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Estimating the Acoustical Parameters and Molecular Interactions of n-Butylammonium perchlorate in Mixed Organic Solvents in the Temperature Range 298-328 K

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The interactions in a non-aqueous system containing n-Butylammonium perchlorate are studied here. The densities and ultrasonic velocities of n-Butylammonium perchlorate in binary mixtures of Acetonitrile and Dimethylsulfoxide at the temperature range of 298-328 K under atmospheric pressure were measured. The binary mixtures contain 20, 40, 60 and 80 mol% of dimethylsulfoxide, and the concentration range taken is 0.03-0.28 mol kg^{-1}. Anton Paar density and sound velocity meter were used to measure the densities and ultrasonic velocities. The experimental data were employed to calculate various acoustical parameters such as isentropic compressibility (βs), intermolecular free length (L_f), relaxation strength (r), specific acoustic impedance (Z), relative association (R_A), Wada's constant (W), Rao's constant (R), Van der Waals constant (b), molar volume (V_m) and free volume (V_f). The results of the derived acoustical parameters have been discussed as a function of salt concentration, solvent composition and temperature. Overall, results show appreciable solute-solvent interactions in dimethylsulphoxide rich region of the binary mixtures studied, and the extent of these interactions were found to be decreasing with temperature.

Keywords: Isentropic compressibility, Acoustic impedance, Acetonitrile, Dimethylsulfoxide, Relative

INTTRODUCTION

The studies of acoustic parameters of non aqueous mixed electrolytic solutions have been found very important in elucidating the specific solute-solute and solute-solvent interactions in solutions. Various studies have been implemented on understanding acoustic behavior of tetraalkylammonium perchlorate [1-5], however, the data available for the solutions of n-butylammonium perchlorates ($C_4H_9NH_3ClO_4$) (BAP) in acetonitrile (AN) and dimethylsulfoxide (DMSO) solvent systems are completely scarce. Therefore, study the acoustic properties of $C_4H_9NH_3ClO_4$ (BAP) in binary mixtures of AN and DMSO could be advantageous. In this article we report the densities (ρ) and speeds of sound (*u*) of the binary mixtures of AN and DMSO solvents with BAP, over the concentration range of 0.03-0.28 mol kg^{-1} at different temperatures, *T* = (298, 308, 318 and 328 K). To explore the nature and type of various molecular interactions in the studied system, some acoustical parameters like isentropic compressibility (β_s), intermolecular free length (L_f), relaxation strength (r), specific acoustic impedance (Z), relative association (R_A), Wada's constant (W), Rao's constant (R), Van der Waals constant (b), molar volume (V_m) and free volume (V_f) have been determined from measured ultrasonic velocities, and densities. The sign and magnitude of these parameters throw light on the various molecular interactions present within the system. Alkyl ammonium perchlorates are used as one of the main ingredients in rocket propellants and explosives [6]. Due to

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high dipole moment, high dielectric constant (μ_{AN} = 3.37D, μ_{DMSO} = 3.90D, D_{AN} = 36.0 and D_{DMSO} = 46.7), low toxicity [7], excellent solvating ability of DMSO and high extraction efficiency of AN, the binary mixtures of these solvents can be used as solvating medium to retrieve the effective components; *i.e.,* alkyl ammonium perchlorates, from waste explosives in ordnances items and munitions. These parameters can be also helpful in choosing the right solvent in development of electrical double layer capacitors where these salts are used as electrolytes [8-10].

MATERIAL AND METHODS

AN (99.8%) (CAS No. 75-05-8) and DMSO (99.8%) (CAS No. 67-68-5) were obtained from E. Merck, and purified by methods as reported earlier [11-14]. Mass fraction purity for AN and DMSO was found to be 0.999[a] and water content was found to be less than 0.00030[b] and 0.00020[b], respectively. Silver perchlorate monohydrate ($AgClO_4.H_2O$) (CAS No.14242-05-8) (Alfa Aesar) purchased for preparation of salt investigated here was used as received without further purification. Solvents were stored over 4 Å molecular sieves for 72 h before use. Preparation and characterization of butylammonium perchlorate (BAP) was done by methods reported [15] in our previously published paper. Thermo Finnigan Flash EA 1112 Series CHNS-O Analyzer was used for elemental analysis. The required data of density and ultrasonic velocity are obtained by digital density and sound velocity meter (Model DSA 5000M, Anton Paar). The sound velocities and densities of pure AN and DMSO were measured using DSA 5000M and the results were compared with literature values available [15]. The experimental data of density (ρ_o) and ultrasonic velocity (u_o) for AN and DMSO binary mixtures at different temperatures used for evaluation of acoustical parameters are reported in Table 2. Temperatures were maintained constant by Peltier-type thermostating unit already built in the instrument. In order to minimize errors, instrument was calibrated with triply distilled water and dry air at atmospheric pressure (0.1 MPa) prior to each series of measurements. The mixtures were prepared by directly weighing solute to give a precision within 0.01 mg by using ACZET-602CY electronic balance. Triply distilled and degassed water was used for preparation of solutions. The probable molality error has been found to be less than $\pm 1 \times 10^{-4}$ mol kg^{-1} (*[a]Gas Chromatography; *[b]Karl Fischer Titration).

RESULTS AND DISCUSSION

Various acoustical parameters were calculated from the experimental data of density and ultrasonic velocity using the following expressions (Eqs. (1)-(10))

$$\text{Isentropic compressibility } (\beta_s) = 1/u^2\rho \quad (1)$$

$$\text{Intermolecular free length } (L_f) = k(\beta_s)^{1/2} \quad (2)$$

$$\text{Specific acoustic impedance } (Z) = \rho.u \quad (3)$$

$$\text{Relative association } (R_A) = (\rho/\rho_o) \times (u_o/u)^{1/3} \quad (4)$$

$$\text{Molar volume } (V_m) = \frac{X_1M_1 + X_2M_2}{\rho_{mix}} = M/\rho_{mix} \quad (5)$$

$$\text{Wada's Constant } (W) = (\beta_s)^{-1/7} V_m \quad (6)$$

$$\text{Rao's Constant } (R) = (u)^{1/3} V_m \quad (7)$$

$$\text{Vander Waal's Constant } (b) = V_m [1 - (RT/Mu^2) \{(1 + Mu^2/3RT)^{1/2} - 1\}] \quad (8)$$

$$\text{Free volume } (V_f) = V_m - b \quad (9)$$

$$\text{Relaxation strength } (r) = 1-(u/u_\infty)^2 \quad (10)$$

where, ρ, ρ_o and u, u_o are the densities and ultrasonic velocities of solution and pure solvent, respectively, u_∞ is Schaff's limiting value taken to be equal to 1600 ms^{-1} for liquids [16], m is the molality, k is temperature dependent constant called Jacobson's constant which can be calculated by the equation $k = (91.368 + 0.3565T) \times 10^{-8}$, T is the experimental temperature, x_1, x_2 and M_1, M_2 are the mass fractions and molar masses of solute and solvent, respectively, and ρ_{mix} is the density of solution.

The measured data of ultrasonic velocity (u) and density (ρ) for BAP at different salt concentrations in AN-DMSO binary mixtures containing 20, 40, 60 and 80 mol% of

Table 1. Density, 10^{-3} ρ_o/(kg m^{-3}) and Ultrasonic Velocity, u_o/(m s^{-1}) of AN-DMSO Binary Mixtures at Temperatures 298 K, 308 K, 318 K and 328 K

mol % DMSO	ρ_o	u_o	ρ_o	u_o	ρ_o	u_o	ρ_o	u_o
	298 K		308 K		318 K		328 K	
20	0.865772	1327.88	0.849555	1284.53	0.838853	1246.93	0.828074	1209.37
	0.857430[x]							
40	0.927716	1360.22	0.921809	1326.90	0.911376	1291.38	0.900867	1255.58
	0.929470[x]							
60	0.988498	1401.78	0.984752	1372.56	0.974541	1338.09	0.964304	1303.78
	0.992680[x]							
80	1.045627	1448.18	1.034326	1413.38	1.024288	1379.76	1.014230	1346.25
	1.046100[x]							

Standard uncertainties are: u(T) = 0.03 K, u(ρ) = 3 × 10^{-2} kg m^{-3}, u(u) = 5 × 10^{-2} m s^{-1} and u(p) = 0.01 MPa. *The u_o and ρ_o values for AN and DMSO binary solvent mixtures are not available at 308, 318 and 318 K; therefore, a comparison of these values could not be made, [x](Ref. [22]).

DMSO at temperatures 298 K, 308 K, 318 K and 328 K are presented in Tables 2-5. A perusal of Tables 2-5 shows that there is an increase in both sound velocity and density of solution with increasing concentration and this trend becomes exactly opposite upon increasing temperature. Increase in sound velocity with concentration supports the structure making property of solute and greater association among the molecules due to the presence of strong solute-solvent interactions [17]. Also it can be seen from Tables 2-5 that the densities exhibit an increase with increasing concentration within the concentration range studied. This concentration dependence of density follows the same pattern for all the temperatures and solvent compositions studied. However, densities decrease with an increase in temperature which may be attributed to the weakening of solute-solvent interactions due to increased thermal agitation. Also, from the plots of isentropic compressibility (β_s) versus molal concentration (m) for BAP [Figs. 1a and 1b], it is clear that isentropic compressibility decreases with increasing salt concentration at all temperatures studied. This linear variation of isentropic compressibility (β_s) with concentration suggests structural effects in solution which become more prominent with further addition of BAP in the solution, or this may be attributed to a phenomenon called electrostriction which results in an increase of internal pressure due to the impact of solute on the surrounding solvent molecules leading to lowering of compressibility or to the predominance of penetration effect of solvent molecules into the intra solute free space over the effect of their solvent intrinsic compressibility [18]. Also, isentropic compressibility increases with increasing the temperature for 20 mol% DMSO and with decreasing DMSO mol % in the solution as analyzed from Figs. 1a and 1b, respectively. Exactly the same trends have been obtained for other binary mixtures studied for all the temperatures applied (Tables 2-5). The increase in β_s values with temperature may be due to enhanced thermal agitation resulting in weakening the solute-solvent interactions leading to higher compressibility of solution.

Table 2. Densities, (ρ)/(kg m^{-3}), Ultrasonic Velocities, (u)/(m s^{-1}), Isentropic Compressibilities, (β_s)/(Pa^{-1}), Specific Acoustic Impedance (Z)/(kg m^{-2} s^{-1}), Inter Molecular Free Lengths (L_f)/(m) and Molar Volume (V_m)/(m^3 mol^{-1}) for BAP in 20 mol% DMSO at 298 K, 308 K, 318 K and 328 K

m	10^{-3} ρ	u	10^{11} β_s	Z/10^6	$L_f/10^{-11}$	10^2 V_m
			298 K			
0.0495	0.870181	1322.35	65.72	1.1507	5.066	5.423
0.0857	0.873143	1326.58	65.08	1.1583	5.041	5.434
0.1237	0.875947	1329.47	64.59	1.1645	5.022	5.446
0.1617	0.878747	1330.65	64.27	1.1693	5.010	5.459
0.1997	0.881191	1332.02	63.96	1.1738	4.997	5.474
			308 K			
0.0495	0.853868	1287.4	70.68	1.0993	5.348	5.529
0.0857	0.856787	1290.56	70.11	1.1057	5.327	5.54
0.1237	0.859580	1293.93	69.53	1.1122	5.305	5.554
0.1617	0.862400	1295.95	69.11	1.1176	5.289	5.567
0.1997	0.864523	1297.13	68.80	1.1214	5.277	5.584
			318 K			
0.0495	0.843014	1247.44	76.23	1.0516	5.653	5.604
0.0857	0.845805	1250.31	75.63	1.0575	5.630	5.617
0.1237	0.848657	1252.98	75.00	1.0634	5.607	5.63
0.1617	0.851154	1254.95	74.60	1.0682	5.592	5.645
0.1997	0.853501	1257.36	74.11	1.0732	5.574	5.661
			328 K			
0.0495	0.831929	1210	82.1	1.0066	5.968	5.683
0.0857	0.8345	1213.84	81.33	1.0129	5.94	5.697
0.1237	0.83702	1215.98	80.8	1.0178	5.921	5.713
0.1617	0.839404	1218.33	80.26	1.0227	5.901	5.729
0.1997	0.841638	1220.29	79.79	1.027	5.884	5.762

Table 3. Densities, (ρ)/(kg m^{-3}), Ultrasonic Velocities, (u)/(m s^{-1}), Isentropic Compressibilities, (β_s)/(Pa^{-1}), Specific Acoustic Impedance, (Z)/(kg m^{-2} s^{-1}), Inter Molecular Free Lengths, (L_f)/(m), and Molar Volume, (V_m)/(m^3 mol^{-1}), for BAP in 40 mol% DMSO at 298 K, 308 K, 318 K and 328 K

m	10^{-3} ρ	u	10^{11} β_s	$Z/10^6$	$L_f/10^{-11}$	10^2 V_m
			298 K			
0.0456	0.932404	1364.66	57.59	1.2724	4.742	5.749
0.0810	0.935191	1367.86	57.15	1.2792	4.724	5.756
0.1163	0.937636	1370.64	56.77	1.2852	4.708	5.766
0.1512	0.939556	1371.9	56.55	1.2890	4.699	5.778
0.1863	0.941126	1372.09	56.44	1.2913	4.695	5.793
			308 K			
0.0456	0.925972	1326.44	61.38	1.2282	4.984	5.793
0.0810	0.928505	1328.64	61.01	1.2336	4.969	5.802
0.1163	0.930933	1330.29	60.7	1.2384	4.956	5.811
0.1512	0.932385	1332.00	60.45	1.2419	4.946	5.827
0.1863	0.933195	1334.96	60.13	1.2458	4.933	5.846
			318 K			
0.0456	0.915393	1291.05	65.54	1.1818	5.241	5.864
0.0810	0.917891	1293.84	65.08	1.1876	5.223	5.874
0.1163	0.919987	1296.05	64.71	1.1924	5.208	5.885
0.1512	0.921703	1298.97	64.3	1.1973	5.192	5.899
0.1863	0.922816	1300.21	64.1	1.1999	5.183	5.917
			328 K			
0.0456	0.904844	1255.25	70.14	1.1358	5.517	5.938
0.0810	0.907404	1257.88	69.65	1.1414	5.497	5.947
0.1163	0.909435	1260.28	69.23	1.1461	5.481	5.959
0.1512	0.911477	1261.97	68.89	1.1503	5.467	5.970
0.1863	0.912835	1265.17	68.44	1.1549	5.449	5.987

Table 4. Densities, (ρ)/(kg m^{-3}), Ultrasonic Velocities, (u)/(m s^{-1}), Isentropic Compressibilities, (β_s)/(Pa^{-1}), Specific Acoustic Impedance, (Z)/(kg m^{-2} s^{-1}), Inter Molecular Free Lengths, (L_f)/(m), and Molar Volume, (V_m)/(m^3 mol^{-1}), for BAP in 60 mol% DMSO at 298 K, 308 K, 318 K and 328 K

m	$\rho\ 10^{-3}$	u	$10^{11}\ \beta_s$	$Z/10^6$	$L_f/10^{-11}$	$10^2\ V_m$
			298 K			
0.0426	0.993017	1407.82	50.81	1.3980	4.454	6.132
0.0756	0.995423	1409.45	50.57	1.4030	4.444	6.141
0.1082	0.99727	1412.34	50.27	1.4085	4.430	6.153
0.1412	0.998293	1412.6	50.20	1.4102	4.427	6.170
0.1745	0.997717	1413.43	50.17	1.4102	4.426	6.196
			308 K			
0.0426	0.989291	1357.14	54.89	1.3426	4.713	6.159
0.0756	0.990976	1358.66	54.67	1.3464	4.704	6.173
0.1082	0.992156	1360.25	54.50	1.3496	4.696	6.189
0.1412	0.992356	1363.17	54.23	1.3527	4.685	6.211
0.1745	0.992856	1364.98	54.08	1.3552	4.678	6.231
			318 K			
0.0426	0.978923	1324.16	58.26	1.2963	4.942	6.230
0.0756	0.980658	1325.95	58.00	1.3003	4.931	6.243
0.1082	0.981093	1327.03	57.88	1.3019	4.926	6.264
0.1412	0.981998	1330.10	57.56	1.3062	4.912	6.282
0.1745	0.982412	1332.95	57.29	1.3095	4.900	6.303
			328 K			
0.0426	0.9686	1289.00	62.13	1.2485	5.192	6.301
0.0756	0.970123	1291.93	61.72	1.2533	5.175	6.316
0.1082	0.970778	1294.14	61.43	1.2563	5.163	6.336
0.1412	0.971513	1295.89	61.20	1.2590	5.153	6.355
0.1745	0.972182	1297.28	61.07	1.2612	5.148	6.374

Table 5. Densities, $(\rho)/(kg\ m^{-3})$, Ultrasonic Velocities, $(u)/(m\ s^{-1})$, Isentropic Compressibilities, $(\beta_s)/(Pa^{-1})$, Specific Acoustic Impedance, $(Z)/(kg\ m^{-2}\ s^{-1})$, Inter Molecular Free Lengths, $(L_f)/(m)$, and Molar Volume, $(V_m)/(m^3\ mol^{-1})$, for BAP in 80 mol% DMSO at 298 K, 308 K, 318 K and 328 K

m	$\rho\ 10^{-3}$	u	$10^{11}\ \beta_s$	$Z/10^6$	$L_f/10^{-11}$	$10^2\ V_m$
			298 K			
0.044	1.04812	1456.9	44.95	1.527	4.19	6.592
0.0766	1.049348	1460.44	44.68	1.5325	4.177	6.607
0.11	1.05004	1464.06	44.43	1.5373	4.165	6.625
0.1423	1.050628	1465.3	44.33	1.5395	4.161	6.644
0.1748	1.050484	1464.08	44.41	1.538	4.164	6.667
			308 K			
0.044	1.036071	1420.1	47.86	1.4713	4.401	6.671
0.0766	1.036468	1423.85	47.59	1.4758	4.389	6.691
0.11	1.036798	1427.83	47.31	1.4804	4.376	6.712
0.1423	1.036386	1430.08	47.18	1.4821	4.37	6.737
0.1748	1.035657	1433.93	46.96	1.4851	4.359	6.765
			318 K			
0.044	1.025906	1385.07	50.81	1.421	4.615	6.741
0.0766	1.026376	1389.96	50.43	1.4266	4.598	6.761
0.11	1.02637	1393.7	50.16	1.4305	4.585	6.784
0.1423	1.02613	1396.65	49.96	1.4331	4.576	6.808
0.1748	1.025341	1401.26	49.67	1.4368	4.563	6.836
			328 K			
0.044	1.015599	1352.97	53.79	1.3741	4.831	6.813
0.0766	1.016142	1357.92	53.37	1.3798	4.812	6.833
0.11	1.016327	1360.22	53.18	1.3824	4.804	6.855
0.1423	1.016473	1362.43	53	1.3849	4.795	6.877
0.1748	1.015901	1365.78	52.77	1.3875	4.785	6.904

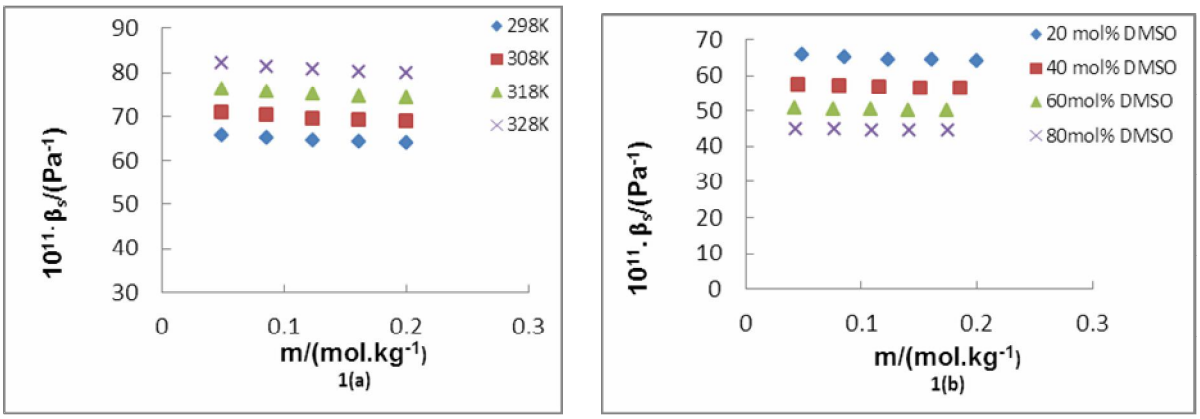

Fig. 1. Plots of (a) isentropic compressibility (β_s) *versus* molal concentration (m) of BAP for 20 mol% DMSO at different temperatures, and (b) isentropic compressibility (β_s) *versus* molal concentration (m) of BAP in binary mixtures of AN + DMSO containing 20, 40, 60 and 80 mol% DMSO at 298 K.

Specific acoustic impedance (Z) is the resistance offered to the sound wave by various components present in the mixture. As indicated by Tables 2-5, the acoustic impedance increases with increase in concentration throughout the composition range for all the temperatures studied. These increasing trends support the possibility of effective solute-solvent interactions occurring with increasing the amount of solute in the solution. This behavior is in a good agreement with the theoretical requirements where the value of both ρ and *u* increases while βs decreases with increasing solute concentration. Also, it can be seen that Z values decreases as DMSO mol% decreases in the solution (Fig. 2a) and temperature rises from 298 to 328 K (Fig. 2b). Decrease in Z values with increase in temperature again may be due to increase in thermal agitation leading to release of solvent molecules from solute, thereby, inhibiting the propagation of ultrasonic waves resulting in reduced values of specific acoustic impedance.

Intermolecular free length (L_f) which depends upon intermolecular attractive and repulsive forces is also an important indicator of various solute-solute or solute-solvent interactions taking place in the system. Analysis of Tables 2-5 shows that L_f values decreases with increasing concentration of BAP at all the temperatures and binary mixtures investigated. Decrease in free length with salt concentration in the solution may be attributed to liquid compression or increasing strength of hydrogen bonding and dipole-dipole interactions due to which molecules comes more close to each other resulting in stronger intermolecular cohesion. Other possible explanation may be clustering the molecules into cage like agglomerates due to polar group's associative effect dominating over other types of interactions. Also, L_f values have been found to increase with increasing temperature for 20 mol% DMSO (Fig. 3b). This may be attributed to weakening the dipolar association and hydrogen bonding due to increased thermal agitation with increase in temperature or due to increase in the mean distance between the molecules, therefore, lowering the potential energy of interactions leading to decrease in u and ρ values. The similar behavior was exactly reported for 40, 60 and 80 mol% DMSO (Tables 2-5). Also, for each of the four ternary mixtures studied at 298 K, L_f values have been found to be in the order; 20 mol% DMSO > 40 mol% DMSO > 60 mol% DMSO > 80 mol% DMSO (Fig. 3a), indicating stronger solute-solvent interactions in DMSO rich region. These trends have been found to be exactly the same for other investigated temperatures (Tables 2-5). According to Erying and Kincaid, regular decrease in free length results in increase of sound velocity which is in accordance with the present results of ultrasonic velocity [19]. This is also supported by relaxation strength (r) (describing various processes in which non equilibrium state of nuclear magnetization returns to equilibrium state) which decreases with increasing concentration throughout

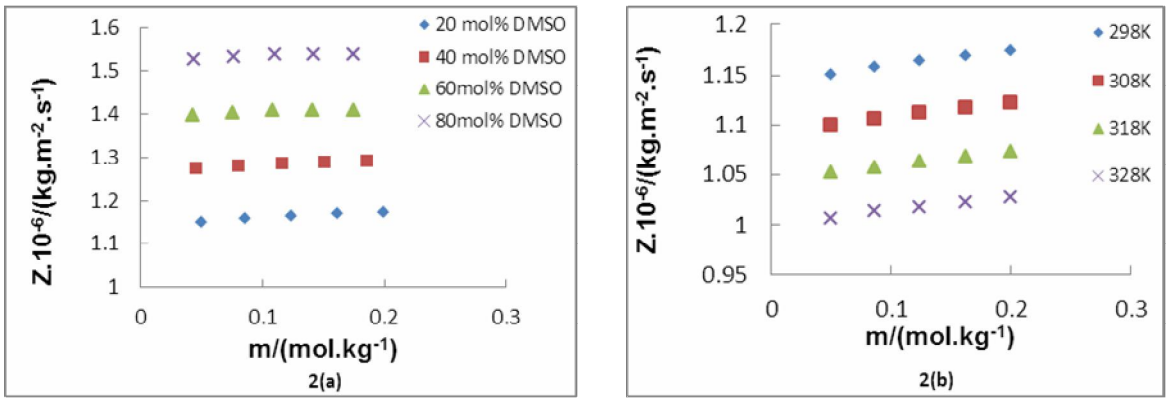

Fig. 2. Plots of (a) specific acoustic impedance (Z) *versus* molal concentration (m) of BAP in binary mixtures of AN + DMSO containing 20, 40, 60 and 80 mol% DMSO at 298 K, and (b) specific acoustic impedance (Z) *versus* molal concentration (m) of BAP for 20 mol% DMSO at different temperatures.

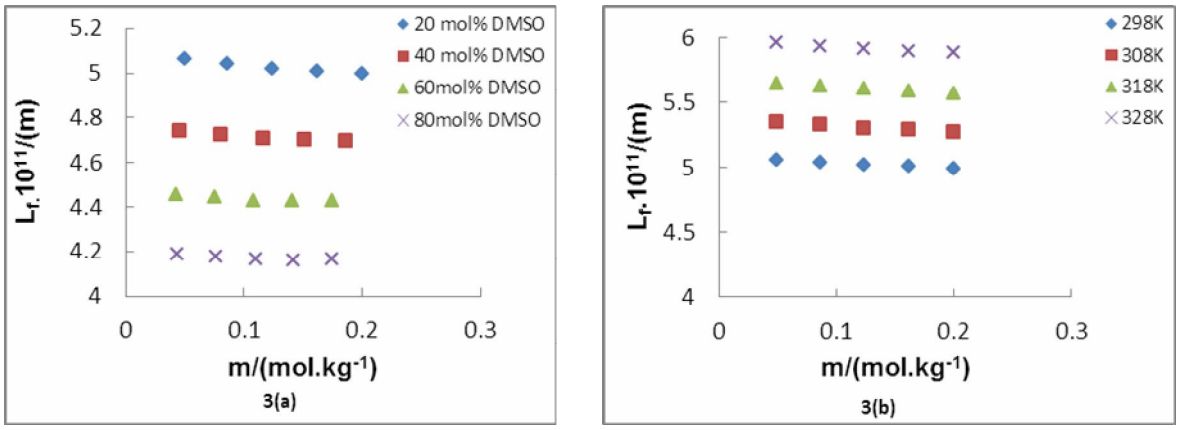

Fig. 3. Plots of (a) intermolecular free length (L_f) *versus* molal concentration (m) of BAP in binary mixtures of AN and DMSO containing 20, 40, 60 and 80 mol% DMSO at 298 K, and (b) intermolecular free length (L_f) *versus* molal concentration (m) of BAP for 20 mol% DMSO at different temperatures.

the composition range and all the temperatures under study (Tables 6-9).

Relative association is the parameter used to assess the extent of association of different components of the mixtures. It mainly depends on either breaking of associated solvent molecules when solute is added, leading to decrease in relative association (R_A), or solvation of the solute by free solvent molecules resulting in increasing the relative association.

It can be seen that relative association (R_A) increases linearly with an increase in concentration at all the studied temperatures (Tables 6-9), however, this variation is negligible at 80 mol% DMSO, indicating poor association which belongs to solute-solvent type interaction [20]. This may be attributed to the predominance over the breaking up of the solvent structure that leads to solvation enhancement of solute by free solvent molecules. However, R_A values show irregular trend with respect to temperature (Fig. 4).

Table 6. Wada's Constant, (W)/(m^3 mol^{-1} $Pa^{1/7}$), Rao's Constant, (R)/(m^3 mol^{-1} (m s^{-1})$^{1/3}$), Van der Waals Constant, (b)/(m^3 mol^{-1}), Free Volume, (V_f)/(m^3 mol^{-1}), Relative Association (R_A), and Relaxation Strength (r) for BAP in 20 mol% DMSO at 298 K, 308 K, 318 K and 328 K

m (mol kg^{-1})	W	R	b	10^3 V_f	R_A	r
			298 K			
0.0495	1.112	0.595	0.0566	3.069	1.0065	0.3169
0.0857	1.115	0.597	0.0569	3.092	1.0088	0.3126
0.1237	1.119	0.599	0.0572	3.115	1.0113	0.3096
0.1617	1.123	0.6	0.0575	3.139	1.0143	0.3083
0.1997	1.127	0.602	0.0577	3.158	1.0168	0.3069
			308 K			
0.0495	1.122	0.602	0.0552	3.052	1.0043	0.3526
0.0857	1.125	0.603	0.0555	3.075	1.0069	0.3494
0.1237	1.129	0.605	0.0558	3.099	1.0093	0.346
0.1617	1.133	0.607	0.0561	3.123	1.0121	0.344
0.1997	1.137	0.609	0.0564	3.149	1.0143	0.3428
			318 K			
0.0495	1.125	0.603	0.0534	2.993	1.0048	0.3921
0.0857	1.129	0.605	0.0537	3.016	1.0074	0.3893
0.1237	1.133	0.607	0.054	3.04	1.0101	0.3867
0.1617	1.136	0.609	0.0541	3.053	1.0125	0.3848
0.1997	1.141	0.611	0.0546	3.091	1.0146	0.3824
			328 K			
0.0495	1.129	0.606	0.0517	2.938	1.0045	0.4281
0.0857	1.133	0.608	0.052	2.962	1.0065	0.4245
0.1237	1.137	0.61	0.0523	2.988	1.009	0.4224
0.1617	1.141	0.612	0.0527	3.019	1.0112	0.4202
0.1997	1.149	0.616	0.0531	3.059	1.0133	0.4183

Standard uncertainties are: $u(\rho) = 3 \times 10^{-2}$ kg m^{-3}, $u(u) = 5 \times 10^{-2}$ m s^{-1}, u(T) = 0.03 K, and u(p) = 0.01 MPa.

Table 7. Wada's Constant, (W)/(m^3 mol^{-1} $Pa^{1/7}$), Rao's Constant, (R)/(m^3 mol^{-1} (m s^{-1})$^{1/3}$), Van der Waals Constant, (b)/(m^3 mol^{-1}), free Volume, (V_f)/(m^3 mol^{-1}), Relative Association (R_A) and Relaxation Strength (r) for BAP in 40 mol% DMSO at 298 K, 308 K, 318 K and 328 K

m (mol kg^{-1})	W	R	b	10^3 V_f	R_A	r
			298 K			
0.0495	1.201	0.638	0.0661	3.800	1.004	0.2725
0.0857	1.204	0.639	0.0664	3.822	1.0062	0.2691
0.1237	1.207	0.640	0.0668	3.852	1.0081	0.2662
0.1617	1.210	0.642	0.0672	3.883	1.0099	0.2648
0.1997	1.214	0.644	0.0675	3.910	1.0115	0.2646
			308 K			
0.0495	1.199	0.637	0.0636	3.684	1.0046	0.3127
0.0857	1.202	0.638	0.0640	3.713	1.0068	0.3104
0.1237	1.205	0.639	0.0643	3.736	1.0090	0.3087
0.1617	1.209	0.641	0.0647	3.770	1.0102	0.3069
0.1997	1.214	0.644	0.0652	3.812	1.0103	0.3039
			318 K			
0.0495	1.203	0.639	0.0617	3.618	1.0045	0.3489
0.0857	1.206	0.64	0.0621	3.648	1.0065	0.3461
0.1237	1.209	0.642	0.0624	3.672	1.0082	0.3438
0.1617	1.213	0.644	0.0629	3.710	1.0094	0.3409
0.1997	1.217	0.646	0.0632	3.740	1.0103	0.3396
			328 K			
0.0495	1.206	0.641	0.0598	3.551	1.0045	0.3845
0.0857	1.209	0.642	0.0602	3.580	1.0066	0.3819
0.1237	1.213	0.644	0.0605	3.605	1.0083	0.3796
0.1617	1.216	0.645	0.0609	3.636	1.0101	0.3779
0.1997	1.220	0.648	0.0613	3.670	1.0107	0.3747

Table 8. Wada's Constant, (W)/(m^3 mol^{-1} $Pa^{1/7}$), Rao's Constant, (R)/(m^3 mol^{-1} (m s^{-1})$^{1/3}$), Van der Waals Constant, (b)/(m^3 mol^{-1}), Free Volume (V_f)/(m^3 mol^{-1}), Relative Association (R_A) and Relaxation Strength (r) for BAP in 60 mol% DMSO at 298 K, 308 K, 318 K and 328 K

m (mol kg^{-1})	W	R	b	10^3 V_f	R_A	r
			298 K			
0.0426	1.304	0.687	0.0775	4.752	1.0031	0.2258
0.0756	1.307	0.689	0.0779	4.784	1.0052	0.2240
0.1082	1.311	0.690	0.0783	4.818	1.0064	0.2208
0.1412	1.314	0.692	0.0787	4.856	1.0073	0.2205
0.1745	1.320	0.695	0.0793	4.913	1.0065	0.2196
			308 K			
0.0426	1.296	0.682	0.0738	4.545	1.0084	0.2805
0.0756	1.299	0.684	0.0742	4.580	1.0097	0.2789
0.1082	1.303	0.686	0.0746	4.617	1.0105	0.2772
0.1412	1.309	0.689	0.0752	4.671	1.010	0.2741
0.1745	1.313	0.691	0.0757	4.717	1.0101	0.2722
			318 K			
0.0426	1.299	0.684	0.0717	4.467	1.0080	0.3151
0.0756	1.303	0.686	0.0721	4.501	1.0093	0.3132
0.1082	1.308	0.688	0.0725	4.541	1.0095	0.3121
0.1412	1.312	0.691	0.0731	4.592	1.0097	0.3089
0.1745	1.318	0.694	0.0736	4.639	1.0094	0.3060
			328 K			
0.0426	1.302	0.686	0.0695	4.379	1.0083	0.351
0.0756	1.306	0.688	0.07	4.421	1.0091	0.348
0.1082	1.311	0.69	0.0705	4.467	1.0092	0.3458
0.1412	1.316	0.693	0.0709	4.506	1.0095	0.3440
0.1745	1.320	0.695	0.0713	4.545	1.0099	0.3426

Table 9. Wada's constant, (W)/(m^3 mol^{-1} $Pa^{1/7}$), Rao's Constant, (R)/(m^3 mol^{-1} (m s^{-1})$^{1/3}$), Van der Waals Constant, (b)/(m^3 mol^{-1}), Free Volume, (V_f)/(m^3 mol^{-1}), Relative Association (R_A) and Relaxation Strength (r) for BAP in 80 mol% DMSO at 298 K, 308 K, 318 K and 328 K

m (mol kg^{-1})	W	R	b	10^3 V_f	R_A	r
			298 K			
0.044	1.427	0.747	0.0919	6.058	1.0004	0.1709
0.0766	1.431	0.75	0.0925	6.111	1.0007	0.1668
0.11	1.436	0.752	0.0932	6.175	1.0006	0.1627
0.1423	1.441	0.755	0.0937	6.225	1.0009	0.1613
0.1748	1.445	0.757	0.0941	6.274	1.001	0.1627
			308 K			
0.044	1.431	0.75	0.0892	5.951	1.0001	0.2122
0.0766	1.436	0.753	0.0899	6.015	0.9996	0.2081
0.11	1.442	0.756	0.0905	6.074	0.999	0.2036
0.1423	1.448	0.759	0.0912	6.144	0.9981	0.2011
0.1748	1.455	0.763	0.092	6.224	0.9965	0.1968
			318 K			
0.044	1.434	0.751	0.0865	5.831	1.0003	0.2506
0.0766	1.439	0.755	0.0872	5.896	0.9996	0.2453
0.11	1.445	0.758	0.0879	5.963	0.9987	0.2413
0.1423	1.451	0.761	0.0886	6.032	0.9977	0.238
0.1748	1.459	0.765	0.0894	6.111	0.9959	0.233
			328 K			
0.044	1.437	0.754	0.0841	5.73	0.9997	0.285
0.0766	1.443	0.757	0.0848	5.794	0.999	0.2797
0.11	1.448	0.76	0.0854	5.854	0.9986	0.2773
0.1423	1.454	0.762	0.0859	5.907	0.9982	0.2749
0.1748	1.46	0.766	0.0866	5.979	0.9969	0.2713

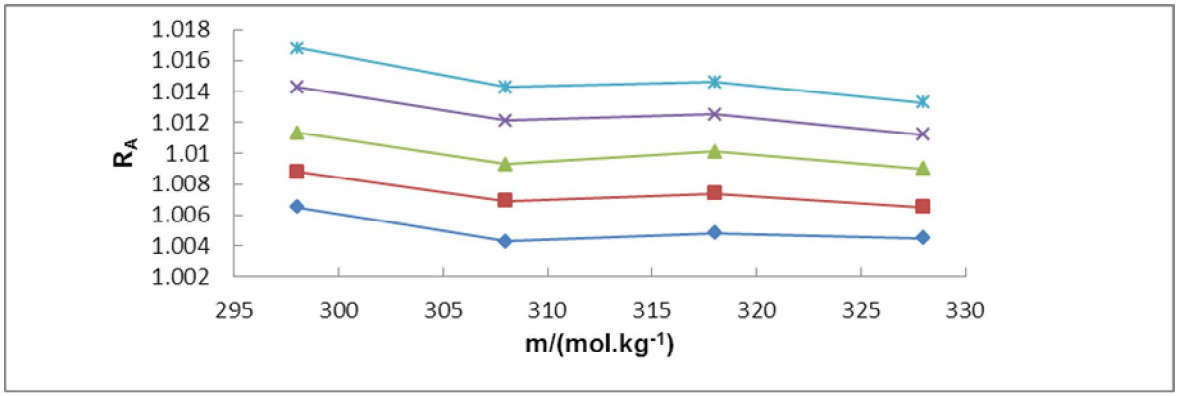

Fig. 4. Plots of relative association (R_A) *versus* temperature for BAP in 20 mol% DMSO with different molalities, ♦ is 0.0495 mol kg^{-1}; ■ is 0.0857 mol kg^{-1}; ▲ is 0.1237 mol kg^{-1}; × is 0.1657 mol kg^{-1}; and ∗ is 0.1997 mol kg^{-1}.

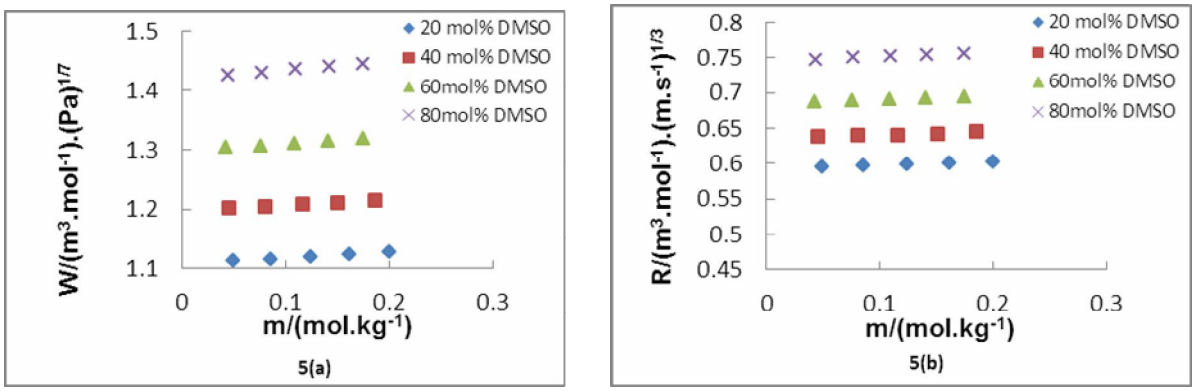

Fig. 5. Plots of (a) Wada's constant (W) *versus* molal concentration (m), and (b) Rao's constant (R) versus molal concentration of BAP in binary mixtures of AN and DMSO containing 20, 40, 60 and 80 mol% DMSO at 298K.

Non linear variation of R_A with temperature may be due to change in orientation and arrangement of molecules of the components due to thermal agitation indicating the dominance of solute-solute interactions rather than solute-solvent interactions with a rise in temperature.

Rao's constant is the distance travelled per unit time by a sound wave propagating in elastic medium. It is the cube root of sound velocity through one molar volume of solution and Wada's constant is the measure of relative volume change of a fluid due to change in pressure. As indicated by Tables 6-9, the Rao's constant and Wada's constant are independent of temperature and their values in general increase with increasing DMSO mol% in the mixtures.

However, no appreciable change has been observed with increasing the concentration of the solution [Figs. 5a and b] indicating weak association between the molecules. The linear variation of W and R with solvent composition indicates (a) absence of complex formation, (b) weak induced dipole-induced dipole interactions, (c) presence of more number of molecules in a given region of space leading to a tight packing hence stronger interactions in the systems under study [20].

It was found that Van der Waals constant decreases with increasing temperature for 20 mol% DMSO and increases with increase in concentration throughout the whole composition range at 298 K (Figs. 6a and b). Similar

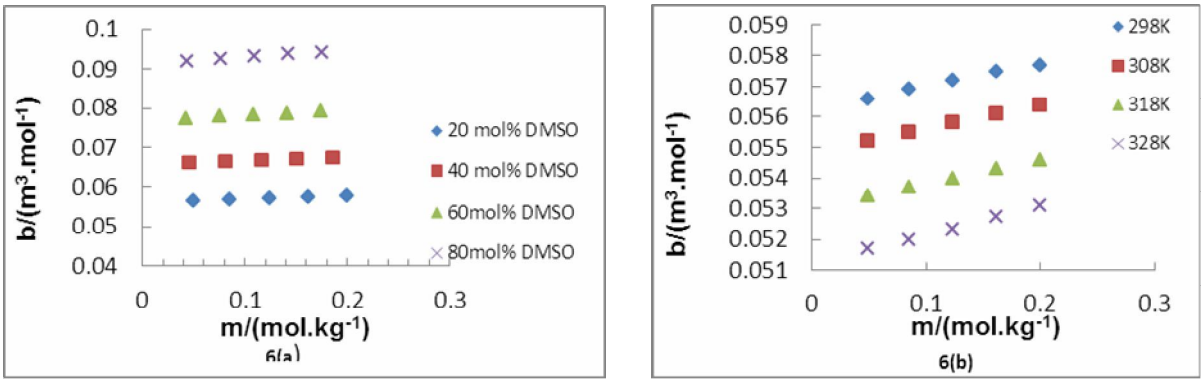

Fig. 6. Plots of (a) Van der Waals constant *versus* molal concentration (m) of BAP in binary mixtures of AN and DMSO containing 20, 40, 60 and 80 mol% DMSO at 298 K, and (b) Van der Waals constant *versus* molal concentration (m) of BAP for 20 mol% DMSO at different temperatures.

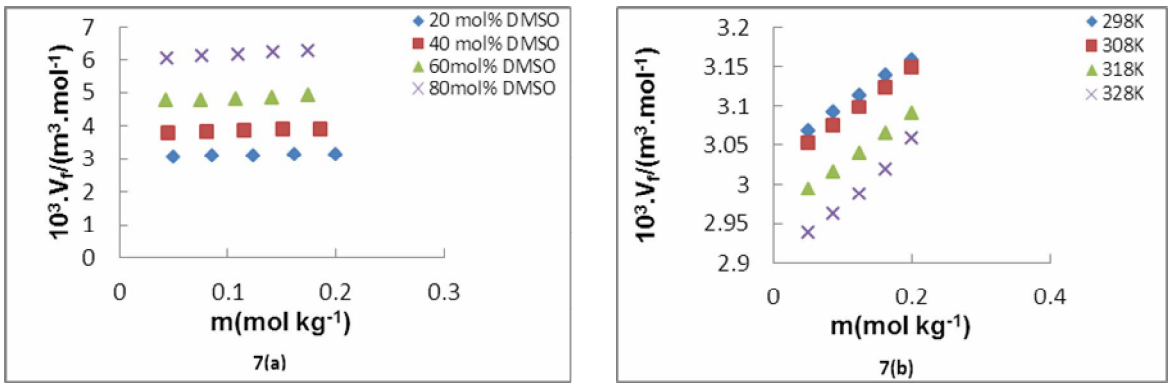

Fig. 7. Plots of (a) free volume (V_f) *versus* molal concentration (m) of BAP in binary mixtures of AN and DMSO containing 20, 40, 60 and 80 mol% DMSO at 298 K, and (b) free volume (V_f) *versus* molal concentration (m) of BAP for 20 mol% DMSO at different temperatures.

behavior was observed for other binary mixtures studied at 308, 318 and 328 K (Tables 6-9). The decrease of b values with rise in temperature is due to weakening the binding forces between solute and solvent that leads to reduced solute-solvent interactions. These results are in a good agreement with the conclusion drawn from the studies of other parameters. Free volume (V_f) is the average volume, in which centre of the molecule can move due to repulsion from other molecules. It can be seen from the plots (Figs. 6a and 6b) that free volume increases with increasing concentration.

Free volume increases due to the decrease in molecular association of solvent molecules in the system causing lowering the internal pressure, hence, weakening the cohesive forces that leads to breaking solvent structure, indicating strong solute-solvent interactions [21]. Also with an increase in temperature free volume decreases, showing that the strength of interaction is decreasing gradually as temperature is increased which is in a good agreement with the results obtained from other parameters. Molar volumes are positive and increase with an increase in concentration and temperature, Tables 6-9. These increasing trends are due to reduced intermolecular interactions between mixture components and dependence of molar volume upon

molecular mass and density of solvent mixtures.

CONCLUSIONS

The ultrasonic velocity and density measurements on binary mixtures of AN and DMSO at different temperatures are carried out. The conclusion drawn is that the solute-solvent interactions become stronger as concentration is increased, representing compact structure and formation of tight solvation layer around BAP ($C_4H_9NH_3ClO_4$) which is supported by a decrease in the values of isentropic compressibility (βs), intermolecular free length (L_f), relaxation strength (r) and an increase in the values of specific acoustic impedance (Z), relative association (R_A), Wada's constant (W), Rao's constant (R), Van der Waals constant (b) and free volume (V_f) with an increase in salt concentration throughout the composition range. Also, increasing DMSO mol% in binary mixtures has made subtle impact on all the acoustical parameters without altering the general trend. Overall, smaller values of βs, L_f, r and more positive values of Z, W, R, b and V_f for 80 mol% DMSO compared to other binary mixtures indicate the stronger solute-solvent interactions in DMSO rich region. All the derived parameters in common indicated that temperature rise results in reduction of solute-solvent interactions due to thermal agitation causing the release of solvent molecules from solute, therefore, reduces interactions. The absence of complex formation is confirmed by the linear variation of βs, Z, R and W values with change in the composition of binary mixtures studied. However, non linear variation of relative association with temperature indicates that solute-solute interaction dominates over solute-solvent interactions in the system investigated. These results are due to different degrees of different solute-solute, solvent-solvent and solute-solvent interactions in the studied ternary systems.

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