the medium with the help of the following equation using the measured data related to ultrasonic velocity and density.

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

### Isentropic Compressibility

The intermolecular free length ( $L_f$ ) is an important physical property of liquid mixtures that mainly affects the sound velocity and depends on intermolecular attractive and repulsive forces. Free length is a reflected behavior of isentropic compressibility ( $K_s$ ) and an important indicator of various solute-solute or solute-solvent interactions taking place in the system.  $L_f$  was calculated using Eq. (2).

$$L_f = k_J \sqrt{K_s} \quad (2)$$

where  $k_J$  is a temperature-dependent constant called Jacobson's constant, which can be calculated by the equation  $k_J = (91.368 + 0.3565T) \times 10^{-8}$ , where T is the experimental temperature.

Specific acoustic impedance (Z), which is the resistance offered to the sound wave by various components present in the mixture, was calculated by Eq. (3).

$$Z = \rho u \quad (3)$$

### Molar Volume

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho} = \frac{M_{eff}}{\rho} \quad (4)$$

where  $x_1$ ,  $x_2$  and  $M_1$ ,  $M_2$  are the mole fractions and molar masses of solvents 1 and 2, respectively.

Free volume ( $V_f$ ), which is the average volume in which the center of the molecule can move due to repulsion from other molecules, was calculated using Eq. (5).

$$V_f = (V_m - b) \quad (5)$$

Van der Waals constant (b), called co-volume in the van der Waal's equation, was calculated by Eq. (6).

$$(b) = V_m \left[ 1 - \left( \frac{RT}{M_{eff}} \right) \left\{ \sqrt{1 + \left( \frac{(M_{eff})^2 u^2}{3RT} \right)} - 1 \right\} \right] \quad (6)$$

Intermolecular forces are responsible for providing a liquid its cohesion. The attractive forces to a large extent consist of hydrogen bonding, multipolar, dipole-dipole, and dispersive

interactions. Repulsive forces, which adhere to very small intermolecular distances, assume a subsidiary role in the cohesion process under normal conditions. Cohesion generates pressure between  $10^3$  and  $10^4$  atmospheres within a liquid. Mixing solvents together experience some of this pressure. In this study, the amount of pressure on the components of the investigated solvents increased whenever they interacted with each other through hydrogen bonding, coulombic or van der Waals, and charge-transfer interactions. Therefore, the binary mixtures of solvents were subjected to a 'structural pressure' from the solvent and a 'chemical pressure' from interactions with the solvent. This perception of internal pressure provides a solid foundation for exploring the solution phenomena. Internal pressure ( $\Pi$ ) was calculated using Eq. (7).

$$\Pi_i = b' RT \sqrt{\frac{k\eta}{u}} \cdot \frac{\rho^{\frac{2}{3}}}{M_{eff}^{\frac{7}{6}}} \quad (7)$$

where  $b'$  is the packing fraction of liquid, assumed to be equal to 2 for most of the liquids, and  $k$  is a dimensionless constant, assumed to be equal to  $4.28 \times 10^9$  and independent of temperature [27].

To elucidate the nature of various types of molecular interactions existing among the components of the binary mixtures of solvents, it is warranted to talk about the same in terms of their excess properties rather than their actual values. The aim of this paper was to estimate and discuss the excess parameters such as viscosity deviation ( $\ln\Delta\eta$ ), excess isentropic compressibility ( $K_s^E$ ), excess molar volume ( $V_m^E$ ), excess intermolecular free length ( $L_f^E$ ), excess free volume ( $V_f^E$ ), excess acoustic impedance ( $Z^E$ ), and excess internal pressure ( $\Pi_i^E$ ) to reveal the existence of intermolecular dipolar interactions in binary solvent mixtures of AN+DMSO and AN+DMA at 298 K, 308 K, 318 K, and 328K. The excess values of all derived parameters, including  $K_s^E$ ,  $V_m^E$ ,  $L_f^E$ ,  $V_f^E$ ,  $Z^E$  and  $\Pi_i^E$ , except  $\ln\Delta\eta$ , were obtained using the following equation [28].

$$Y^E = Y - (x_1 Y_1 + x_2 Y_2) \quad (8)$$

where  $Y^E$  is  $K_s^E$ ,  $V_m^E$ ,  $L_f^E$ ,  $V_f^E$ ,  $Z^E$ , and  $\Pi_i^E$ .

Viscosity deviations ( $\ln\Delta\eta$ ) were obtained from the

empirical relationship as shown below [29]:

$$\ln \Delta\eta = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \quad (9)$$

where  $\eta$  is the viscosity of the mixtures, and  $x_1$ ,  $\eta_1$  and  $x_2$ ,  $\eta_2$  are the mole fraction and viscosity of pure components 1 and 2, respectively.

The evaluated excess functions, *viz.* viscosity deviation ( $\ln\Delta\eta$ ), excess isentropic compressibility ( $K_s^E$ ), excess molar volume ( $V_m^E$ ), excess intermolecular free length ( $L_f^E$ ), excess free volume ( $V_f^E$ ), acoustic impedance ( $Z$ ), and excess internal pressure ( $\Pi_i^E$ ), for AN+DMSO and for AN+DMA solvent mixtures at 298 K, 308 K, 318 K, and 328 K are reported in Tables 1 and 2, respectively.

**Table 1.** Excess Viscosity ( $\eta^E/\text{mPa s}$ ), Excess Isentropic Compressibility- $K_s^E \times 10^6/(\text{bar}^{-1})$ , Excess Specific Acoustic Impedance- $Z^E \times 10^{-6}/(\text{kg m}^{-2} \text{s}^{-1})$ , Excess Intermolecular Free length- $L_f^E \times 10^{11}/(\text{m})$ , Excess Free Volume- $10^3 \times V_f^E/(\text{m}^3 \text{mol}^{-1})$ , Excess Molar Volume- $10^3 \times V_m^E/(\text{m}^3 \text{mol}^{-1})$ , and Excess Internal Pressure- $\Pi_i \times 10^{-6}/(\text{N m}^{-2})$  for Pure AN, DMSO, and AN+DMSO Mixtures at Different Temperatures

Mole fraction DMSO	0.0	0.2	0.4	0.6	0.8	1.0
<b><math>\ln\Delta\eta</math></b>						
298 K	0	0.07	0.197	0.165	0.05	0
308 K	0	0.044	0.04	0.011	0.016	0
318 K	0	-0.042	-0.187	-0.266	-0.214	0
328 K	0	-0.116	-0.235	-0.356	-0.341	0
<b><math>K_s^E</math></b>						
298 K	0	-5.02	-5.38	-4.68	-3.08	0
308 K	0	-4.9	-6.41	-5.9	-3.19	0
318 K	0	-6.21	-7.88	-7.15	-3.97	0
328 K	0	-7.176	-9.082	-8.228	-4.584	0
<b><math>Z^E</math></b>						
298 K	0	0.016	0.017	0.02	0.011	0
308 K	0	0.0122	0.0184	0.0216	0.0058	0
318 K	0	0.0156	0.0222	0.0248	0.0094	0
328 K	0	0.0148	0.0216	0.0244	0.0092	0
<b><math>L_f^E</math></b>						
298 K	0	-0.154	-0.158	-0.139	-0.097	0
308 K	0	-0.139	-0.187	-0.178	-0.094	0
318 K	0	-0.174	-0.226	-0.212	-0.116	0
328 K	0	-0.194	-0.251	-0.236	-0.13	0
<b><math>V_f^E</math></b>						
298 K	0	-0.338	-0.416	-0.424	-0.282	0
308 K	0	-0.28	-0.45	-0.47	-0.28	0
318 K	0	-0.268	-0.426	-0.444	-0.252	0
328 K	0	-0.268	-0.416	-0.434	-0.252	0
<b><math>V_m^E</math></b>						
298 K	0	-0.534	0.012	0.108	-0.006	0
308 K	0	-0.154	-0.278	-0.312	0.084	0
318 K	0	-0.200	-0.330	-0.370	0.050	0
328 K	0	-0.236	-0.382	-0.418	0.016	0
<b><math>\Pi_i^E</math></b>						
298 K	0	6.29	37.03	29.02	-0.74	0
308 K	0	-2.5	-9.58	-17.79	-10.4	0
318 K	0	-25.63	-71.09	-93.42	-77.69	0
328 K	0	-42	-64.55	-106.6	-	0

**Table 2.** Excess Viscosity ( $\eta^E$ /mPa.s), Excess Isentropic Compressibility- $K_s^E \times 10^6$ /(bar<sup>-1</sup>), Excess Specific Acoustic Impedance- $Z^E \times 10^{-6}$ /(kg m<sup>-2</sup> s<sup>-1</sup>), Excess Intermolecular Free length- $L_f^E \times 10^{11}$ /(m), Excess Free Volume- $10^3 \times V_f^E$ /(m<sup>3</sup> mol<sup>-1</sup>), Excess Molar Volume- $10^3 \times V_m^E$ /(m<sup>3</sup> mol<sup>-1</sup>), and Excess Internal Pressure- $\Pi_i 10^{-6}$ /(Nm<sup>-2</sup>) for Pure AN, DMA, and AN+DMA Mixtures at Different Temperatures

Mole fraction DMSO	0.0	0.2	0.4	0.6	0.8	1.0
<b>lnΔη</b>						
298 K	0	0.103	0.118	0.109	0.131	0
308 K	0	0.064	0.099	0.112	0.144	0
318 K	0	0.066	0.029	0.047	0.123	0
328 K	0	-0.02	0.024	-0.059	0.055	0
<b>K<sub>s</sub><sup>E</sup></b>						
298 K	0	-3.748	-5.446	-4.404	-2.842	0
308 K	0	-4.104	-5.158	-5.642	-3.796	0
318 K	0	-5.092	-6.114	-6.476	-4.328	0
328 K	0	-5.584	-6.588	-6.832	-4.236	0
<b>Z<sup>E</sup></b>						
298 K	0	0.024	0.048	0.032	0.026	0
308 K	0	0.026	0.032	0.048	0.034	0
318 K	0	0.028	0.026	0.044	0.032	0
328 K	0	0.026	0.032	0.038	0.024	0
<b>L<sub>f</sub><sup>E</sup></b>						
298 K	0	-0.121	-0.183	-0.149	-0.099	0
308 K	0	-0.127	-0.163	-0.189	-0.134	0
318 K	0	-0.153	-0.185	-0.209	-0.146	0
328 K	0	-0.158	-0.188	-0.207	-0.133	0
<b>V<sub>f</sub><sup>E</sup></b>						
298 K	0	-0.852	-1.324	-1.326	-0.928	0
308 K	0	-0.83	-1.24	-1.31	-0.86	0
318 K	0	-0.796	-1.192	-1.268	-0.824	0
328 K	0	-0.802	-1.204	-1.286	-0.868	0
<b>V<sub>m</sub><sup>E</sup></b>						
298 K	0	-0.166	-0.402	-0.158	-0.244	0
308 K	0	-0.200	-0.030	-0.490	-0.340	0
318 K	0	-0.222	-0.024	-0.466	-0.288	0
328 K	0	-0.256	-0.062	-0.528	-0.354	0
<b>Π<sub>i</sub><sup>E</sup></b>						
298 K	0	-1.39	-8.61	-8.77	9.19	0
308 K	0	-12.24	-15.13	-8.81	9.8	0
318 K	0	-11.96	-31.3	-23.11	4.27	0
328 K	0	-31.3	-30.46	-42.3	-8.33	0

The dependence of excess parameters on the solvent composition was then fitted to the Redlich-Kister equation, as shown below, using the least square method [30].

$$Y^E = x_2(1 - x_2)[A_0 + A_1(2x_2 - 1) + A_2(2x_2 - 1)^2 + A_3(2x_2 - 1)^3] \quad (10)$$

where  $A_0$ ,  $A_1$ ,  $A_2$ , and  $A_3$  are the coefficients of the polynomial equation, and the corresponding standard deviations were obtained by the following equation [31]:

$$\sigma(Y)^E = \sqrt{\frac{\sum (Y_{obs}^E - Y_{cal}^E)^2}{n - m}} \quad (11)$$

where  $n$  is the total number of experimental points and  $m$  is the number of coefficients.

The values of coefficients in Eq. (10), along with their standard deviations, for AN-DMSO and AN-DMA (excluding  $\ln\Delta\eta^E$  and  $V_m^E$  coefficients in case of AN-DMA\*) solvent systems are presented in Tables 3 and 4,

respectively.

\*High standard error values, which indicate poor fit, were obtained using the Redlich-Kister equation when  $\ln\Delta\eta^E$  and  $V_m^E$  values were plotted against solvent composition in the AN-DMA system.

**Table 3.** Coefficients of the Redlich-Kister Equation and Standard Deviation ( $\sigma$ ) Values for Excess Viscosity ( $\eta^E/\text{mPa s}$ ), Excess Isentropic Compressibility- $K_s^E \times 10^6/(\text{bar}^{-1})$ , Excess Specific Acoustic Impedance- $Z^E \times 10^{-6}/(\text{kg m}^{-2} \text{s}^{-1})$ , Excess Intermolecular Free Length- $L_f^E \times 10^{11}/(\text{m})$ , Excess Free Volume- $10^3 \times V_f^E/(\text{m}^3 \text{mol}^{-1})$ , and Excess Internal Pressure- $\Pi_i \times 10^{-6}/(\text{N m}^{-2})$  for Pure AN-DMSO Solvent System at Different Temperatures

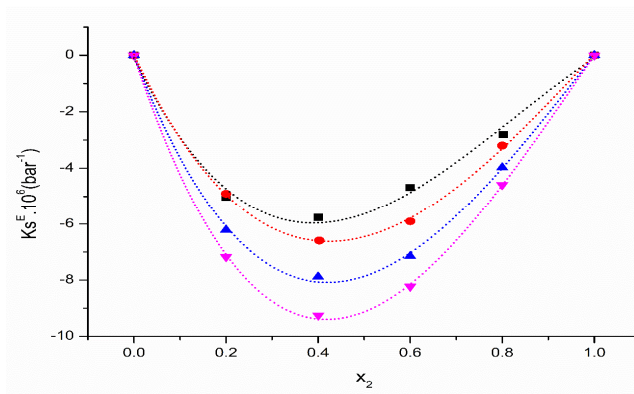
Temp (K)	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma$
$\ln\Delta\eta$					
298 K	0.6466	-0.0391	-0.0068	0.0396	0.0888
308 K	0.1321	-0.0499	0.0013	0.0500	0.0172
318 K	-0.9026	-0.2250	0.0028	0.2251	0.0351
328 K	-1.287	-0.3070	-0.0047	0.3067	0.0605
$K_s^E$					
298 K	-22.526	2.8459	-0.0960	-2.8461	1.2149
308 K	-25.802	2.1337	0.0248	-2.1269	0.4110
318 K	-31.453	2.7065	-0.0171	-2.6909	0.6308
328 K	-36.509	3.2285	-0.0115	-3.2177	0.4384
$Z^E$					
298 K	0.0791	-0.0044	0.0002	0.0042	0.0064
308 K	0.0771	-0.0046	-0.0008	0.0044	0.0109
318 K	0.0923	-0.0046	-0.0005	0.0045	0.0070
328 K	0.0886	-0.0047	-0.0006	0.0046	0.0084
$L_f^E$					
298 K	-0.6776	0.0651	-0.0029	-0.0652	0.0378
308 K	-0.7435	0.0547	0.0007	-0.0543	0.0249
318 K	-0.9108	0.0668	0.0002	-0.0663	0.0434
328 K	-1.0277	0.0785	0.0007	-0.0782	0.0354
$V_f^E$					
298 K	-1.7911	0.0399	-0.0049	-0.0388	0.0778
308 K	-1.8659	-0.0197	0.0034	0.0198	0.0432
318 K	-1.7373	0.0152	0.0054	-0.0148	0.0701
328 K	-1.7300	0.0068	0.0050	-0.0058	0.0749
$\Pi_i^E$					
298 K	103.82	-11.375	-1.8977	11.489	24.673
308 K	-51.942	-12.214	0.4902	12.331	7.685
318 K	-355.75	-69.079	1.3502	69.025	17.782
328 K	-405.37	-95.360	-1.5484	95.833	27.192
$V_m^E$					
298 K	-0.2589	0.6223	-0.0681	-0.6196	0.8811
308 K	-0.9745	0.2677	0.0376	-0.2661	0.4804
318 K	-1.1835	0.2546	0.0329	-0.2522	0.4291
328 K	-1.4128	0.2679	0.0322	-0.2649	0.4157

**Table 4.** Coefficients of the Redlich-Kister Equation and Standard Deviation ( $\sigma$ ) Values for Excess Isentropic Compressibility- $K_s^E \times 10^6/(\text{bar}^{-1})$ , Excess Specific Acoustic Impedance- $Z^E \times 10^{-6}/(\text{kg m}^{-2} \text{s}^{-1})$ , Excess Intermolecular Free Length- $L_f^E \times 10^{11}/(\text{m})$ , Excess Free Volume- $10^3 \times V_f^E/(\text{m}^3 \text{mol}^{-1})$ , and Excess Internal Pressure- $\Pi_i \times 10^{-6}/(\text{Nm}^{-2})$  for Pure AN-DMA Solvent System at Different Temperatures

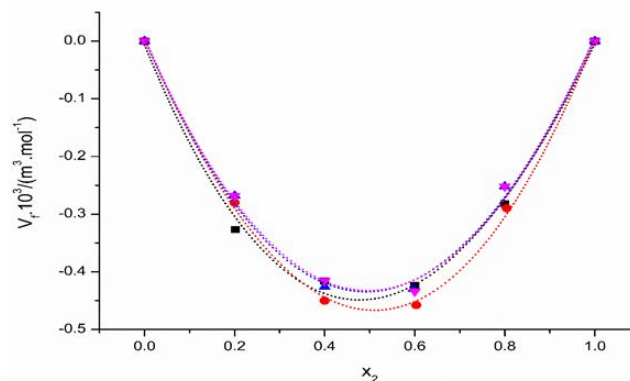
Temp (K)	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma$
$K_s^E$					
298 K	-20.083	1.3333	-0.0244	-1.3446	0.5298
308 K	-23.197	0.2924	-0.0711	-0.2844	0.9571
318 K	-27.439	0.7103	-0.0954	-0.6893	1.4597
328 K	-29.069	1.3793	-0.0766	-1.3517	1.4323
$Z^E$					
298 K	0.1656	-0.0045	0.0002	0.0046	0.0029
308 K	0.1733	0.0161	0.0003	-0.0163	0.0069
318 K	0.1609	0.0139	0.0004	-0.0141	0.0070
328 K	0.1483	0.0013	0.0008	-0.0014	0.0037
$L_f^E$					
298 K	-0.6912	0.0350	0.0002	-0.0356	0.0207
308 K	-0.7567	-0.0147	-0.0028	0.0152	0.0401
318 K	-0.8481	0.0275	-0.0029	-0.0271	0.0407
328 K	-1.0199	0.0757	0.0003	-0.0752	0.0192
$V_f^E$					
298 K	-5.5325	-0.0796	-0.0014	0.0781	0.0576
308 K	-5.3038	-0.0687	0.0011	0.0709	0.0846
318 K	-5.1075	-0.0699	0.0021	0.0723	0.0979
328 K	-5.1962	-0.1123	-0.0011	0.1143	0.0756
$\Pi_i^E$					
298 K	-19.102	9.9157	0.3140	-9.9127	4.009
308 K	-41.128	25.593	0.4194	-25.588	5.279
318 K	-99.616	28.050	0.5366	-27.995	7.149
328 K	-161.00	19.785	0.3720	-19.719	5.345

To understand the nature of AN+DMSO and AN+DMA solvent systems at different compositions and temperatures, the above calculated excess parameters were plotted as a function of the mole fraction of DMSO and DMA, respectively. The variation in all the investigated excess parameters as a function of the mole fraction of DMSO and DMA was found to be non-linear (Figs. S1-S4 and Figs. 1-10, respectively). Solvent structural effects, which are responsible for the non-linear variation in the solvent excess parameters with solvent composition, are said to be even stronger when a solvent excess parameter passes through a maximum or minimum.

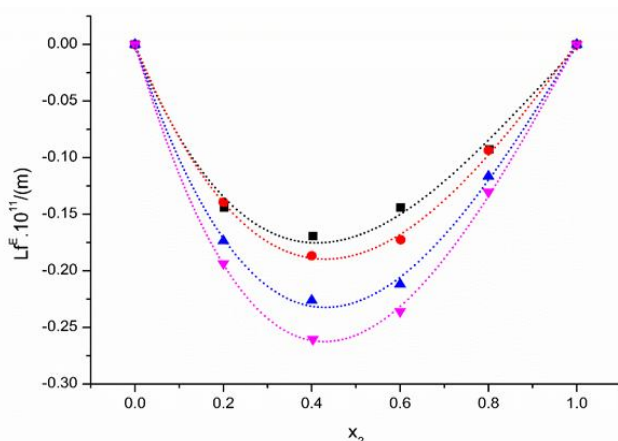
An examination of plots in Figs. 1-3 and 6-8 reveals that excess isentropic compressibility ( $K_s^E$ ), excess intermolecular free length ( $L_f^E$ ) and excess free volume ( $V_f^E$ ) are negative over the entire composition range for the binary mixtures of AN+DMSO and AN+DMA. In other words, excess functions  $K_s^E$ ,  $L_f^E$ , and  $V_f^E$  show negative deviations; that is, they increased negatively in magnitude, reaching broad minima at around 0.4-0.6 mole fraction of DMSO and DMA, respectively, and then further increased with the addition of DMSO and DMA. Negative values of these excess parameters led to much stronger interactions among the component molecules of the solvent.



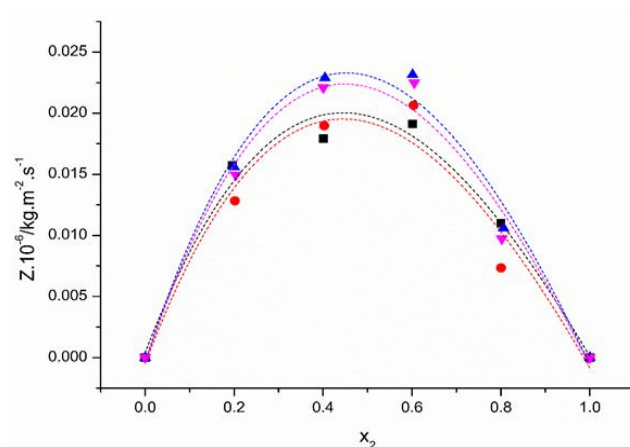
**Fig. 1.** Curves of excess isentropic compressibility ( $K_s^E$ ) versus the mole fraction for the binary mixture of AN+DMSO at different temperatures, including 298 K (black square), 308 K (red circle), 318 K (blue triangle), and 328 K (purple triangle).



**Fig. 3.** Curves of excess free volume ( $V_f^E$ ) versus the mole fraction for the binary mixture of AN+DMSO at different temperatures, including 298 K (black square), 308 K (red circle), 318 K (blue triangle), and 328 K (purple triangle).



**Fig. 2.** Curves of excess intermolecular free length ( $L_f^E$ ) versus the mole fraction for the binary mixture of AN+DMSO at different temperatures, including 298 K (black square), 308 K (red circle), 318 K (blue triangle), and 328 K (purple triangle).



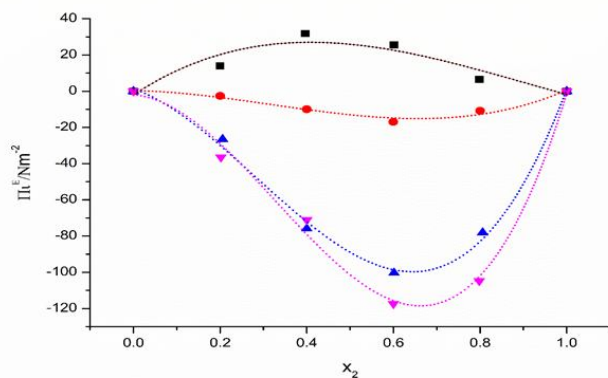
**Fig. 4.** Curves of excess specific acoustic impedance ( $Z^E$ ) versus the mole fraction for the binary mixture of AN+DMSO at different temperatures, including 298 K (black square), 308 K (red circle), 318 K (blue triangle), and 328 K (purple triangle).

Quantitatively, this can be explained in terms of the closer approach of unlike molecules, which, in turn, reduced the compressibility and volume of the studied binary solvent system. This may also be attributed to the relative strength of the below-mentioned effects, which are responsible for influencing the free spaces among the component molecules

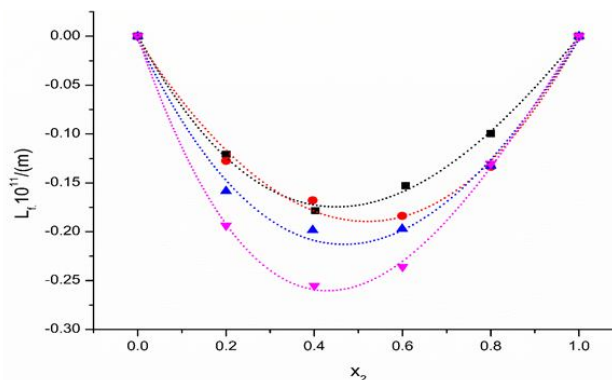
in the binary solvent mixtures [32-33]:

(a) Different sizes and shapes of the component molecules, loss of dipolar association and the break-up of hydrogen bonding, which together decrease ultrasonic velocity and increase isentropic compressibility and free length, as defined by Jacobson;

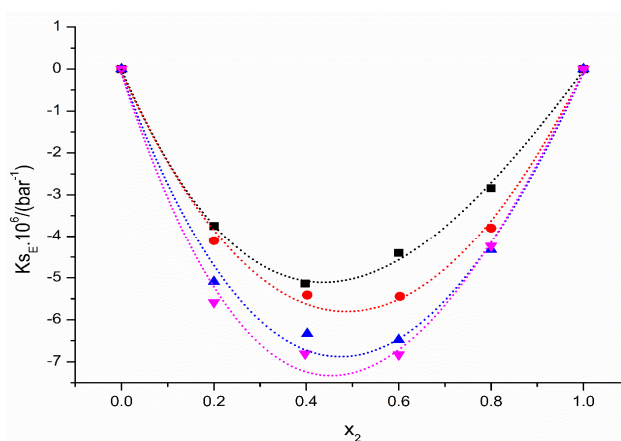




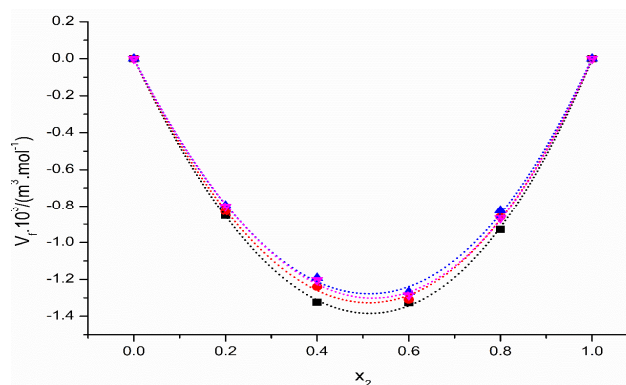
**Fig. 5.** Curves of excess internal pressure ( $\pi_i^E$ ) versus the mole fraction for the binary mixture of AN+DMSO at different temperatures, including 298 K (black square), 308 K (red circle), 318 K (blue triangle), and 328 K (purple triangle).



**Fig. 7.** Curves of excess intermolecular free length ( $L_i^E$ ) versus the mole fraction for the binary mixture of AN+DMA at different temperatures, including 298 K (black square), 308 K (red circle), 318 K (blue triangle), and 328 K (purple triangle).



**Fig. 6.** Curves of excess isentropic compressibility ( $K_s^E$ ) versus the mole fraction for the binary mixture of AN+DMA at different temperatures, including 298 K (black square), 308 K (red circle), 318 K (blue triangle), and 328 K (purple triangle).



**Fig. 8.** Curves of excess free volume ( $V_f^E$ ) versus the mole fraction for the binary mixture of AN+DMA at different temperatures, including 298 K (black square), 308 K (red circle), 318 K (blue triangle), and 328 K (purple triangle).

(b) Dipole-dipole interactions, electron donor-acceptor interactions, or charge-transfer complexes among unlike molecules, which together bring about association complex formation among the component molecules, leading to an increase in ultrasonic velocity and a decrease in isentropic compressibility.

Negative excess free volume ( $V_f^E$ ) for the given solvent composition reflects strong dipole-dipole interactions occurring between the unlike molecules of the components [32]. Moreover, the negative deviations in excess intermolecular free length ( $L_i^E$ ) suggest the presence of strong interactions in the mixtures, which is further supported by the Kerr effect [34-35]. The observed isentropic compressibility ( $K_s^E$ ), excess intermolecular free

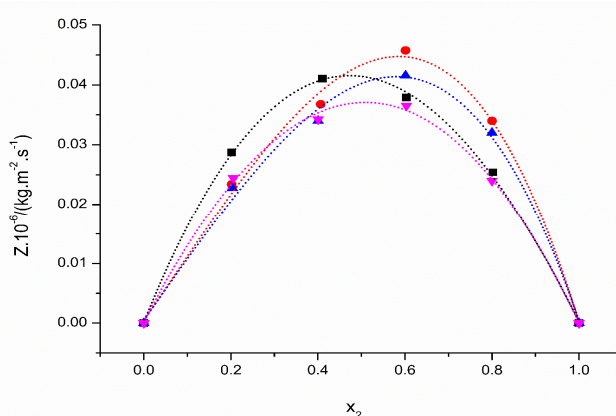
length ( $L_f^E$ ) and excess free volume ( $V_f^E$ ) values are the net result of the above-mentioned two effects. Pal and Das also observed the same trends in excess intermolecular lengths ( $L_f^E$ ) in their studies of ultrasonic velocity. The plots of  $L_f^E$  versus the mole fraction of the solvent were found to be negative for the system investigated, which suggests that the effect of complex formation among unlike molecules must have been more dominant than the structural effects in the studied mixtures. Negative deviations in intermolecular free length ( $L_f^E$ ) were caused due to dipolar association taking place in the solvent mixtures as a result of which longer distances were traveled by sound waves in the binary mixtures of solvents [36]. Negative values of the excess functions  $K_s^E$ ,  $L_f^E$ , and  $V_f^E$  can also be attributed to the decrease in free length between the molecules caused by the interstitial accommodation of AN molecules in DMSO and DMA.

Figures S1 and S3 show the plots of deviation in viscosity ( $\ln\Delta\eta$ ) for the binary mixtures AN-DMSO and AN-DMA, respectively, at different temperatures, including 298 K, 308 K, 318 K, and 328 K. While in the AN-DMSO system (Fig. S1), viscosity deviations ( $\ln\Delta\eta$ ) were positive throughout the whole composition range at 298 K and 308 K, showing maxima at around 0.4 mole fraction of DMSO, they were negative in magnitude at 318 K and 328 K and approached broad minima at around 0.6-0.8 mole fraction of DMSO. However, in AN+DMA solvent systems (Fig. S3), while the viscosity deviations ( $\ln\Delta\eta$ ) were found to be positive over the entire composition range at 298 K, 308 K and 318 K, with two maxima at 0.4 and 0.8 mole fraction of DMA, they were negative at 328 K and approached two minima at 0.2 and 0.6 mole fraction of DMA. Negative deviation in viscosity (reduction in viscosity of liquid mixture with respect to an ideal mixture) can be attributed to the deterioration of the association among different component molecules, resulting in higher fluidity of the system. Similar behavior was observed in DMF + MeOH solvent systems [37]. In these solvent systems, a broad minimum corresponding to a negative deviation was obtained at around 60-80% mol MeOH. Since both these systems represent much stronger hydrogen bond interactions; therefore, the results need to be explicated with regard to the strong structural outcome of intermolecular interactions. Since all the three investigated solvents (*i.e.*,

AN, DMSO, and DMA) were non-hydrogen bonded, the structural changes caused due to hydrogen bonding were not considered with viscosity deviations here. The variation in  $\ln\Delta\eta$  values in the solvent composition yields a qualitative assessment of the strength of the intermolecular interactions prevailing in the solvent mixtures. Fort and Moore [38] obtained positive values for excess viscosity ( $\ln\Delta\eta$ ) and suggested that the specific interactions which involved the formation of hetero-molecular complexes were the main causes of positive deviations in viscosity. Also, the positive viscosity deviation, or the positive excess viscosity ( $\ln\Delta\eta$ ), values for the studied binary mixtures indicate that the viscosities of associates formed among unlike molecules were relatively more significant than those of the pure components. The viscosity deviation [38] can be analyzed by taking into account the following points:

- (i) The loss of dipolar association in the pure component and different sizes and shapes of the component molecules may lead to decreased viscosity of the solution and hence negative deviations in viscosity;
- (ii) Certain interactions among unlike component molecules, including charge transfer complexes or dipole-dipole interactions, can also increase the viscosity of the mixtures compared to that of pure components, leading to positive deviations in viscosity.

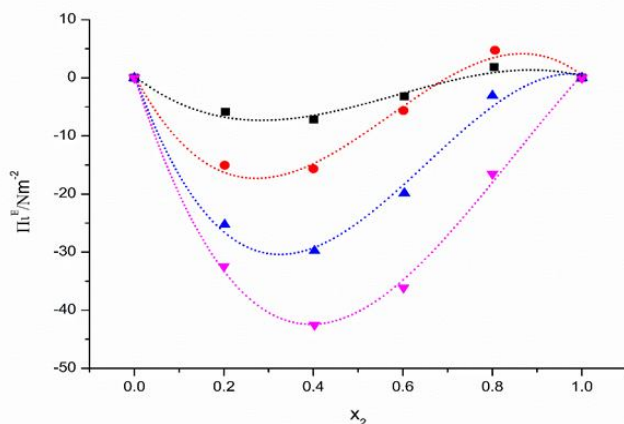
An examination of Figs. 4 and 9 shows that the excess acoustic impedance ( $Z^E$ ) values were positive over the entire solvent composition range for both investigated solvent systems (*i.e.*, AN+DMSO and AN+DMA) at all studied temperatures. In the AN+DMSO system,  $Z^E$  values increased in magnitude with the increase in DMSO mole fraction, reached a maximum at around 0.6 mole fraction of DMSO, and then started to decrease with the increase in the DMSO content in the solvent mixture (Fig. 4). However, in the AN+DMA solvent system, one maximum was obtained at 298 K at 0.4 mole fraction of DMA, and another maximum was obtained at 308 K, 318 K, and 328 K at 0.6 mole fraction of DMA (Fig. 9). The positive deviation in acoustic impedance ( $Z^E$ ) can possibly reflect firm molecular interactions among unlike molecules, or it can suggest that the specific interactions among the unlike molecules in the solvent mixtures were controlling the shattering of dipolar interactions among like molecules in the binary mixture of solvents [39].



**Fig. 9.** Curves of excess specific acoustic impedance ( $Z^E$ ) versus the mole fraction for the binary mixture of AN+DMA at different temperatures, including 298 K (black square), 308 K (red circle), 318 K (blue triangle), and 328 K (purple triangle).

Compared to other studied excess functions, the behaviors of excess molar volume ( $V_m^E$ ) and excess internal pressure ( $\Pi_i^E$ ) were different. These two excess parameters showed both negative and positive deviations. An examination of Fig. S2 shows that  $V_m^E$  values were negative throughout the whole solvent composition range in AN+DMSO solvent mixtures, except at 0.4-0.6 mole fraction of DMSO at 298 K and 0.8 mole fraction of DMSO at 308 K, 318 K and 328 K. At 298 K, the minima corresponding to negative deviation in  $V_m^E$  values were obtained at around 0.2 mole fraction, and the maxima were obtained at 0.6 mole fraction of DMSO. However, at 308 K, 318 K and 328 K, the minima and maxima were obtained at 0.6 and 0.8 mole fraction of DMSO, respectively. However, in the AN+DMA solvent system (Fig. S4), the values of excess molar volume ( $V_m^E$ ) were negative throughout the whole solvent composition range at 298 K, showing two minima at 0.4 and 0.8 mole fraction of DMA and a maximum at 0.6 mole fraction of DMA. However, at 308 K, 318 K, and 328 K, both positive and negative deviations were observed, with one minimum corresponding to the negative deviation at 0.6 mole fraction of DMA and one maximum corresponding to the positive deviation at 0.8 mole fraction of DMA. Overall, a sigmoid change was observed from negative to positive in excess  $V_m^E$  values. In

other words, the  $V_m^E$  curve at all investigated temperatures was sigmoidal and tended to change from negative to positive values at higher mole fractions of DMA. Excess molar volumes ( $V_m^E$ ) were found to be very subtle concerning mutual interactions among component molecules of the binary mixtures of solvents. The degree of deviations in these excess parameters from ideal behavior relies on the strength of interactions between unlike molecules. Also, for any system, the type of deviation in excess molar volume ( $V_m^E$ ), whether positive or negative, depends on the extent of expansion and contraction of different solvents after being mixed. In cases where the contraction factors are overshadowed by expansion factors, the excess molar volume ( $V_m^E$ ) turns positive. Conversely, if the contraction factors dominate the expansion factors, the excess molar volume ( $V_m^E$ ) becomes negative. Therefore, it is fascinating to note that the results obtained until now indicate that the excess molar volume ( $V_m^E$ ) values for the current systems are substantially affected by various physical and chemical forces, which, as described in the literature, include the following [40]: (i) the disruption of the order of liquid after mixing with the second component or the break-up of dipolar association existing in the solvent component molecules; (ii) unfavorable and non-specific physical interactions among unlike molecules; (iii) steric hindrance, which prevents the closeness of different constituents of the component molecules; (iv) different molar volumes causing geometrical fitting of smaller component molecules into the voids generated by bigger molecules; (v) hydrogen bonding, which causes the appearance of specific interactions in the solvent mixture between unlike molecules; (vi) the existence of specific dipole-dipole type interactions among solvent and co-solvent molecules in the binary mixture; (vii) chemical interaction taking place between the constituent chemicals; and (viii) the settlement of one component molecules into the interstitial sites of the other component molecules. The first four factors are responsible for the volume expansion while the latter four contract the volume of the liquid mixture. The negative excess molar volumes at specified solvent compositions, as discussed above, suggest that either the volume contraction factors play an important role in dissimilar molecules or that the interactions among molecules of mixtures are much stronger compared to those



**Fig. 10.** Curves of excess internal pressure ( $\Pi_i^E$ ) versus the mole fraction for the binary mixture of AN+DMA at different temperatures, including 298 K (black square), 308 K (red circle), 318 K (blue triangle), and 328 K (purple triangle).

among the molecules of pure liquids and that associative force influence the behavior of the solution under investigation. Initially, the negative excess molar volume ( $V_m^E$ ) values seemed to have been caused by the interstitial accommodation of AN molecules in the bigger DMSO molecules, but later, the excess molar volume ( $V_m^E$ ) started to become positive, suggesting the dissociation of self-associated AN molecule by further addition of DMSO, which cannot be explained by the interaction occurring in AN and DMSO, resulting in rapid expansion in volume until it reaches maxima. Further decrease in the excess molar volume ( $V_m^E$ ) may be due to the lower packing forces of the mixed liquids compared to those of the pure liquids. As can be seen in Fig. 5, excess internal pressure ( $\Pi_i^E$ ) values for the AN+DMSO solvent system at 298 K were positive throughout the whole solvent composition range, with broad maxima at around 0.4-0.6 mole fraction of DMSO; however, at 308 K, 318 K and 328 K, the values of  $\Pi_i^E$  showed negative deviations, with a minimum at around 0.6 mole fraction of DMSO. Also, excess internal pressure ( $\Pi_i^E$ ) values decreased with an increase in temperature. However, in the AN+DMA solvent system (Fig. 10),  $\Pi_i^E$  values showed a sigmoidal change from negative to positive, that is,  $\Pi_i^E$  showed a negative deviation, which

corresponded to a minimum at 0.6 mole fraction of DMA, and a positive deviation, which corresponded to a maximum at 0.8 mole fraction of DMA. Positive excess internal pressure ( $\Pi_i^E$ ) values reveal the existence of strong interactions between component molecules in the binary mixtures of solvents [41].

## CONCLUSIONS

In the present investigation, the calculated excess parameters suggested the existence of strong molecular interactions in both solvent systems studied. However, AN-DMA solvent system, compared to the AN-DMSO solvent system, exhibited more deviation towards a stronger interaction mode. Furthermore, the rise of temperature had a significant role in altering molecular interactions. Negative and positive deviations in the excess properties were examined in terms of molecular interactions. Negative deviation in viscosity ( $\ln\Delta\eta$ ) can be explained by the loss of the association among the different component molecules, which resulted in higher fluidity of the system. Positive deviations in  $\ln\Delta\eta$  values may be the result of dipole-dipole interactions. Positive deviations in  $V_m^E$  values in the studied binary systems can be attributed to the dispersion forces, disturbance of the order of liquid when mixed with the other component, and different molar volumes causing geometrical fitting of the smaller component molecules into the voids generated by the bigger molecules. Furthermore, negative deviations in  $L_f^E$ ,  $V_f^E$ ,  $V_m^E$ , and  $K_S^E$  can be attributed to dipole-dipole and induced dipole interactions. Dispersion forces were functional in all the solvent systems, which explains the existence of numerous sorts of interactions between the unlike components of the binary solvent mixtures. It can also be stated that the excess values were the outcome of all types of contributions. The observed positive deviation in  $Z^E$  values and the opposite behavior in  $L_f^E$ ,  $V_f^E$ , and  $K_S^E$  over the entire solvent composition range further support the existence of molecular interactions between unlike molecules. Various molecular interactions occurring in the binary mixtures can be attributed to the overall impact of the steric hindrance of the solvent molecules, solvent structure, and different dielectric constants developing from the effect of the ions on the solvent structure.

## ACKNOWLEDGMENTS

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## REFERENCES

- [1] Chand, G. P.; Sankar, M. G.; Ramchandran, D., Densities, Viscosities and speeds of sound of binary mixtures of 2-chloroaniline with o-chlorotoluene, m-chlorotoluene and p-Chlorotoluene at different temperatures. *J. Sol. Chem.* **2016**, *45*, 153-187, DOI: 10.1007/s10953-016-0439-0.
- [2] Kaur, M., Thermodynamic and physicochemical properties and the excess functions of binary mixtures of dimethylsulfoxide with pyridine and nitromethane at variable temperatures-298 to 318 K. *Conf. Ser.: Mater. Sci. Eng.* **2021**, 1033, DOI: 10.1088/1757-899X/1033/1/012079.
- [3] Palani, R.; Geetha, A., Acoustical and excess thermodynamic studies of molecular interaction in aqueous mixed solvent systems at 303, 308 and 313 K. *Phys. Chem. Liquids.* **2009**, *47*, 542-552. DOI: 10.1080/00319100802562862.
- [4] Raza, M. A.; Valtz, A.; Coquelet, C.; Hallett, P. D.; Afzal, W., Volumetric properties of furan and 2-5-dimethylfuran in different industrial solvents at temperatures from 278 to 343 K. *J. Chem. Eng. Data.* **2021**, *66*, 2666-2680. DOI: 10.1021/acs.jced.0c01060.
- [5] Chaudhary, N.; Nain, A. K., Densities, ultrasonic speeds, viscosities, refractive indices, and excess properties of 1-butyl-3-methylimidazolium tetrafluoroborate + N-methylacetamide binary mixtures at different temperatures. *J. Chem. Eng. Data.* **2020**, *65*, 1447-1459. DOI: 10.1021/acs.jced.9b00875.
- [6] Wang, Y.; Ma, C.; Liu, C.; Lu, X.; Feng, X.; Ji, X., Thermodynamic study of choline chloride-based deep eutectic solvents with water and methanol. *J. Chem. Eng. Data.* **2020**, *65*, 2446-2457. DOI: 10.1021/acs.jced.9b01113.
- [7] Shekaari, H.; Zafarani-Moattar, M. T.; Mohammadi, B., Thermophysical characterization of aqueous deep eutectic solvent (choline chloride/urea) solutions in full ranges of concentration at T = (293.15-323.15) K. *J. Mol. Liq.* **2017**, *243*, 451-461. DOI: 10.1016/j.molliq.2017.08.051.
- [8] Zarei, H. A.; Lavasani, M. Z.; Iloukhani, H., Densities and volumetric properties of binary and ternary Liquid mixtures of water (1) + acetonitrile (2) + dimethyl sulfoxide (3) at temperatures from (293.15 to 333.15) K and at ambient pressure (81.5 KPA). *J. Chem. Eng. Data.* **2008**, *53*, 578-585. DOI: 10.1021/je700645p.
- [9] Ciocirlan, O.; Iulian, O., Properties of pure 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ionic liquid and its binary Mixtures with dimethyl sulfoxide and acetonitrile. *J. Chem. Eng. Data.* **2012**, *57*, 3142-3148. DOI: 10.1021/je3007474.
- [10] Roy, M.; Sarkar, B.; Chanda, R., Viscosity, density, and speed of sound for the binary mixtures of formamide with 2-methoxyethanol, acetophenone, acetonitrile, 1,2-dimethoxyethane, and dimethylsulfoxide at different temperatures. *J. Chem. Eng. Data.* **2007**, *52*, 1630-1637. DOI: 10.1021/je700026d.
- [11] Kabir, M. H.; Motin, M. A.; Huque, M. E., Densities and excess molar volumes of methanol, ethanol and n-propanol in pure water and in water + surf excel solutions at different temperatures. *Phys. Chem. Liquids.* **2004**, *42*, 279-290. DOI: 10.1080/0031910042000205346.
- [12] Sadeghi, R.; Shekaari, H.; Hosseini, R., Volumetric and isentropic compressibility behavior of ionic liquid, 1-propyl-3-methylimidazolium bromide in acetonitrile, dimethylformamide, and dimethylsulfoxide at T = (288.15 to 308.15) K. *Int. J. Thermophys.* **2009**, *30*, 1491-1509. DOI: 10.1007/s10765-009-0648-5.
- [13] Bhagour, S.; Solanki, S.; Hooda, N.; Sharma, D.; Sharma, V. K., Thermodynamic properties of binary mixtures of the ionic liquid [Emim][BF<sub>4</sub>] with acetone and dimethylsulfoxide. *J. Chem. Thermodyn.* **2013**, *60*, 76-86. DOI: 10.1016/j.jct.2013.01.010.
- [14] Raghuram, N.; Suresh, R.; Ramesh, G.; Sowjanya, G.; Jyostna, T. S., Excess parameters for the binary mixtures of sulfolane with chloroethanes at different temperatures. *J. Therm. Anal. Calorim.* **2015**, *119*,

- 2107-2117. DOI: 10.1007/s10973-015-4399-1.
- [15] Sastry, S. S.; Babu, S.; Vishwam, T.; Tiong, H. S., Excess parameters for binary mixtures of alkyl benzoates with 2-propanol at different temperatures. *J. Therm. Anal. Calorim.* **2013**, *116*, 923-935. DOI: 10.1007/s10973-013-3570-9.
- [16] Narendra, K.; Srinivasu, C.; Fakruddin, S.; Narayanamurthy, P., Excess parameters of binary mixtures of anisaldehyde with o-cresol, M-cresol and p-cresol at T = (303.15, 308.15, 313.15, and 318.15) K. *J. Chem. Thermodyn.* **2011**, *43*, 1604-1611. DOI:10.1016/j.jct.2011.05.018.
- [17] Nikam, P. S.; Sawant, A. B., Viscosity of potassium halides and symmetrical tetraalkylammonium bromides in acetonitrile + water mixtures at 298.15 K. *J. Chem. Eng. Data.* **1997**, *42*, 1151-1156. DOI: 10.1021/je970067a.
- [18] Gill, D.; Pathania, V.; Kumari, A.; Anand, H.; Jauhar, S., Compressibility behaviour of some copper(I) perchlorate complexes in binary mixtures of acetonitrile with nitromethane and dimethylsulfoxide at 298.15 K. *Z. Phys. Chem.* **2004**, *218*, 857-865. DOI: 10.1524/zpch.218.7.857.3572.
- [19] Galavo, J.; Davis, B.; Tilley, M.; Normando, E. R.; Duchon, M.; Cordeiro, Unexpected low dose toxicity of the universal solvent DMSO. *The FASEB J.* **2014**, *28*, 1317-1330, DOI:10.1096/fj.13-235440.
- [20] Pathania, V.; Sharma, S.; Vermani, S. K.; Vermani, B. K., Ultrasonic velocity and isentropic compressibility studies of monoalkylammonium salts in binary mixtures of acetonitrile and N,N-dimethylacetamide at variable temperature and atmospheric pressure. *J. Solution. Chem.* **2020**, *49*, 798-813, DOI: 10.1007/s10953-020-00991-3.
- [21] Wypych-Stasiewicz, A.; Borun, A.; Benko, J.; Bald, A., Conductance studies of KI, LiBr, LiNO<sub>3</sub>, AgNO<sub>3</sub>, Et<sub>4</sub>NI and the limiting ionic conductance in water + propan-1-ol mixtures at 298.15 K. *J. Mol. Liq.* **2013**, *178*, 84-87, DOI: 10.1016/j.molliq.2012.11.028.
- [22] Roy, M. N.; Banerjee, A.; Das, R. K., Conductometric study of some alkali metal halides in (dimethylsulfoxide + acetonitrile) at T = 298.15 K. *J. Chem. Thermodyn.* **2009**, *41*, 1187-1192, DOI: 10.1016/j.jct.2009.03.005.
- [23] Wypych-Stasiewicz, A.; Borun, A.; Benko, J.; Bald, A., Conductance studies of Et<sub>4</sub>NIO<sub>4</sub>, Et<sub>4</sub>NClO<sub>4</sub>, Bu<sub>4</sub>NI, Et<sub>4</sub>NI and the limiting ionic conductance in water + acetonitrile mixtures at 298.15 K. *J. Mol. Liq.* **2014**, *190*, 54-58, DOI: 10.1016/j.molliq.2013.10.023.
- [24] Riddick, A.; Bunger, W. B.; Sakano, T. K., Organic solvents, Physical Properties and Methods of Purification. Wiley Interscience, New York, 4th Ed., **1986**.
- [25] Pathania, V.; Sharma, S.; Vermani, S. K.; Vermani, B. K.; Grover, N., Physicochemical study of solvation behavior of n-butylammonium perchlorate in binary mixtures of acetonitrile and dimethylsulfoxide at variable temperatures. *J. Sol. Chem.* **2021**, *50*, 1204-1235, DOI: 10.1007/s10953-021-01113-3.
- [26] Pathania, V.; Sharma, S.; Vermani, S. K.; Vermani, B. K.; Grover, N., Estimating the acoustical parameters and molecular interactions of n-butylammonium perchlorate in mixed organic solvents in the temperature range 298-328 K. *Phys. Chem. Res.* **2020**, *8*, 737-753, DOI: 10.22036/PCR.2020.229730.1772.
- [27] Praharaj, M. K.; Satapathy, A.; Mishra, P.; Mishra, S., Ultrasonic analysis of intermolecular interaction in the mixtures of benzene with N,N-dimethylformamide and cyclohexane at different temperatures. *J. Chem. Pharm. Res.* **2013**, *5*, 49-56, <https://www.jocpr.com/archive/jocpr-volume-5-issue-1-year-2013.html>.
- [28] Nain, A. K.; Chand, D.; Chandra, P.; Pandey, J. T., Excess internal pressures, excess free volumes and excess thermodynamic parameters of some non-aqueous binary mixtures from ultrasonic speed, density and viscosity data. *Phys. Chem. Liq.* **2009**, *47*, 195-209, DOI: 10.1080/00319100802072664.
- [29] Venkatesulu, D.; Venkatesu, P.; Rao, M. V. R., Viscosities and densities of trichloroethylene or tetrachloroethylene with 2-alkoxyethanols at 303.15 K and 313.15 K. *J. Chem. Eng. Data.* **1997**, *42*, 365-367, DOI: 10.1021/je960316f.
- [30] Nagarjun, A.; Babu, S., Excess thermodynamic and acoustic properties for equimolar mixtures of benzyl benzoate with 1-butanol at different temperatures. *Mater. Today: Proc.* **2018**, *5*, 26322-26328, DOI: 10.1016/j.matpr.2018.08.083.



- [31] Babavali, S. F.; Punyaseshudu, D.; Narendra, K.; Yesaswi, C. R.; Srinivasu, C., Study of molecular interaction using excess thermo-acoustic parameters at different temperatures. *J. Mol. Liq.* **2016**, *224*, 47-52, DOI: 10.1016/j.molliq.2016.09.079.
- [32] Dahire, S. L.; Morey, Y. C.; Agrawal, P. S., Excess molar volumes, intermolecular free lengths, adiabatic compressibilities and acoustic impedance of binary mixtures of anisole, toluene and ethylbenzene with dioxane at different temperatures. *Int. Let. Chem.* **2014**, *42*, 72-83, DOI: 10.18052/www.scipress.com/ILCPA.42.72.
- [33] Jeyaumar, J. E.; Vinayagam, S. C.; Murugan, J. S.; Ibrahim, P. S. S., An ultrasonic study on acoustical and excess properties of ternary liquid mixtures of 2-bromoanisole + 1-butanol + n-hexane at different temperatures 303 K, 308 K and 313 K and a frequency 2 MHz. *J. Chem. Soc. Pak.* **2020**, *42*, 798-806.  
[https://link.gale.com/apps/doc/A641278858/AONE?u=tacoma\\_comm&sid=googleScholar&xid=72cf4c1c](https://link.gale.com/apps/doc/A641278858/AONE?u=tacoma_comm&sid=googleScholar&xid=72cf4c1c)
- [34] Deosarkar, S. D.; Tawde, P. D.; Kalyankar, T. M., Partial molar volumes and compressibilities of metformin hydrochloride in aqueous-NaCl/sucrose solutions at 30 °C. *J. Mol. Liq.* **2018**, *251*, 40-44, DOI: 10.1016/j.molliq.2017.12.038.
- [35] Mohabansi, N. P., Study of excess parameters and partial molar volume for the molecular interactions of an aqueous 2-(tert-butylamino)-1-(3-chlorophenyl)propan-1-one and NaCl solution at different temperatures. *J. Sci. Res.* **2020**, *64*, 352-358, Retrieved from [https://www.bhu.ac.in/research\\_pub/jsr/Volumes/JSR\\_64\\_02\\_2020/48.pdf](https://www.bhu.ac.in/research_pub/jsr/Volumes/JSR_64_02_2020/48.pdf)
- [36] Nagarjun, B.; Sarma, A. V.; Rao, G. V.; Rambabu, C., Thermodynamic and acoustic study on molecular interactions in certain binary liquid systems Involving ethyl benzoate. *J. Thermodyn.* **2013**, *2013*, 1-9, DOI: 10.1155/2013/285796.
- [37] Bhuiyan, M. M. H.; Uddin, M. H., Excess molar volumes and excess viscosities for mixtures of N,N-dimethylformamide with methanol, ethanol and 2-propanol at different temperatures. *J. Mol. Liq.* **2008**, *138*, 139-146. DOI: 10.1016/j.molliq.2007.07.006.
- [38] Fort, R. J.; Moore, W. R., Viscosities of binary liquid mixtures. *Trans. Faraday Soc.* **1966**, *62*, 1112-1119, DOI: 10.1039/TF9666201112.
- [39] Singh, S.; Vibhu, I.; Gupta, M.; Shukla, J. P., Excess acoustical and volumetric properties and the theoretical estimation of the excess thermodynamic functions of binary liquid mixtures. *Chin. J. Phys.* **2007**, *45*, 412-423, Retrieved from <https://www.airitilibrary.com/Publication/alDetailedMesh?docid=05779073-200708-45-4-412-424-a>.
- [40] Mahajan, A. R.; Mirgane, S. R., Excess molar volumes and viscosities for the binary mixtures of n-octane, n-decane, n-dodecane, and n-tetradecane with octan-2-ol at 298.15 K. *J. Thermodyn.* **2013**, DOI: 10.1155/2013/571918.
- [41] Rao, G. V.; Sarma, A. V.; Ramchandran, D.; Rambabu, C., Evaluation of excess free volumes and excess internal pressures of binary solutions of o-chlorophenol at different temperatures. *IJPAP.* **2005**, *43*, 602-608, DOI: <http://nopr.niscair.res.in/handle/123456789/8851>.