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Thermo-acoustic Parameters of Tetrabutylammonium borate and Perchlorate in Non-aqueous Solvents

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ABSTRACT

Interactions of electrolytes in a binary mixture can be determined by various techniques. Ultrasonic velocity measurements prove to be one of the important tools for measuring various acoustic properties at variable temperature. Thermo-acoustic parameters like Isentropic compressibility (κ_s), Acoustic impedance (Z), Free volume (V_f), Absorption coefficient (Ab_{scoeff}), Intermolecular free length (L_f), Gibb's free energy (ΔG), Relaxation time (τ), Rao's constant (R_m), Internal pressure (π_i), Wada's constant (w), and Entropy (H) for Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) and Tetrabutylammonium perchlorate (Bu_4NClO_4) was calculated using experimental ultrasonic velocities, viscosities and densities at three different temperatures (298K, 308 K and 318K) and 1 atmospheric pressure in non-aqueous solvents like Dimethylsulfoxide (DMSO), Pyridine (Py) and their binary mixtures at 0, 20, 40, 60, 80 and 100 mol% of Py at variable temperatures ranging from 298K to 318K. Both Bu_4NBPh_4, Bu_4NClO_4, showed an increase in the ultrasonic velocity values at all the temperatures. This shows that molecular interactions are taking place in both the electrolytes. These increases in the molecular interactions with increase in the concentration of electrolytes in the solvent mixture were discussed in terms of solvent structural effects. And results showed the greater molecular interaction in DMSO rich regions.

Keywords: Acoustic studies, Non-aqueous solvents, Molecular interaction, Ultrasonic velocity, Density.

INTRODUCTION

The structure and interactions of electrolytes in a binary mixture can be determined using a variety of approaches and spectroscopic techniques. X-ray crystallography, chromatography, NMR, EPR, vibration and Raman spectroscopy, neutron and light scattering, circular dichroism (CD), infrared spectroscopy, and ultrasonic velocity measurements are among them. Ultrasonic velocity measurements have been discovered to be the most important method in the investigation of structure and molecular interactions occurring in solutions among these techniques. Ultrasonic wave propagation in a material has become a basic test for determining its properties[1]. Many researchers have demonstrated the critical and fundamental function of molecular specifics of the solvent species in determining particular interactions, which are responsible for macroscopic thermodynamic and other associated properties in non-electrolyte solutions[2,3]. Materials are typically treated in fluid

form in the chemical process industries, so their physical, chemical, and transport properties are essential[4,5]. The ultrasonic technique is a fast and non-destructive way to characterize materials[6]. The ultrasonic velocity in a liquid is fundamentally related to the binding forces between atoms or molecules, and it has been successfully used to characterize the physicochemical activity of liquid mixtures in the field of interactions and structural aspect studies[7-9]. The ultrasonic velocity, in combination with density and viscosity, provides a wealth of knowledge about ion interactions, dipoles, hydrogen bonding, multipolar and dispersive forces[10]. Since intermolecular and intramolecular association, complex formation, dipolar interactions, and related structural changes affect the system's compressibility, which causes corresponding variations in ultrasonic velocity, ultrasonic propagation parameters provide useful information about the behavior of liquid systems[11]. The various acoustic parameters are used to interpret the type and frequency of molecular interactions in the system[12]. Intermolecular interactions have an effect on the structural arrangement and form of molecules[13,14]. In the present studies thermo acoustic parameters like Isentropic compressibility (κ_s), Acoustic impedance (Z), Free volume (V_f), Absorption coefficient (Ab_{scoeff}), Intermolecular free length (L_f), Gibb's free energy (ΔG), Relaxation time (τ), Rao's constant (R_m), Internal pressure (πi), Wada's constant (w), and Entropy (H) for Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) and Tetrabutylammonium perchlorate (Bu_4NClO_4) was calculated using experimental velocities, viscosities and densities at three different temperatures (298K, 308 K and 318K) and 1 atmospheric pressure in non-aqueous solvents like Dimethylsulfoxide (DMSO), Pyridine (Py) and their binary mixtures at 0, 20, 40, 60, 80 and 100 mol% of Py at variable temperatures ranging from 298K to 318K.

MATERIALS AND METHODS

Apparatus

Using experimental densities, the necessary proportion of solvents were mixed with the preliminary conversion of the required mass of each solvent to a volume at 298 K. The solvents were mixable throughout. An electronic balance (SAG 285, Mettler Toledo) with a precision of $\pm 10^{-7}$ kg was used for the mass measurements. Each solvent were kept in an air tight container to avoid any kind of contamination. Density and ultrasonic velocity were measured by DSA 5000M from Anton Parr at 298K using long tube of borosilicate glass (U shaped). The sample was then excited to oscillate at its characteristic frequency of 2MHz. Apparatus was calibrated at the beginning of every set of reading with distilled water and air. For calibration, the density & ultrasonic velocity of known liquids like water (ρ = 0.99705 g cm^{-3}, u = 1496.68 ms^{-1}) and acetonitrile (ρ = 0.77687 g cm^{-3}, u = 1280.9 ms^{-1}) were measured at 298K and it agreed well with literature values of ρ = 0.99707 g cm^{-3} [15], u = 1496.6 ms^{-1} [16] for water and ρ = 0.77685 g cm^{-3}, u = 1280.8 ms^{-1} [17] for acetonitrile. Accuracy in the density value was $\pm$ 1 x 10^{-5} g.cm^{-3} and for ultrasonic velocity was $\pm$ 0.1 ms^{-1}. All the experiments were performed in temperature controlled DSA apparatus ($\pm$ 0.01K). Viscosity was measured by SV-10 viscometer (A&D Co. Ltd.) at a frequency of 30Hz. The apparatus was calibrated prior every reading with distilled water. Each set of reading was repeated twice for better reproducibility of result. The accuracy in the viscosity value was found to be $\pm$ 1%. Dielectric constant meter (DCL-01) (SES Instruments Pvt. Ltd., Roorkee, India) operating at 1 Mhz frequency was used to measure dielectric constant (ε) with an accuracy of $\pm$ 1%[18].

Solvent Purification

Dimethylsulfoxide (DMSO), (Merck)[19] with boiling point 181-189^{0}C was purified by repeated crystallisations. The crystallised solvent was further kept over 4A^o molecular sieves for 2-3 days with occasional shaking and fractionated through a long vertical column under reduced pressure and middle fraction with density 1.0960 g cm^{-3} and viscosity 1.990 mPa.s was collected and stored. Pyridine (Py), (Merck)[19] with boiling point of 114-115^{0}C was refluxed over KOH for 3 h and was distilled at atmospheric pressure and middle fraction with density 0.9786 g cm^{-3} and viscosity 0.881 mPa.s was collected and stored.

Table 1: Source and Purity of Solvents

Solvent	Provenance	CAS-No	Molecular Formula	Molar Mass (g mol^{-1})	Grade	Densitya (g cm^{-3})	Mass Fraction Purity	Water Content
Dimethylsulfoxide (DMSO)	E.Merck	67-68-5	C_2H_6OS	78.13	ACS	1.0953	0.998[b]	0.0002[c]
Pyridine (Py)	E.Merck	110-86-1	C_5H_5N	79.1	ACS, Reag.	0.9786	0.995[b]	0.0001[c]

[a]density at 298 K by Anton Parr density meter (DSA 5000 M) with a precision of 0.0004 g cm^{-3}

[b]From Gas Chromatography Analysis

[c]Karl-Fischer Titration Method

Preparation of Tetrabutylammonium perchlorates and Tetrabutylammonium tetraphenyl borate

Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) was prepared by mixing the aqueous solutions of tetrabutylammonium bromide (Bu_4NBr) and sodium tetraphenylborate ($NaBPh_4$) in 1:1 molar ratio. The white powder of Bu_4NBPh_4 precipitated out which was filtered and dissolved in acetone and again was precipitated on adding distilled water in excess. Process of precipitation was repeated twice. The salt was dried under vacuum at 60°C over P_2O_5 for 2 days. Purity was checked by measuring its melting point. The measured melting point was 222-224°C which agreed well with the reported value of 223-225°C[19]. Tetrabutylammonium perchlorate (Bu_4NClO_4) was prepared by prepared by dissolving silver perchlorate monohydrate ($AgClO_4.H_2O$) (sisco research laboratories) and tetrabutyl ammonium bromide (Bu_4NBr) in aqueous acetone mixtures in 1:1 molar ratio. After mixing, the solution was filtered, concentrated by evaporation and again filtered and heated till salt separated out. The process of dissolving in acetone and recrystallizing was repeated twice and salt was dried under P_2O_5 for 2 days at 60°C.

Theory

The Isentropic compressibility (κ_s) and Acoustic parameters like Acoustic impedance (Z), Free volume (V_f), Absorption coefficient (Ab_{scoeff}), Internal pressure (πi), Gibb's free energy (ΔG), Relaxation time (τ), Rao's constant (R_m), Intermolecular free length (L_f), Wada's constant (w), and Entropy (H) was calculated using experimental velocities, viscosities and densities at three different temperatures (298K, 308 K and 318K) and 1 atmospheric pressure.

Isentropic compressibility (κ_s) was measured by[20]

$$\kappa_s = \frac{1}{\rho \times u^2} \quad [1]$$

where ρ denotes density and u, ultrasonic velocity.

The acoustic impedance (Z) of a medium was calculated by a relation.[21]

$$Z = \rho \times u \quad [2]$$

Intermolecular free length (L_f)[21] between the molecules in the liquid state was determined by the relation.

$$L_f = K\sqrt{\kappa_s} \quad [3]$$

Where K is constant whose value is taken as 1.995×10^{-6} at 298K, 2.095×10^{-6} at 308K and 2.115×10^{-6} at 318K.

Relaxation time (τ) was using the following relationship.[22]

$$\tau = \frac{4\eta}{3\kappa_s} \quad [4]$$

where η is the viscosity coefficient.

Free Volume (V_f) has been calculated from the relation.[21]

$$V_f = \left(\frac{M_{eff.}\, u}{K\eta}\right)^{3/2} \quad [5]$$

Where, M_{eff} is the effective molecular mass, K is temperature dependent constant.

Absorption coefficient (Ab_{scoeff}) of the medium was found by a relation.[21]

$$Abs_{coeff} = \frac{8\pi^2 \eta}{3\rho \times u^2} \quad [6]$$

The internal pressure (πi) was calculated by the relation.[21]

$$\pi_i = bRT\left(\frac{K.\eta}{u}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \quad [7]$$

Where b refers to cubic packing of solvent taken to be equal to 2, K is dimensionless constant having a value 4.281×10^9, T is absolute temperature, η is viscosity in $Nm^{-2}s$, R is gas constant, u is ultrasonic velocity in $m\ s^{-1}$, M_{eff} is effective molecular weight and ρ is density in $kg\ m^{-3}$.

Gibbs free energy (ΔG) was determined from acoustic relaxation time (τ).[20]

$$\Delta G = RT \ln\left(\frac{K.T.\tau}{\hbar}\right) \quad [8]$$

Where K is Boltzmann constant, ħ is planck constant and τ is relaxation time.

Molar sound velocity or Rao's constant (R_m) has been evaluated from the relation.[20]

$$R_m = \frac{M_{eff}}{\rho} \cdot u^{1/3} \quad [9]$$

Wada's constant (w) has been calculated using isentropic compressibility values.[20]

$$W = (\kappa_s)^{-1/7} \cdot \frac{M_{eff}}{\rho} \quad [10]$$

Enthalpy (H) has been calculated by the relation.

$$H = \pi_i \times V_m \quad [11]$$

where $V_m = \frac{M_{eff}}{\rho}$

RESULTS AND DISCUSSIONS

In the present studies the Isentropic compressibility (κ_s) and Acoustic parameters like Acoustic impedance (Z), Free volume (V_f), Absorption coefficient (Ab_{scoeff}), Internal pressure (π_i), Gibb's free energy (ΔG), Relaxation time (τ), Rao's constant (R_m), Intermolecular free length (L_f), Wada's constant (w), and Entropy (H) was calculated using experimental velocities, viscosities and densities at three different temperatures (298K, 308 K and 318K) and 1 atmospheric pressure for Bu_4NClO_4 and Bu_4NBPh_4 in a binary mixtures of DMSO+Py at 0, 20, 40, 60, 80 and 100 mol% composition of Py.

Table 2: Density (ρ), viscosity (η), and ultrasonic velocity (u) for DMSO and Py at 298K

Solvents	ρ/(g cm^{-3})		η/(mPa s)		u/(m s^{-1})	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
DMSO	1.0953	1.09530[18]; 1.09533[19]; 1.09537[23]	1.99	2.012[24]; 1.99[18];	1486.49	1486.74[19]
Py	0.9786	0.9782[19,25]	0.88	0.88[19]; 0.89[26]	1418.14	1419.2[19]

Table 3: Density (ρ), Viscosity (η) and ultrasonic velocity (u) for DMSO+Py binary mixture at various temperaturesa

	DMSO+Py								
Mol % Py	ρ (g.cm^{-3})			η (mPa.s)			u (m.s^{-1})		
	298 K	308 K	318 K	298 K	308 K	318 K	298 K	308 K	318 K
0	1.0953	1.0852	1.0753	1.99	1.645	1.385	1486.49	1467.07	1434.18
20	1.0702	1.0633	1.0535	1.61	1.455	1.236	1471.21	1453.97	1419.78
40	1.0494	1.0441	1.0342	1.32	1.284	1.089	1457.83	1442.84	1408.32
60	1.0233	1.0197	1.0099	1.12	1.093	0.932	1444.98	1428.76	1392.62
80	1.0033	0.9972	0.9873	1.01	0.942	0.787	1432.41	1407.8	1370.3
100	0.9786	0.9695	0.9594	0.88	0.771	0.655	1418.14	1381.7	1341.87

[a]Ref:[19]

The previous investigations of the solvation of Me_4N^+, Et_4N^+, Pr_4N^+ and Bu_4N^+ ions are limited to 2-methoxyethanol, water[27], N,N-dimethylformamide, acetonitrile, DMSO and n-butyronirile and their binary mixtures[28,29]. Since there is a limited data available for DMSO and Py, it is expected to be good solvents for a comparative study of the solvation behaviour of tetraalkylammonium ions. As evident from Tables 4-9, with the increase in the concentration of electrolytes (Bu_4NBPh_4, Bu_4NClO_4), the density shows an increase in trend and moreover ultrasonic velocity (u) increases. Increment in the ultrasonic velocity is related to compactness of medium as the number of molecules per unit volume increases, thus the medium becomes denser. It has been further supported by the fact that the electrolytes show two types of behaviour either structure maker or structure breaker. Increase in ultrasonic velocity corresponds to structure making tendency of electrolytes and decrease in velocity refers to structure breaking tendency.

Table 4: Concentration and calculated Acoustic parameters of Bu_4NBPh_4 in DMSO+Py at 298 K

Conc mol.Kg^{-3}	ρ g.cm^{-3}	u m.s^{-1}	κ_s.10^6 bar^{-1}	$K_{s\Phi}$	Z.10^6 Kg m-^{2}s^{-1}	L_f.10^{-5} m	R_A	τ.10^{-12} s	ΔG. 10^{24} J mol^{-1}	Ab_{scoeff} 10^{-8} Npm^{-1}s^2	V_f. 10^{-5} m^3 mol^{-1}	π_i. 10^3 Nm^{-2}	R_m	W	H. 10^{-3} KJ mol^{-1}
								100 mol% Py							
0.0389	0.9796	1424.01	50.34	152.67	1.41	0.014	0.9988	5.79	3.484	114.174	1.68	4234.65	923.59	46.9	34.76
0.0814	0.9801	1430.62	49.85	155.59	1.436	0.0138	0.9949	5.59	3.479	110.231	1.69	4226.29	924.55	46.94	34.67
0.1239	0.9819	1434.84	49.46	157.88	1.455	0.0136	0.9927	5.45	3.475	107.469	1.7	4225.24	923.76	46.91	34.6
0.1664	0.9827	1440.29	49.05	159.71	1.478	0.0134	0.9888	5.29	3.47	104.314	1.7	4219.53	924.18	46.93	34.53
0.2089	0.9838	1444.78	48.69	161.13	1.499	0.0132	0.9855	5.15	3.466	101.554	1.71	4216.11	924.1	46.92	34.46
								80 mol% Py							
0.0373	1.0036	1437.53	48.21	167.79	1.459	0.0137	0.9954	6.41	3.501	126.4	1.35	4639.09	899.72	45.83	36.98
0.0798	1.0051	1440.39	47.95	178.55	1.484	0.0135	0.9918	6.2	3.495	122.259	1.36	4639.1	898.97	45.79	36.92
0.1223	1.0068	1442.97	47.71	181.75	1.509	0.0133	0.9884	6.01	3.49	118.512	1.36	4640.17	897.99	45.75	36.87
0.1648	1.0076	1445.36	47.51	187.87	1.533	0.0131	0.9843	5.83	3.485	114.926	1.36	4638.79	897.77	45.74	36.83
0.2073	1.0084	1447.48	47.33	192.02	1.552	0.0129	0.9812	5.69	3.482	112.202	1.37	4637.84	897.5	45.73	36.79
								60 mol% Py							
0.0355	1.0245	1447.78	46.56	171.43	1.501	0.0135	0.9966	6.79	3.51	133.854	1.18	4926.44	881.08	44.99	38.36
0.078	1.0257	1450.31	46.35	182.61	1.528	0.0132	0.9923	6.57	3.504	129.457	1.19	4925.98	880.56	44.97	38.32
0.1205	1.0265	1452.49	46.17	189.06	1.554	0.013	0.9878	6.35	3.499	125.237	1.19	4924.84	880.31	44.96	38.28
0.163	1.0278	1453.74	46.04	193.34	1.578	0.0128	0.9842	6.16	3.494	121.471	1.21	4926.88	879.45	44.92	38.24
0.2055	1.0286	1455.46	45.89	195.59	1.602	0.0126	0.9804	5.99	3.49	118.019	1.22	4926.52	879.11	44.91	38.21
								40 mol% Py							
0.0338	1.0507	1458.83	44.72	189.64	1.533	0.1334	1.001	7.87	3.533	155.204	0.93	5434.92	859.04	44.01	41.16
0.0763	1.0512	1459.71	44.65	205.31	1.534	0.1333	1.0013	7.86	3.533	154.961	0.93	5435.01	858.81	44	41.14
0.1188	1.0521	1460.34	44.57	207.12	1.536	0.1332	1.002	7.84	3.533	154.683	0.93	5436.93	858.19	43.97	41.12
0.1613	1.0529	1460.88	44.5	208.57	1.538	0.1331	1.0026	7.83	3.532	154.441	0.93	5438.69	857.65	43.95	41.1
0.2038	1.0534	1461.11	44.47	211.93	1.539	0.133	1.0031	7.83	3.532	154.336	0.93	5439.98	857.29	43.93	41.09
								20 mol% Py							
0.0322	1.0724	1469.78	43.17	200.41	1.576	0.1311	1.0024	9.27	3.561	182.741	0.7	6084.76	841.05	43.2	45.01
0.0747	1.0717	1471.55	43.09	208.29	1.577	0.131	1.0013	9.25	3.559	182.402	0.71	6078.45	841.94	43.24	44.99
0.1172	1.0709	1473.12	43.03	212.29	1.578	0.1309	1.0002	9.24	3.559	182.148	0.72	6072.18	842.87	43.28	44.98
0.1597	1.0698	1474.43	42.99	216.12	1.577	0.1308	0.9989	9.23	3.559	181.979	0.73	6065.33	843.98	43.33	44.97
0.2022	1.0686	1475.98	42.95	218.56	1.577	0.1307	0.9974	9.22	3.558	181.809	0.73	6057.61	845.23	43.38	44.96
								0 mol% Py							
0.0306	1.0947	1486.89	41.32	218.67	1.628	0.1282	0.9994	10.96	3.586	216.193	0.51	6878.07	820.98	42.27	49.47
0.0731	1.0937	1487.93	41.3	217.15	1.627	0.1282	0.9982	10.96	3.586	216.088	0.52	6871.47	821.92	42.31	49.47
0.1156	1.0929	1489.04	41.26	214.47	1.627	0.1281	0.9972	10.95	3.586	215.878	0.53	6865.56	822.73	42.35	49.46
0.1581	1.0903	1493.24	41.13	211.81	1.628	0.1279	0.9939	10.91	3.585	215.198	0.54	6845.02	825.47	42.47	49.43
0.2006	1.0881	1496.71	41.02	210.44	1.629	0.1278	0.9912	10.88	3.585	214.623	0.55	6827.88	827.78	42.57	49.41

Standard Uncertainty: u(T) = ± 0.01 K, u (mole %) = ± 0.01, u(ρ) = ± 0.0004 g•cm^{-3}, u(P) = 0.1 MPa

Table 5: Concentration and calculated Acoustic parameters of Bu4NBPh4 in DMSO+Py at 308 K

Conc mol.Kg^{-3}	ρ g.cm^{-3}	u m.s^{-1}	κ_s.10^6 bar^{-1}	$K_{s\Phi}$	Z. 10^6 Kg m^{-2} s^{-1}	L_f .10^{-5} m	R_A	τ . 10^{-12} s	ΔG.10^{24} J mol^{-1}	Ab_{scoeff}.10^8 Npm^{-1}s^2	V_f .10^5 m^3 mol^{-1}	π_i. 10^3 N m^{-2}	R_m	W	H. 10^{-3} KJ mol^{-1} m.s^{-1}
							100 mol% Py								
0.0389	0.9703	1387.18	53.56	171.01	1.345	0.1533	0.9995	5.5	3.843	108.573	1.96	4124.45	924.33	46.93	34.18
0.0814	0.9717	1391.48	53.15	180.47	1.352	0.1527	0.9999	5.46	3.842	107.742	1.97	4122.03	923.95	46.91	34.11
0.1239	0.9725	1395.09	52.83	191.66	1.356	0.1522	0.9998	5.43	3.841	107.093	1.98	4118.95	923.99	46.91	34.06
0.1664	0.9731	1399.17	52.49	195.48	1.361	0.1517	0.9995	5.39	3.84	106.404	1.99	4114.63	924.32	46.93	34
0.2089	0.9737	1403.22	52.16	197.45	1.366	0.1513	0.9991	5.36	3.839	105.735	1.99	4110.38	924.64	46.94	33.94
							80 mol% Py								
0.0373	0.9976	1412.84	50.22	175.12	1.409	0.1484	0.9992	6.3	3.833	124.381	1.48	4629.33	899.92	45.83	37.12
0.0798	1.0003	1414.14	49.99	185.83	1.414	0.1481	1.0016	6.27	3.832	123.811	1.48	4635.55	897.76	45.74	37.07
0.1223	1.0017	1416.47	49.76	191.76	1.418	0.1477	1.0024	6.24	3.831	123.242	1.48	4636.05	897	45.7	37.02
0.1648	1.0024	1419.02	49.54	198.06	1.422	0.1474	1.0025	6.22	3.831	122.697	1.49	4634.04	896.91	45.7	36.98
0.2073	1.0027	1421.86	49.33	202.29	1.425	0.1471	1.0021	6.19	3.83	122.177	1.49	4630.34	897.24	45.71	36.94
							60 mol% Py								
0.0355	1.0189	1432.98	47.79	200.75	1.46	0.1448	0.9982	6.96	3.825	137.336	1.2	5037.47	882.89	45.07	39.44
0.078	1.0196	1434.52	47.66	212.36	1.462	0.1446	0.9985	6.94	3.825	136.962	1.2	5037.07	882.6	45.06	39.41
0.1205	1.0208	1435.28	47.55	215.59	1.465	0.1444	0.9995	6.92	3.824	136.646	1.21	5039.69	881.71	45.02	39.39
0.163	1.0223	1435.72	47.46	218.61	1.467	0.1443	1.0009	6.91	3.823	136.387	1.21	5043.85	880.51	44.96	39.36
0.2055	1.0231	1436.87	47.34	218.98	1.47	0.1441	1.0014	6.89	3.822	136.043	1.21	5044.46	880.06	44.94	39.34
							40 mol% Py								
0.0338	1.0429	1446.54	45.82	207.88	1.508	0.1418	0.9979	7.84	3.819	154.684	0.958	5536.09	863.02	44.18	42.24
0.0763	1.0425	1448.49	45.72	217.42	1.51	0.1416	0.9971	7.82	3.818	154.347	0.96	5530.94	863.74	44.21	42.22
0.1188	1.0422	1449.28	45.68	226.3	1.51	0.1415	0.9967	7.82	3.813	154.212	0.961	5528.38	864.15	44.23	42.21
0.1613	1.0418	1450.33	45.63	229.43	1.51	0.1415	0.996	7.81	3.811	154.043	0.962	5524.96	864.69	44.25	42.2
0.2038	1.0412	1451.28	45.59	232.69	1.511	0.1414	0.9952	7.8	3.81	153.908	0.963	5521.03	865.38	44.29	42.19
							20 mol% Py								
0.0322	1.0641	1453.99	44.45	213.18	1.548	0.1396	1.0007	8.62	3.814	170.044	0.796	5979.87	844.56	43.35	44.57
0.0747	1.0629	1456.33	44.36	220.01	1.548	0.1395	0.999	8.6	3.8137	169.7	0.798	5970.57	845.97	43.41	44.56
0.1172	1.0606	1458.82	44.3	228.41	1.547	0.1394	0.9963	8.59	3.8134	169.47	0.8	5956.87	848.28	43.51	44.55
0.1597	1.0587	1460.74	44.27	233.24	1.546	0.1393	0.9941	8.58	3.8133	169.355	0.802	5945.84	850.18	43.6	44.55
0.2022	1.0556	1462.91	44.27	241.39	1.544	0.1393	0.9907	8.58	3.8133	169.355	0.804	5929.82	853.1	43.72	44.56
							0 mol% Py								
0.0306	1.0851	1467.18	42.81	220.72	1.592	0.137	0.9998	9.38	3.808	185.156	0.664	6468.52	824.56	42.42	46.93
0.0731	1.0846	1469.42	42.7	213.24	1.593	0.1368	0.9989	9.36	3.8076	184.68	0.665	6461.6	825.36	42.46	46.91
0.1156	1.0835	1472.22	42.58	209.72	1.595	0.1367	0.9972	9.33	3.8071	184.161	0.667	6451.09	826.73	42.52	46.88
0.1581	1.0832	1473.79	42.5	206.88	1.596	0.1365	0.9966	9.32	3.8068	183.815	0.668	6446.46	827.25	42.54	46.86
0.2006	1.0829	1475.34	42.43	206.76	1.597	0.1364	0.996	9.3	3.8066	183.513	0.671	6441.88	827.77	42.56	46.84

Standard Uncertainty: u(T) = ± 0.01 K, u(mole %) = ± 0.01, u(ρ) = ±0.0004 g•cm^{-3}, u(P) = 0.1 MPa

Table 6: Concentration and calculated Acoustic parameters of Bu_4NBPh_4 in DMSO+Py at 318 K

Conc mol.Kg^{-3}	P g.cm^{-3}	U m.s^{-1}	κ_s.10^6 bar^{-1}	$K_{s\phi}$	Z. 10^6 Kg m^{-2}s^{-1}	L_f.10^{-5} m	R_A	τ . 10^{-12} s	ΔG . 10^{24} J mol^{-1}	Ab_{scoeff}. 10^{-8} Npm^{-1}s^2	V_f. 10^{-5} m^3 mol^{-1}	π_i . 10^3 N m^{-2}	R_m	W	H. 10^{-3} KJ mol^{-1}
								100 mol% Py							
0.0389	0.9603	1347.25	57.37	183.82	1.294	0.1602	0.9996	5.01	3.86	98.799	2.4	3955.3	924.91	46.96	33.12
0.0814	0.9614	1350.11	57.06	211.88	1.298	0.1598	1	4.98	3.859	98.266	2.4	3954.12	924.51	46.94	33.08
0.1239	0.9627	1352.52	56.78	221.53	1.302	0.1594	1.0008	4.96	3.858	97.783	2.41	3954.16	923.81	46.91	33.03
0.1664	0.9632	1355.37	56.52	229.81	1.305	0.159	1.0006	4.94	3.857	97.336	2.42	3951.37	923.98	46.92	32.99
0.2089	0.9641	1357.96	56.25	232.21	1.309	0.1586	1.0009	4.91	3.857	96.871	2.43	3950.06	923.7	46.9	32.95
								80 mol% Py							
0.0373	0.9881	1374.29	53.58	195.04	1.358	0.1548	0.9998	5.62	3.849	110.868	1.86	4401.43	900.23	45.85	35.64
0.0798	0.9898	1375.55	53.39	210.05	1.362	0.1545	1.0013	5.6	3.848	110.475	1.86	4404.46	898.96	45.79	35.6
0.1223	0.9919	1377.06	53.17	216.89	1.366	0.1542	1.003	5.58	3.848	110.019	1.87	4408.27	897.39	45.72	35.56
0.1648	0.9922	1378.83	53.01	226.84	1.368	0.154	1.0029	5.56	3.847	109.688	1.87	4406.33	897.5	45.73	35.53
0.2073	0.9927	1381.19	52.81	229.56	1.371	0.1537	1.0028	5.54	3.847	109.275	1.87	4404.04	897.56	45.73	35.49
								60 mol% Py							
0.0355	1.0103	1395.69	50.81	207.14	1.41	0.1508	0.9997	6.31	3.84	124.507	1.47	4839.03	882.61	45.06	38.22
0.078	1.0109	1397.76	50.63	220.37	1.413	0.1505	0.9998	6.29	3.84	124.066	1.47	4837.36	882.53	45.06	38.18
0.1205	1.0112	1399.52	50.49	228.29	1.415	0.1503	0.9996	6.27	3.839	123.723	1.48	4835.28	882.63	45.06	38.15
0.163	1.0125	1400.02	50.39	230.97	1.418	0.1501	1.0008	6.26	3.839	123.478	1.48	4838.56	881.61	45.02	38.13
0.2055	1.0136	1401.07	50.26	231.13	1.42	0.1499	1.0016	6.25	3.839	123.159	1.48	4840.25	880.87	44.98	38.1
								40 mol% Py							
0.0338	1.033	1412.29	48.53	217.07	1.459	0.1473	0.9979	7.05	3.833	138.952	1.18	5293.62	864.37	44.25	40.78
0.0763	1.0329	1413.81	48.44	231.85	1.46	0.1472	0.9974	7.03	3.833	138.695	1.185	5290.43	864.76	44.26	40.76
0.1188	1.0326	1414.93	48.37	238.28	1.461	0.1471	0.9969	7.02	3.833	138.494	1.187	5287.31	865.24	44.28	40.75
0.1613	1.0323	1416.16	48.3	241.16	1.462	0.147	0.9963	7.01	3.832	138.294	1.188	5283.99	865.74	44.31	40.74
0.2038	1.0319	1417.69	48.22	241.89	1.463	0.1469	0.9956	7	3.832	138.065	1.19	5279.78	866.39	44.33	40.72
								20 mol% Py							
0.0322	1.0522	1422.98	46.94	220.44	1.497	0.1449	0.998	7.74	3.828	152.542	0.985	5709.15	848	43.5	43.04
0.0747	1.0517	1424.16	46.88	233.88	1.498	0.1448	0.9973	7.73	3.828	152.347	0.986	5704.98	848.64	43.53	43.03
0.1172	1.0509	1425.83	46.81	236.89	1.498	0.1447	0.9961	7.71	3.827	152.12	0.988	5698.75	849.62	43.58	43.02
0.1597	1.0491	1427.27	46.79	244.34	1.497	0.1447	0.9941	7.71	3.827	152.055	0.989	5689.36	851.36	43.65	43.02
0.2022	1.0481	1428.61	46.75	246.38	1.497	0.1446	0.9928	7.7	3.827	151.925	0.991	5683.08	852.44	43.7	43.01
								0 mol% Py							
0.0306	1.0752	1434.78	45.18	228.18	1.543	0.1422	0.9998	8.34	3.822	164.522	0.831	6159.12	825.99	42.49	45.11
0.0731	1.0747	1436.61	45.09	222.27	1.544	0.142	0.9989	8.33	3.821	164.194	0.833	6153.29	826.73	42.52	45.08
0.1156	1.0737	1439.39	44.95	219.62	1.545	0.1418	0.9973	8.3	3.821	163.684	0.835	6143.53	828.03	42.58	45.05
0.1581	1.0733	1441.18	44.86	218.45	1.547	0.1417	0.9965	8.28	3.821	163.357	0.837	6138.19	828.68	42.61	45.03
0.2006	1.0727	1443.22	44.76	218.02	1.548	0.1415	0.9955	8.27	3.82	162.993	0.839	6131.56	829.54	42.65	45.01

Standard Uncertainty: u(T) = ± 0.01 K, u(mole %) = ± 0.01, u(ρ) = ± 0.0004 g•cm^{-3}, u(P) = 0.1 MPa

Table 7: Concentration and calculated Acoustic parameters of Bu_4NClO_4 in DMSO+Py at 298 K

Conc. mol.Kg^{-3}	ρ g.cm^{-3}	u m.s^{-1}	κ_s.10^6 bar^{-1}	K_{svb}	Z. 10^6 Kg m^{-2}s^{-1}	L_f.10^{-5} m	R_A	τ . 10^{-12} s	ΔG.10^{24} J mol^{-1}	Ab_{scoeff}. 10^{-8} Npm^{-1}s^2	V_f. 10^{-5} m^3 mol^{-1}	π_i. 10^3 N m^{-2}	R_m	W	H. 10^{-3} KJ mol^{-1}
								100 mol% Py							
0.0474	0.9799	1421.21	50.53	100.31	1.393	0.1418	1.0006	5.92	3.829	116.912	1.66	4261.32	918.69	46.66	34.82
0.0899	0.9813	1424.13	50.24	94.55	1.397	0.1414	1.0014	5.89	3.828	116.241	1.67	4261	918.01	46.63	34.76
0.1324	0.9827	1427.8	49.92	88.72	1.403	0.141	1.0019	5.85	3.827	115.501	1.67	4259.57	917.49	46.61	34.7
0.1749	0.9842	1430.85	49.63	86.97	1.408	0.1405	1.0027	5.82	3.826	114.83	1.68	4259.35	916.74	46.57	34.65
0.2174	0.9853	1434.89	49.29	83.84	1.414	0.1401	1.0029	5.78	3.825	114.043	1.68	4256.52	916.58	46.57	34.59
								80 mol% Py							
0.0449	1.0044	1434.96	48.35	102.78	1.441	0.1387	1.0005	6.57	3.822	129.666	1.34	4661.976	895.78	45.63	37.02
0.0879	1.0049	1438.86	48.06	95.88	1.446	0.1383	1.0001	6.53	3.821	128.888	1.35	4657.199	896.15	45.65	36.96
0.1304	1.0054	1443.17	47.75	91.32	1.451	0.1379	0.9996	6.49	3.82	128.056	1.35	4651.782	896.59	45.67	36.9
0.1729	1.0069	1446.19	47.48	88.03	1.456	0.1375	1.0004	6.45	3.819	127.332	1.36	4651.543	895.88	45.64	36.85
0.2154	1.0074	1450.93	47.16	85.48	1.462	0.137	0.9998	6.41	3.818	126.474	1.36	4645.476	896.41	45.66	36.78
								60 mol% Py							
0.0409	1.0233	1446.77	46.68	124.91	1.48	0.1363	0.9996	6.97	3.817	137.46	1.2	4879.534	888.84	45.38	38.34
0.0834	1.0239	1447.95	46.58	125.39	1.483	0.1362	0.9999	6.96	3.816	137.166	1.2	4879.452	888.56	45.37	38.32
0.1259	1.0242	1449.29	46.48	126.38	1.484	0.136	0.9999	6.94	3.816	136.871	1.2	4878.148	888.57	45.37	38.3
0.1684	1.0248	1449.82	46.42	128.29	1.486	0.1359	1.0004	6.93	3.816	136.695	1.2	4879.161	888.16	45.35	38.28
0.2109	1.0254	1450.01	46.4	131.31	1.487	0.1359	1.0009	6.93	3.816	136.636	1.2	4880.746	887.68	45.33	38.27
								40 mol% Py							
0.0384	1.0501	1457.88	44.8	128.53	1.531	0.1335	1.0007	7.88	3.81	155.482	0.92	5471.896	854.33	43.77	41.22
0.0809	1.0496	1459.7	44.71	129.33	1.532	0.1334	0.9998	7.87	3.81	155.17	0.92	5466.748	855.09	43.8	41.2
0.1234	1.0491	1461.55	44.63	130.22	1.533	0.1333	0.9989	7.85	3.809	154.892	0.93	5461.551	855.86	43.83	41.18
0.1659	1.0488	1461.97	44.61	133.68	1.533	0.1332	0.9985	7.85	3.808	154.823	0.93	5459.726	856.18	43.85	41.18
0.2084	1.0476	1463.34	44.58	137.11	1.533	0.1332	0.997	7.85	3.807	154.718	0.93	5453.006	857.43	43.9	41.18
								20 mol% Py							
0.0359	1.0705	1471.26	43.15	129.04	1.575	0.131	1.0003	9.26	3.804	182.656	0.69	6095.34	840.36	43.15	45.03
0.0784	1.0703	1471.77	43.11	130.08	1.575	0.131	1	9.25	3.803	182.487	0.69	6093.525	840.61	43.17	45.03
0.1209	1.0692	1473.33	43.09	134.73	1.575	0.131	0.9986	9.25	3.802	182.402	0.7	6086.125	841.77	43.21	45.02
0.1634	1.0688	1473.86	43.07	135.29	1.575	0.1309	0.9981	9.25	3.801	182.318	0.7	6083.513	842.19	43.23	45.02
0.2059	1.0682	1474.7	43.05	136.01	1.575	0.1309	0.9973	9.24	3.8	182.233	0.7	6079.503	842.82	43.26	45.01
								0 mol% Py							
0.0334	1.0949	1486.97	41.31	130.39	1.628	0.1282	0.9995	10.96	3.797	216.141	0.51	6873.556	821.38	42.29	49.46
0.0759	1.0942	1487.52	41.3	131.64	1.628	0.1282	0.9988	10.96	3.795	216.088	0.51	6869.356	822	42.32	49.46
0.1184	1.0933	1488.44	41.29	132.64	1.627	0.1282	0.9977	10.96	3.794	216.036	0.51	6863.467	822.85	42.36	49.46
0.1609	1.0917	1489.63	41.28	135.74	1.626	0.1282	0.996	10.95	3.793	215.984	0.51	6854.029	824.27	42.42	49.46
0.2034	1.0901	1490.94	41.26	136.55	1.625	0.1281	0.9943	10.95	3.791	215.879	0.51	6844.322	825.73	42.48	49.47

Standard Uncertainty: u(T) = ± 0.01 K, u(mole %) = ± 0.01, u(ρ) = ± 0.0004 g•cm^{-3}, u(P) = 0.1 MPa

Table 8: Concentration and calculated Acoustic parameters of Bu_4NClO_4 in DMSO+Py at 308 K

Conc. mol.Kg^{-3}	ρ g.cm^{-3}	u m.s^{-1}	κ_s.10^6 bar^{-1}	$K_{s\phi}$	Z. 10^6 Kg m^{-2}s^{-1}	L_f.10^{-5} m	R_A	τ. 10^{-12} s	ΔG.10^{24} J mol^{-1}	Ab_{scoeff}. 10^{-8} Npm^{-1}s^2	V_f. 10^{-5} m^3 mol^{-1}	π_i.10^3 N m^{-2}	R_m	W	H. 10^{-3} KJ mol^{-1}
							100 mol% Py								
0.0474	0.9704	1385.31	53.69	107.35	1.344	0.154	1	5.52	3.84	108.837	1.96	4127.52	923.83	46.91	34.21
0.0899	0.9723	1387.14	53.45	103.75	1.349	0.153	1.002	5.49	3.84	108.35	1.96	4130.178	922.43	46.85	34.16
0.1324	0.9747	1388.82	53.19	99.05	1.354	0.153	1.004	5.47	3.84	107.823	1.97	4134.469	920.53	46.77	34.11
0.1749	0.9761	1391.49	52.91	98.18	1.358	0.152	1.004	5.44	3.84	107.256	1.97	4134.455	919.8	46.74	34.06
0.2174	0.9772	1394.88	52.59	96.02	1.363	0.152	1.005	5.41	3.84	106.607	1.98	4132.53	919.51	46.72	34.01
							80 mol% Py								
0.0449	0.9979	1410.66	50.36	110.29	1.408	0.149	1	6.33	3.83	124.728	1.48	4633.839	899.19	45.8	37.15
0.0879	0.9987	1413.81	50.09	105.86	1.412	0.148	1	6.29	3.83	124.059	1.49	4631.148	899.14	45.8	37.1
0.1304	0.9999	1416.43	49.85	103.19	1.416	0.148	1.001	6.26	3.83	123.465	1.49	4630.568	898.61	45.78	37.05
0.1729	1.0005	1419.77	49.58	101.37	1.42	0.148	1	6.23	3.83	122.796	1.49	4626.968	898.78	45.79	37
0.2154	1.0012	1423.25	49.31	99.63	1.425	0.147	1	6.19	3.83	122.128	1.5	4623.463	898.88	45.79	36.95
							60 mol% Py								
0.0409	1.0205	1430.12	47.91	124.34	1.459	0.145	1	6.98	3.83	137.681	1.2	5047.789	880.92	44.99	39.47
0.0834	1.0217	1430.49	47.83	125.36	1.462	0.145	1.002	6.97	3.82	137.451	1.2	5051.092	879.96	44.94	39.45
0.1259	1.0223	1431.62	47.73	126.03	1.464	0.145	1.002	6.96	3.81	137.164	1.21	5051.074	879.68	44.93	39.42
0.1684	1.0238	1431.68	47.65	127.92	1.466	0.145	1.003	6.94	3.8	136.934	1.21	5055.908	878.4	44.88	39.4
0.2109	1.0242	1432.81	47.56	128.73	1.467	0.144	1.003	6.93	3.8	136.675	1.21	5055.23	878.29	44.87	39.38
							40 mol% Py								
0.0384	1.0433	1445.54	45.87	132.18	1.5081	0.1419	0.9986	7.85	3.82	154.854	0.957	5539.422	862.5	44.16	42.26
0.0809	1.0424	1447.71	45.77	133.55	1.5091	0.1417	0.9973	7.84	3.82	154.516	0.96	5532.085	863.68	44.21	42.24
0.1234	1.0417	1449.12	45.71	134.92	1.5095	0.1416	0.9963	7.83	3.82	154.314	0.961	5526.917	864.54	44.25	42.22
0.1659	1.0402	1450.98	45.66	139.75	1.5093	0.1416	0.9944	7.82	3.82	154.145	0.963	5518.07	866.15	44.32	42.22
0.2084	1.0399	1451.78	45.63	140.54	1.5097	0.1415	0.9939	7.81	3.82	154.044	0.964	5515.489	866.56	44.34	42.21
							20 mol% Py								
0.0359	1.0629	1454.92	44.45	134.23	1.546	0.14	0.999	8.62	3.81	170.045	0.798	5973.472	845.7	43.4	44.58
0.0784	1.0614	1456.97	44.38	138.76	1.546	0.14	0.998	8.61	3.81	169.777	0.799	5963.651	847.29	43.47	44.57
0.1209	1.0605	1457.89	44.36	142.02	1.546	0.14	0.996	8.61	3.81	169.7	0.8	5958.398	848.19	43.51	44.57
0.1634	1.0597	1458.65	44.35	143.71	1.546	0.14	0.996	8.6	3.81	169.662	0.801	5953.849	848.98	43.55	44.57
0.2059	1.0584	1459.79	44.33	145.27	1.545	0.139	0.994	8.6	3.81	169.586	0.802	5946.656	850.24	43.6	44.57
							0 mol% Py								
0.0334	1.0851	1467.15	42.81	134.99	1.592	0.137	1	9.39	3.81	185.157	0.664	6468.588	824.56	42.43	46.94
0.0759	1.0849	1467.41	42.8	135.11	1.592	0.137	1	9.39	3.81	185.113	0.665	6467.22	824.76	42.44	46.94
0.1184	1.0847	1467.72	42.79	136.85	1.592	0.137	0.999	9.39	3.81	185.07	0.665	6465.742	824.97	42.45	46.94
0.1609	1.084	1468.38	42.78	137.93	1.592	0.137	0.999	9.38	3.81	185.027	0.665	6461.507	825.63	42.48	46.94
0.2034	1.0831	1469.13	42.77	138.95	1.591	0.137	0.998	9.38	3.81	184.984	0.666	6456.282	826.46	42.51	46.94

Standard Uncertainty: u(T) = ±0.01 K, u(mole %) = ±0.01, u(ρ) = ±0.0004 g•cm-3, u(P) = 0.1 MPa.

Table 9: Concentration and calculated Acoustic parameters of Bu_4NClO_4 in DMSO+Py at 318 K

Conc. mol.Kg^{-3}	ρ g.cm^{-3}	u m.s^{-1}	κ_s.10^6 bar^{-1}	$K_{s\phi}$	Z. 10^6 Kg m^{-2}s^{-1}	L_f.10^{-5} m	R_A	τ . 10^{-12} s	ΔG.10^{24} J mol^{-1}	Ab_{scoeff}. 10^{-8} Npm^{-1}s^2	V_f 10^{-5} m^3 mol^{-1}	π_i.10^3 N m^{-2}	R_m	W	H.10^{-3} KJ mol^{-1}
								100 mol% Py							
0.0474	0.9625	1349.25	57.07	112.31	1.299	0.16	1.001	4.98	3.86	98.283	2.41	3958.4	923.26	46.89	33.07
0.0899	0.9638	1357.97	56.26	109.11	1.309	0.159	1.001	4.91	3.86	96.888	2.43	3949.22	923.99	46.92	32.95
0.1324	0.9651	1366.76	55.47	106.53	1.319	0.158	1	4.84	3.85	95.527	2.45	3940.04	924.73	46.95	32.83
0.1749	0.9662	1375.43	54.71	105.58	1.329	0.156	0.999	4.78	3.85	94.218	2.48	3930.59	925.63	46.99	32.72
0.2174	0.9675	1383.68	53.99	104.25	1.339	0.155	0.998	4.72	3.85	92.979	2.5	3922.37	926.23	47.01	32.6
								80 mol% Py							
0.0449	0.9878	1373.28	53.68	115.02	1.357	0.155	1	5.63	3.85	111.075	1.86	4402.16	900.29	45.85	35.66
0.0879	0.9884	1376.32	53.41	111.84	1.36	0.155	1	5.6	3.85	110.516	1.87	4399.07	900.4	45.86	35.61
0.1304	0.9907	1377.87	53.17	109.52	1.365	0.154	1.002	5.58	3.85	110.019	1.87	4403.42	898.65	45.78	35.56
0.1729	0.9916	1380.71	52.9	108.04	1.369	0.154	1.002	5.55	3.85	109.461	1.88	4401.55	898.45	45.77	35.51
0.2154	0.9925	1383.78	52.62	106.24	1.373	0.153	1.002	5.52	3.85	108.881	1.88	4399.32	898.3	45.76	35.46
								60 mol% Py							
0.0409	1.0105	1394.29	50.9	127.67	1.409	0.151	1	6.33	3.84	124.727	1.47	4842.1	882.14	45.04	38.23
0.0834	1.0113	1395.55	50.77	129.88	1.411	0.151	1.001	6.31	3.84	124.409	1.47	4842.47	881.71	45.02	38.21
0.1259	1.0122	1396.38	50.66	131.43	1.413	0.151	1.001	6.3	3.84	124.139	1.48	4843.9	881.1	45	38.18
0.1684	1.0137	1396.41	50.59	132.47	1.416	0.15	1.003	6.29	3.84	123.968	1.48	4848.64	879.81	44.94	38.17
0.2109	1.0146	1396.81	50.52	133.91	1.417	0.15	1.004	6.28	3.84	123.796	1.48	4850.81	879.11	44.91	38.15
								40 mol% Py							
0.0384	1.0331	1411.02	48.62	141.21	1.4577	0.1475	0.9983	7.06	3.83	139.21	1.18	5296.34	864.03	44.23	40.8
0.0809	1.0326	1411.96	48.58	148.31	1.458	0.1474	0.9976	7.05	3.83	139.096	1.18	5292.87	864.64	44.26	40.79
0.1234	1.0317	1413.41	48.52	151.99	1.4582	0.1473	0.9964	7.05	3.83	138.924	1.19	5287.08	865.69	44.3	40.78
0.1659	1.0304	1414.66	48.49	156.17	1.4577	0.1473	0.9948	7.04	3.83	138.838	1.19	5280.31	867.03	44.36	40.78
0.2084	1.0293	1415.78	48.47	158.22	1.4573	0.1472	0.9935	7.04	3.83	138.781	1.19	5274.46	868.19	44.41	40.78
								20 mol% Py							
0.0359	1.0524	1421.13	47.05	155.28	1.496	0.145	0.999	7.75	3.83	152.9	0.983	5713.59	847.47	43.48	43.07
0.0784	1.0517	1421.87	47.03	155.38	1.495	0.145	0.998	7.75	3.83	152.835	0.984	5709.57	848.18	43.51	43.07
0.1209	1.0503	1422.98	47.02	157.82	1.495	0.145	0.996	7.75	3.83	152.802	0.985	5702.28	849.54	43.57	43.07
0.1634	1.0497	1423.56	47	158.36	1.494	0.145	0.996	7.75	3.83	152.737	0.986	5698.95	850.14	43.6	43.07
0.2059	1.0481	1424.75	46.98	160.34	1.493	0.145	0.994	7.74	3.83	152.672	0.987	5690.77	851.67	43.67	43.07
								0 mol% Py							
0.0334	1.0753	1427.92	45.61	145.03	1.5354	0.1428	1.0015	8.42	3.82	166.088	0.826	6174.28	824.59	42.43	45.21
0.0759	1.0747	1436.18	45.11	146.61	1.5435	0.1421	0.999	8.33	3.82	164.267	0.833	6154.21	826.64	42.52	45.09
0.1184	1.0737	1436.83	45.1	148.94	1.5427	0.142	0.9979	8.33	3.82	164.231	0.834	6149	827.54	42.56	45.09
0.1609	1.0724	1438.09	45.08	150.81	1.5422	0.142	0.9964	8.32	3.82	164.158	0.835	6141.34	828.78	42.61	45.09
0.2034	1.0708	1440.02	45.03	153.68	1.542	0.1419	0.9945	8.32	3.82	163.976	0.836	6131.12	830.39	42.69	45.09

Standard Uncertainty: u(T) = ± 0.01 K, u(mole %) = ± 0.01, u(ρ) = ± 0.0004 g•cm^{-3}, u(P) = 0.1 MPa

Both Bu_4NBPh_4, Bu_4NClO_4, shows an increase in the ultrasonic velocity values at all the temperatures. This shows that molecular interactions are taking place in both the electrolytes. This increase in the molecular interactions with increase in the concentration of electrolytes in the solvent mixture may be due to solvent structural effects. Density measurements further supports these molecular interactions. With the increase in density, the interactions between solvent-solvent and solute-solvent is also increased. This could be attributed to the reduction in the free space per unit volume as more and more solute molecules occupied it. Isentropic compressibility (κ_s) shows the decreasing trend. When the solute molecule is added to the solvent, there are large numbers of solvent molecules available to interact and surround the incoming solute molecules. But on addition of more solute molecules in the solvent, the availability of solvent molecules in the bulk decreases. Because addition of an ion to the solvent attracts the solvent molecules towards itself, by pulling the molecules from surroundings. The electrostatic forces between incoming ions and the solvent molecule results in decrease in the availability of solvent molecules for next incoming ions. This process is defined as compressibility. Every solvent has a limit for compression called limiting compressibility. The solvent's compressibility is generally more than that of a solute and is inversely related to concentration. κs decreases with increase in concentration because as the concentration of solutes increases, a larger portion of solvent molecules being electrostatic attract towards solute molecules and there is reduction in the amount of solvent molecules in the bulk which inversely decreases. Bu_4NBPh_4, Bu_4NClO_4, both shows the same decreasing trend at all compositions of Py solvents and trend is followed at high temperatures also.

The Acoustic Impedance (Z), for the electrolyte is related to density and ultrasonic velocity of the medium. Z values increases with the increase in the concentration of Bu_4NBPh_4, Bu_4NClO_4, at 298 K, 308 K and 318 K. The value of Z further increases when we move to DMSO rich regions than in Py rich regions. This behaviour suggests the possibility of molecular interactions between solutes and solvent through hydrogen bonding. Intermolecular free length (L_f), decreases with increase in the concentration of electrolytes which indicates less number of solvent molecules available in the bulk but the value increases with the increase in temperature[30]. Thus intermolecular free length shows inverse relationships with the ultrasonic velocity. Lesser the intermolecular distance between the solvent and solute molecules, more will be the free length. Thus this leads to high ultrasonic velocity of the medium. Both Bu_4NBPh_4, Bu_4NClO_4, shows approximately same trend in the L_f values.

Relative association (R_A), is further influenced either by the breaking up of the solvent structures on addition of solutes or by the relative solvation of the solutes. The former trend refers to decrease in the R_A values and latter corresponds to increase in the R_A values. These values show no regular trend in both the electrolytes studied. These values were found to be maximum at 80 mol% Py for Bu_4NBPh_4, which is greater than one. This indicates that Bu_4NBPh_4, is solvated to greater extent at 80 mol% Py. But both in Pure Py or pure DMSO, the R_A values are less than one which indicates the breaking up of the solvent structures with addition of solute molecules. This trend remains same at all the temperatures studied. But the R_A values for Bu_4NClO_4 is positive and greater than one which indicates that for Bu_4NClO_4, shows more molecular interactions in DMSO as well as in Py at all compositions and at all three temperatures. Relaxation time (τ) decreases with increase in the concentration of Bu_4NBPh_4, Bu_4NClO_4, and shows a decreasing trend as we move to Py rich regions. The relaxation time further shows a decreasing trend with increase in temperature. Relaxation time indicates the time taken by solute molecules to undergo any structural changes[31,32]. Gibbs free energy (ΔG) measures the close packing of molecules which might be due to some kind of bonding (hydrogen or van der wall) between electrolyte and the solvent molecules. The decrease in the trend of free energy values suggest that less time is required for the cooperation process or rearrangement of molecules in the solvent[33]. Values of absorption coefficient (α/f^2) decreases with increase in the concentration of electrolytes and also decreases with the increase in the temperature. This indicates that the interaction in Py rich regions is less for both the electrolytes and same trend is followed at high temperature also[34]. Thus it shows greater molecular interaction in DMSO rich regions and Entropy (H) follows the same pattern.

Internal Pressure (π_i) value decreases when the concentration of both Bu_4NBPh_4, Bu_4NClO_4, increases indicating that the molecular interactions is greater at lower concentration of solute and these interactions are more for DMSO than for Py[35]. It is also very interesting to see that free volume of the system increases as the internal pressure decreases. The higher value of free volume indicates weak solute-solute interactions and vice-versa. Decrease in the internal pressure might be attributed to the loosening of cohesive forces which leads to breaking up of solvent structure at Py rich regions for Bu_4NBPh_4 and Bu_4NClO_4. Rao constant (R_m) and Wada constant (W) did not show much change in the values with increase in the concentration of solute. But this increase in the Py rich region indicating the presence of higher number of molecules in same region which lead to compact packing of medium thus increasing the interaction.

CONCLUSION

Acoustic studies of tetrabutylammonium tetraphenylborate and tetrabutylammonium perchlorate in a mixture of dimethylsulfoxide and pyridine at 298 K, 308 K and 318 K were carried out for the present studies. Tetraalkylammonium salts exclusively find an application as electrolytes in developing super capacitors also known as electrical double layer capacitors (EDLCs). Results showed greater molecular interaction in DMSO rich regions for both Bu_4NBPh_4 and Bu_4NClO_4, at all temperatures. This increase in the molecular interactions with increase in the concentration of electrolytes in the solvent mixture may be attributed to solvent structural effects.

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Conflict of interest

The author declare that we have no conflict of interest.

REFERENCES

1. Gill, D.S.; Anand, H.; Pathania, V., Z. *Phys. Chem.*, **2004**, *218*, 857-865.
2. Gill, D.S.; Rodehueser, L.; Rubini, P.; Delpuech, J. J., *J. Chem. Soc. Faraday Trans.*, **1995**, *91*, 2307.
3. Gill, D.S.; Kemp, U.; Dölle, A.; Zeidler, M.D., *Ind. J. Chem.*, **2001**, *40A*, 693-699.
4. Saravanakumar, K.; Baskaran, R.; Kubendran, T.R., *Russ. J. Phys. Chem. A.*, **2012**, *86*(13), 1947–1952.
5. Bedare, G.R.; Bhandakkar, V.D.; Suryavanshi, B.M., *Euro. J. Appl. Eng. Sci. Res.*, **2012**, *1*(1), 1-4.
6. Amrutia, R.R.; Mehta, N.M.; Karia, F.D.; Parsania. P.H., *J. Sci. Ind. Res.*, **2006**, *65*, 905-911.
7. Praharaj, M.K.; Satapathy, A.; Mishra. P.; Mishra, S., *J. Chem. Pharma. Res.*, **2013**, *5*(1), 49-56.
8. Bhandakkar, V.D.; Bhat, V.R.; Chimankarand, O.P.; Asole. A.W., *Adv. Appl. Sci. Res.*, **2014**, *5*(2), 80-85.
9. Rawat, M.K.; Sangeeta., *Ind. J. Pure and Appl. Phys.*, **2008**, *46*(3), 187-192.
10. Jasmine, E.; Rani, V.; Kannagi, K.; Padmavathy, R.; Radha, N., *J. Bas. Appl. Phys.,* **2012***, 1*, 96-101.
11. Singh, P.K.; Bhatt, S. C., *Appl. Phys. Res.,* **2010**, *2*(1), 35-41.
12. Tabhane, P.; Chimankar, O.P.; Dudhe, C.M.; Tabhane; V.A., *Der. Chemica. Sinica.*, **2012**, *3*(4), 944-947.
13. Wadekar, M.P., *J. Chem. Pharma. Res.*, **2013**, *5*(8), 37-41.
14. Kaur, B.; Juglan, K. C., *J. Poly. Eng.,* **2013**, *33*, 851-856.
15. Rodrıguez,. H.; Brennecke, J. F., *J. Chem. Eng. Data.*, **2006**, *51*, 2145-2155.
16. Del Grosso, V.A.; Mader, C.W., *J. Acoust. Soc. Am.*, **1972**, *52*, 1442–46.
17. Gill, D.S.; Rohitash.; Anand, H.; Puri, J.K., *J. Mol. Liq.*, **2002**, *15*, 98-99.
18. Pathania, V.; Kaur, M.; Vermani, B.K.; Veneeta,; Gill, D.S., *J. Soln. Chem.,* **2021**. https://doi.org/10.1007/s10953-021-01086-3

19. Kaur, M., IOP Conf. Ser.: *Mater. Sci. Eng.,* **2021**, *1033*, 012079.
20. Mehra, R.; Malav, B.B., *Arab. J. Chem.*, **2013**, DOI: 10.1016/j.arabjc.2013.07.018.
21. Godhani, D.R.; Dobariya, P.B.; Sanghani, A.M.; Mehta, J.P., *Arab. J. Chem.,* **2012**, *10*, 422-430. http://dx.doi.org/10.1016/j.arabjc.2012.10.002.
22. Dash, U.N.; Roy, G.S.; Talukdar, M.; Moharatha, D., *Ind. J. of Pure & Appl. Phys.,* **2010**, *48*, 651-657.
23. Markarian, S.A.; Asatryan, A.M.; Zatikyan, A.L., *J. Chem. Thermodyn.*, **2005**, *37*, 768–777.
24. Zhao, T.; Zhang, J.; Guo, B.; Zhang, F.; Sha, F.; Xie, X,; Wei, X., *J. Mol. Liq.,* **2005**, *207*, 315-322.
25. Kinart, C.M.; Kinart, W.J.; Aewiklinska, A,; Kinart, Z., *Phys. Chem. Chem. Phys.*, **2014**, *52*, 627-635.
26. Kijevcanin, M.L.; Zivkovic, E.M.; Djordjevic, B.D.; Radovic, R.; Jovanovic, J.; Serbanovic, S., *J. Chem. Thermodyn.*, **2013**, *56*, 49-56.
27. Gill, D.S.; Kumari, A.; Kumar, S.; Jauhar, S.P., *Z Naturforsch.*, **2005**, *60A*, 70-74.
28. Kratochvil, B.; Yeager, H.L., *Topic in Current Chemistry.,* **1972**, *27*, 1.
29. Anand, H.; Verma, R., *Chem Sci Trans.*, **2018**, *7*(3), 488-498.
30. Shinde, B.R.; Jadhav, S.S.; Shinde, S.U.; Shengule, D.R.; Jadhav, K.M., *J. Chem. Pharm. Res.*, **2011**, *3*(3), 432-438.
31. Sharma, P.; Chauhan, S.; Chauhan, M.S.; Syal, V.K., *Ind J Pure and Appl Phys.*, **2008**, *46*, 839-843.
32. Ali, A.; Hyde, S.; Nain, A.K., *Ind. J. Phys.,* **2000**, *74*(B), 63-67.
33. Naik, A.B.; *Ind. J. Pure and Appl. Phys.*, **2015**, *53*, 27-34.
34. Kannappan, A.N.; Ali, S.J.A.; Mahaboob, A., *Ind J Pure and Appl Phys.,* **2009**, *47*, 97.
35. Kolhe, R.K.; Bhosale, B.B., *Int. J. Scient. And Resc. Pub.*, **2017**, *7*, 494-511.