Ultrasonic Studies on Ion-Solvent Interactions of Tetra-*n*-butylammonium Bromide in Aqueous Solution of 1,3-Dioxolane and 2,2-Dimethoxypropane at Different Temperatures

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Tetra-*n*-butylammonium bromide (TBAB) is made soluble in different solvents like 10 % 1,3-dioxolane-water and 10 % dimethoxypropane-water. Ultrasonic velocity (U), density (ρ) and coefficient of viscosity (η) are determined at different temperatures *i.e.* at 298.15, 303.15, 308.15 and 313.15 K. These values of ultrasonic velocity (U), density (ρ) and co-efficient of viscosity (η) are used to calculate the thermo acoustic properties like isentropic compressibility (β_s), molar compressibility (W), acoustic impedance (Z), molar sound velocity (R), relative association (R_A), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i), isothermal compressibility (β_T). The results obtained were analyzed to interpret the ion-ion and ion-solvent interactions occurring in the solutions.

Keywords: Tetra-*n*-butylammonium bromide, 1,3-Dioxolane, 2,2-Dimethoxy propane, Ion-solvent interaction, Ultrasonic.

INTRODUCTION

In recent years, the ultrasonic measurements have gained a lot of importance which is being intensively used in the field of agriculture, medical science engineering and industries. Such types of studies being used for the investigation of different chemical processes, play vital roles in the field of synthetic works [1]. The density and viscosity of tetra-*n*-butylammonium bromide is useful in elucidating the nature of ion-solvent interaction in aqueous and non-aqueous solutions [2]. Tetra alkylammonium salts are one of the important classes of organic compounds which are used as phase transfer catalyst [3]. As they contain both hydrophilic and hydrophobic groups their solution behaviour is very much attractive. Tetra-*n*-butylammonium bromide is commonly used as a phase transfer catalyst which is used in various C-C, C-N, C-O, C-S and C-P bond forming reactions which are carried out by liquid-liquid and liquid-solid conditions [4]. Tetra-*n*-butyl-ammonium bromide is used to synthesize different tetrabutyl-ammonium salts through salt metathesis. When it is dissolved in aqueous solutions of 1,3-dioxolane (1,3-DO) and 2,2-dimethoxy-propane (DMP), it affects the geometrical nature of water molecules. Thus a clathrate like structure is formed between water molecules and ammonium ions of tetra-*n*-butylammonium bromide [5]. These ions do not form any hydrogen bond but contain hydrophilic and hydrophobic groups. Aqueous solutions of

tetra-*n*-butylammonium bromide show many properties like high viscosity with high temperature coefficients [6], high apparent molar heat capacities [7,8], low surface charge densities, high apparent molar volume [9] which are unusual. Tetra-alkylammonium halides are large in size and are capable to arrange water particles around themselves subject to their alkyl group. 2,2-Dimethoxypropane is used for the dehydration of animal tissue because it scavenges water molecules more effectively in water-sensitive area and any trace quantity of water will react with 2,2-dimethoxypropane to form methanol and acetone. Similarly 1,3-dioxolane is a dominant aprotic solvent, used in formulations, in production methods or even as a reactant itself. Several applications of 1,3-dioxolane are due to its capability to quickly dissolve polar polymers, like epoxies, polyesters and urethanes *etc*. Due to its small size, it rapidly penetrates into the polymer, causing in fast application rates for several coating methods [10]. The present work aims at the measurement of ultrasonic velocity, density and viscosity of the solutions of tetra-*n*-butylammonium bromide in 10 % (v/v) aqueous 1,3-dioxolane and 10 % (v/v) aqueous 2,2-dimethoxy-propane at 298.15-313.15 K. Tetra alkylammonium salts are bigger in size and are known to adjust water molecules around them depending on their alkyl chain [11,12]. The aqueous solutions of tetra alkylammonium bromide show high viscosities and large temperature coefficients [13]. The ion-solvent and ion-ion interactions for tetra alkylammonium salts have been

reported from density and viscosity measurements by Nikam *et al.* [14,15]. Thermo-acoustic properties of tetra-*n*-butyl-ammonium bromide in aqueous solution has recently been done [16,17]. There is mild studies about these properties of tetra-*n*-butylammonium bromide in mixed solvents like 1,3-dioxolane and 2,2-dimethoxypropane.

EXPERIMENTAL

The chemicals used are tetra-*n*-butylammonium bromide, 1,3-dioxlane and 2,2-dimethoxy propane. These are of Sigma Aldrich, German variety with 99 % purity. 10 % solutions of 1,3-dioxolane and 2,2-dimethoxypropane in water were prepared which were used as solvents. Tetra-*n*-butylammonium bromide was purified by recrystallization from acetone and the recrystallized salt was dried at 333.15 K for 48 h. The sample description is presented in Table-1.

The tetra-*n*-butylammonium bromide solutions in 10 % aqueous solutions of each of 1,3-dioxolane and 2,2-dimethoxy-propane were prepared by mass in molar basis. Electronic balance of model ABJ-220-4NM (KERN, Germany) was used to record the masses of solute and solvents with a precision of ± 0.01 mg. The density (ρ) of mixture solutions were measured with Rudolph DDM 2911 laboratory density meter. It was calibrated with the samples provided by the manufacturer to confirm the accuracy of the measurement. The uncertainty in density measurements was determined to be 0.00125 g cm^{-3}. The molarity of solutions was converted to molality using standard expressions [18-21] and density values. The ultrasonic velocity of solutions were measured with ultrasonic interfero-meter, model-M-84 (Mittal Enterprises, India,) with a frequency of 2 MHz. Uncertainty in ultrasonic velocity measurements were precise to ± 0.1 m s^{-1}. The instrument was calibrated with triply distilled water. The temperature of the test liquids was maintained at 298.15-313.15 K to an accuracy of ± 0.01 K [22].

Theory

The velocity of sound is affected by parameters like tempe-rature, frequency, density and concentration of solution. This paper reports the various parameters from the experimentally measured values *viz.*, isentropic compressibility (β_S) = $1/U^2\rho$; isothermal compressibility (β_T) = $17.1 \times 10^{-4}/(T^{4/9} \rho^{4/3} U^2)$; molar compressibility (W) = $M_{eff} \times \rho^{-1} \times \beta_s^{-1/7}$; acoustic impendance (Z) = $U \times \rho$; molar sound velocity (R) = $M_{eff} \times \rho$; relative association (R_A) = $(\rho/\rho_0) \times (U_0/U)^{1/3}$; intermolecular free length (L_f) = $K_T\beta_s^{1/2}$; where K_T is the Jacobson's constant [23] and is equal to $(93.875 + 0.375T) \times 10^{-8}$ and is equal to 207.5×10^{-8} at 303.15 K. Free volume (V_f) = $[(M_{eff \times} U)/(K \times \eta)]^{3/2}$; where K = 4.28×10^9 for all types of liquids and M_{eff} is called effective molecular mass *i.e.* $M_{eff} = \Sigma m_i x_i$, where m_i and x_i represent the molar mass and the mole fraction of the components respectively. Internal pressure (π_i) = $b' R \times T (K\eta/U)^{1/2} (\rho^{2/3}/M_{eff}^{7/6})$.

RESULTS AND DISCUSSION

Density, speed of sound and compressibility: The ultra-sonic velocity, density and viscosity of tetra-*n*-butylammonium bromide in aqueous solution of 1,3-dioxolane and 2,2-dimethoxy-propane at 298.15-313.15 K are given in Table-2. The analysis of the data from the table, reveals that with increase in concentra-tion of tetra-*n*-butylammonium bromide, the value of density (ρ) increases. As the concentration increases number of particles in a particular area increases which results in contraction of volume of solution, thereby increase of density. Due to this, there is quick transfer of sound velocity in the solution. Hence ultrasonic velocity increases with the increase in concentration of tetra-*n*-butylammonium bromide (Fig. 1). This indicates that there is a strong interaction between the molecules of tetra-*n*-butyl-ammonium bromide in solution. The values of isentro-pic compressibility (β_s), isothermal compressibility (β_T) and molar compressibility (W) were determined (Table-3). The decrease of β_s values with increase in tetra-*n*-butylammonium bromide concentration is due to the influence of the interaction of ammonium ions with 1,3-dioxolane and 2,2-dimethoxy-propane, so called electrostriction. In these solutions, the solute dissociated in to oppositely charged ions due to ion solvent interactions and there will be a sphere of positive and negative charged ions around a charged ion in solution [24]. Tetra *n*-butylammonium bromide ions associate themselves with water molecules as well as the complex of 1,3-dioxolane-water or 2,2-dimethoxy propane-water mixture, resulting in the decrease in compressibility and hence increase in ultrasonic velocity. The decrease in compressibility is expected due to the structure-making ability of tetra-*n*-butylammonium bromide [25]. As the solvent molecules are oriented in presence of electrostatic forces of ions, the solvent particles are more rigidly packed in case of primary solvation of solvent in comparison to the packing which occurs in absence of ions. Due to this fact the solvent-molecules are compressed when ions are introduced into them. This compression of medium caused by electrostatic force of ions is called as electrostriction. Solvent particles do not respond to any further use of pressure as these are compacted. As a result the isentropic compre-ssibility (β_s) as well as isothermal compressibility (β_T) decreases due to which the solution becomes harder to compress. So the two factors which are used to describe the arrangement of molecules in liquid medium are isentropic compressibility and internal pressure. The value of molar compressibility increases with increase in temperature. This may be due to the decrease in bulkiness of tetra-*n*-butylammonium bromide which is due to the reason that organic co-solvents filled the interstitial spaces of water.

TABLE-1 SAMPLE DESCRIPTION				
Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity
Tetra-*n*-butylammonium bromide	Sigma	0.99	Used as procured	0.99
1,3-Dioxolane	Sigma	0.99	Purified by standard methods	0.99
2,2-Dimethoxy propane	Sigma	0.99	Purified by standard methods	0.99

TABLE-2
DENSITY (ρ), ULTRASONIC VELOCITY (U) AND VISCOSITY (η) OF TETRA-*n*-BUTYLAMMONIUM BROMIDE
IN 10 % 1,3-DIOXOLANE + WATER AND 10 % 2,2-DIMETHOXYPROPANE + WATER SOLUTIONS
AT DIFFERENT TEMPERATURES AND ATMOSPHERIC PRESSURE

Conc. (mol kg⁻¹)	298.15 K			303.15 K			308.15 K			313.15 K		
	ρ (kg m⁻³)	U (m s⁻¹)	η (NS m⁻³)	ρ (kg m⁻³)	U (m s⁻¹)	η (NS m⁻³)	ρ (kg m⁻³)	U (m s⁻¹)	η (NS m⁻³)	ρ (kg m⁻³)	U (m s⁻¹)	η (NS m⁻³)
Tetra-*n*-butylammonium bromide in 10 % 1,3-dioxolane + water												
0.000	1009.0	1553.5	0.9362	1008.1	1558.0	0.8356	1006.7	1564.0	0.7495	1005.2	1568.8	0.6750
0.001	1009.0	1554.7	0.9374	1008.1	1559.0	0.8366	1006.7	1565.2	0.7504	1005.2	1569.6	0.6759
0.005	1009.0	1558.0	0.9462	1008.1	1562.2	0.8430	1006.7	1568.4	0.7563	1005.2	1572.8	0.6812
0.008	1009.1	1558.8	0.9480	1008.2	1563.0	0.8457	1006.8	1568.9	0.7588	1005.2	1573.4	0.6835
0.010	1009.2	1559.2	0.9492	1008.2	1563.3	0.8476	1006.8	1569.4	0.7606	1005.2	1574.8	0.6852
0.021	1009.3	1562.1	0.9524	1008.4	1566.2	0.8511	1006.8	1572.0	0.7637	1005.3	1578.3	0.6880
0.042	1009.8	1564.5	0.9580	1008.7	1568.2	0.8557	1007.0	1573.6	0.7680	1005.4	1580.0	0.6918
0.064	1010.2	1567.0	0.9655	1009.0	1570.8	0.8613	1007.2	1577.0	0.7737	1005.6	1583.8	0.6970
0.087	1010.6	1570.2	0.9685	1009.3	1574.2	0.8636	1007.4	1580.5	0.7763	1005.8	1587.0	0.6994
0.110	1011.1	1573.0	0.9752	1009.7	1576.8	0.8694	1008.0	1582.4	0.7803	1006.0	1589.0	0.7030
0.133	1011.6	1577.2	0.9749	1010.1	1580.9	0.8690	1008.5	1586.0	0.7798	1006.3	1592.0	0.7024
Tetra-*n*-butylammonium bromide in 10 % 2,2-dimethoxypropane + water												
0.000	981.45	1500.0	0.9448	979.81	1505.5	0.8384	976.53	1514.0	0.7483	974.64	1521.7	0.6707
0.001	981.46	1501.0	0.9482	979.81	1506.5	0.8422	976.54	1514.8	0.7518	974.65	1522.5	0.6742
0.005	981.53	1504.8	0.9546	979.87	1509.5	0.8473	976.58	1517.5	0.7564	974.68	1524.9	0.6781
0.008	981.58	1506.5	0.9564	979.92	1511.0	0.8496	976.62	1518.6	0.7585	974.72	1525.7	0.6794
0.011	981.64	1507.4	0.9581	979.97	1512.0	0.8504	976.67	1519.0	0.7592	974.75	1526.5	0.6807
0.021	981.91	1509.5	0.9617	980.19	1514.3	0.8536	976.85	1521.0	0.7622	974.90	1528.7	0.6834
0.044	982.45	1511.0	0.9676	980.61	1516.0	0.8589	977.25	1523.5	0.7670	975.20	1531.2	0.6877
0.066	983.01	1513.0	0.9751	981.02	1518.0	0.8656	977.65	1526.0	0.7730	975.50	1533.9	0.6931
0.090	983.62	1515.5	0.9842	981.52	1521.3	0.8736	978.05	1529.3	0.7804	975.80	1537.2	0.6998
0.113	984.34	1517.5	0.9949	982.08	1523.0	0.8832	978.50	1530.6	0.7891	976.20	1538.6	0.7077
0.137	984.91	1519.1	1.0016	982.64	1525.5	0.8891	978.95	1533.5	0.7945	976.60	1541.6	0.7126

Uncertainty in the density values ± 0.00125 g cm⁻³; Uncertainties in the molality is ± 0.0002 (mol kg⁻¹)

TABLE-3
ISENTROPIC COMPRESSIBILITY (β$_S$), MOLAR COMPRESSIBILITY (W), ISOTHERMAL COMPRESSIBILITY (β$_T$) OF
TETRA-*n*-BUTYLAMMONIUM BROMIDE IN 10 % 1,3-DIOXOLANE + WATER AND 10 % 2,2-DIMETHOXYPROPANE +
WATER SOLUTIONS AT DIFFERENT TEMPERATURES AND ATMOSPHERIC PRESSURE

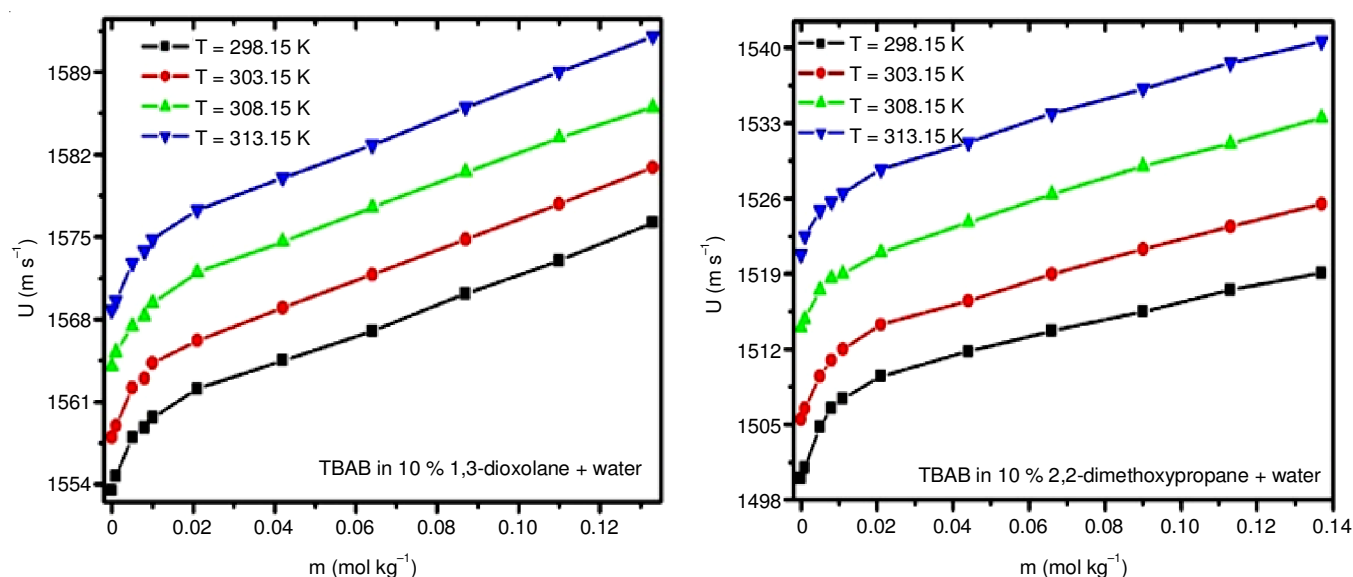| Conc. (mol kg⁻¹)	298.15 K			303.15 K			308.15 K			313.15 K		
	β$_s$×10¹⁰ (m² N⁻¹)	W×10⁴ (N⁻¹ m⁻¹)	β$_T$×10¹⁵ (m² N⁻¹)	β$_s$×10¹⁰ (m² N⁻¹)	W×10⁴ (N⁻¹ m⁻¹)	β$_T$×10¹⁵ (m² N⁻¹)	β$_s$×10¹⁰ (m² N⁻¹)	W×10⁴ (N⁻¹ m⁻¹)	β$_T$×10¹⁵ (m² N⁻¹)	β$_s$×10¹⁰ (m² N⁻¹)	W×10⁴ (N⁻¹ m⁻¹)	β$_T$×10¹⁵ (m² N⁻¹)
Tetra-*n*-butylammonium bromide in 10 % 1,3-dioxolane + water												
0.0000	4.107	4.253	5.565	4.092	4.259	5.498	4.071	4.269	5.427	4.058	4.278	5.366
0.0010	4.101	4.266	5.556	4.087	4.273	5.491	4.065	4.283	5.418	4.054	4.292	5.360
0.0051	4.083	4.321	5.532	4.070	4.328	5.469	4.048	4.338	5.396	4.037	4.347	5.339
0.0076	4.078	4.355	5.526	4.065	4.361	5.463	4.046	4.371	5.393	4.034	4.381	5.334
0.0102	4.076	4.388	5.523	4.064	4.395	5.460	4.043	4.405	5.389	4.032	4.415	5.325
0.0207	4.060	4.524	5.501	4.048	4.532	5.439	4.029	4.542	5.371	4.019	4.553	5.301
0.0423	4.046	4.799	5.481	4.037	4.807	5.423	4.021	4.819	5.359	4.009	4.831	5.288
0.0644	4.031	5.079	5.461	4.022	5.088	5.403	4.003	5.101	5.334	3.990	5.114	5.262
0.0870	4.013	5.362	5.435	4.000	5.372	5.377	3.984	5.387	5.309	3.973	5.401	5.240
0.1099	3.997	5.648	5.412	3.983	5.659	5.357	3.965	5.673	5.292	3.952	5.689	5.224
0.1332	3.974	5.937	5.380	3.961	5.949	5.326	3.945	5.962	5.265	3.936	5.980	5.203
Tetra-*n*-butylammonium bromide in 10 % 2,2-dimethoxypropane + water												
0.000	4.528	4.265	6.193	4.506	4.276	6.116	4.491	4.295	6.031	4.478	4.308	5.943
0.001	4.522	4.279	6.184	4.500	4.290	6.108	4.486	4.309	6.024	4.473	4.322	5.936
0.005	4.499	4.336	6.153	4.482	4.346	6.083	4.470	4.365	6.003	4.459	4.379	5.918
0.008	4.489	4.371	6.139	4.473	4.382	6.071	4.464	4.401	5.994	4.454	4.414	5.911
0.011	4.483	4.406	6.131	4.469	4.417	6.062	4.461	4.435	5.990	4.449	4.449	5.905
0.021	4.470	4.546	6.112	4.455	4.557	6.042	4.448	4.576	5.973	4.436	4.591	5.886
0.044	4.458	4.829	6.095	4.440	4.842	6.025	4.432	4.863	5.950	4.420	4.878	5.865
0.066	4.444	5.117	6.074	4.427	5.131	6.006	4.416	5.154	5.927	4.403	5.171	5.842
0.090	4.426	5.409	6.049	4.405	5.425	5.976	4.395	5.449	5.899	4.382	5.468	5.814
0.113	4.412	5.702	6.027	4.389	5.719	5.958	4.378	5.745	5.885	4.365	5.765	5.801
0.137	4.400	5.997	6.010	4.376	6.017	5.934	4.367	6.045	5.859	4.351	6.067	5.775

Fig. 1. Plot of ultrasonic velocity (U) *vs.* molality (m) of solutions of tetra-*n*-butylammonium bromide in (a) 10 % 1,3-dioxolane + water and (b) in 10 % 2,2-dimethoxypropane + water at 298.15-313.15 K

Acoustic impedance, molar sound velocity and relative association: Thermo acoustic parameters were calculated from their formulae. The values of acoustic impedance (Z), molar sound velocity (R) and relative association (R_A) of tetra-*n*-butylammonium bromide in aqueous solution of 1,3-dioxolane and 2,2-dimethoxypropane at 298.15-313.15 K has been obtained (Table-4). From the data, it is analyzed that the value of acoustic impedance (Z) increase in all solutions with increase

in concentration of tetra-*n*-butylammonium bromide [26]. The acoustic impedance explains the elastic property of the medium whose value is influenced by the geometric distortion of the solution. The elastic property of the solution increases with increase in concentration of tetra-*n*-butylammonium bromide in 1,3-dioxolane and 2,2-dimethoxypropane. It has been observed that with increase in concentration of tetra-*n*-butylammonium bromide in solvents like 1,3-dioxolane and 2,2-dimethoxy-

TABLE-4
MOLAR COMPRESSIBILITY (W), MOLAR SOUND VELOCITY (R) AND RELATIVE ASSOCIATION (R_A) OF
TETRA-*n*-BUTYLAMMONIUM BROMIDE IN 10 % 1,3-DIOXOLANE + WATER AND 10 % 2,2-DIMETHOXYPROPANE +
WATER SOLUTIONS AT DIFFERENT TEMPERATURES

Conc. (mol kg⁻¹)	298.15 K			303.15 K			308.15 K			313.15 K		
	$Z \times 10^{-6}$ (Kg m⁻² s⁻¹)	R_A	$R \times 10^4$ (m⁻⁸/³ s⁻¹/³)	$Z \times 10^{-6}$ (Kg m⁻² s⁻¹)	R_A	$R \times 10^4$ (m⁻⁸/³ s⁻¹/³)	$Z \times 10^{-6}$ (Kg m⁻² s⁻¹)	R_A	$R \times 10^4$ (m⁻⁸/³ s⁻¹/³)	$Z \times 10^{-6}$ (Kg m⁻² s⁻¹)	R_A	$R \times 10^4$ (m⁻⁸/³ s⁻¹/³)
Tetra-*n*-butylammonium bromide in 10 % 1,3-dioxolane + water												
0.0000	1.567	1.000	2.246	1.571	1.000	2.251	1.574	1.000	2.257	1.577	0.999	2.262
0.0010	1.569	1.000	2.254	1.572	0.999	2.258	1.576	0.999	2.264	1.578	0.999	2.269
0.0051	1.572	0.999	2.283	1.575	0.998	2.287	1.579	0.998	2.293	1.581	0.999	2.299
0.0076	1.573	0.999	2.301	1.576	0.998	2.305	1.579	0.998	2.311	1.582	0.998	2.317
0.0102	1.573	0.999	2.318	1.576	0.998	2.323	1.580	0.998	2.329	1.583	0.998	2.335
0.0207	1.577	0.999	2.390	1.579	0.998	2.395	1.583	0.998	2.401	1.585	0.997	2.408
0.0423	1.580	0.998	2.536	1.582	0.998	2.541	1.585	0.998	2.548	1.589	0.997	2.555
0.0644	1.583	0.998	2.684	1.585	0.998	2.689	1.588	0.997	2.697	1.593	0.997	2.705
0.0870	1.587	0.998	2.833	1.589	0.998	2.840	1.592	0.997	2.849	1.596	0.996	2.857
0.1099	1.591	0.998	2.984	1.592	0.998	2.991	1.595	0.997	3.000	1.600	0.996	3.010
0.1332	1.596	0.998	3.137	1.597	0.998	3.145	1.600	0.997	3.153	1.604	0.996	3.164
Tetra-*n*-butylammonium bromide in 10 % 2,2-dimethoxypropane + water												
0.000	1.472	1.000	2.258	1.475	1.000	2.265	1.478	0.999	2.277	1.483	0.998	2.285
0.001	1.473	1.000	2.266	1.476	1.000	2.272	1.479	0.999	2.284	1.484	0.998	2.292
0.005	1.477	0.999	2.296	1.479	0.999	2.302	1.482	0.998	2.314	1.486	0.998	2.322
0.008	1.479	0.999	2.315	1.481	0.999	2.321	1.483	0.998	2.333	1.487	0.997	2.341
0.011	1.480	0.999	2.333	1.482	0.999	2.340	1.484	0.998	2.351	1.488	0.997	2.360
0.021	1.482	0.998	2.408	1.484	0.998	2.414	1.486	0.998	2.426	1.490	0.997	2.435
0.044	1.484	0.999	2.557	1.487	0.998	2.565	1.489	0.998	2.578	1.493	0.997	2.588
0.066	1.487	0.999	2.710	1.489	0.998	2.718	1.492	0.998	2.732	1.496	0.996	2.743
0.090	1.491	0.999	2.864	1.493	0.998	2.874	1.496	0.997	2.889	1.500	0.996	2.901
0.113	1.494	0.999	3.019	1.496	0.998	3.030	1.499	0.998	3.046	1.503	0.996	3.059
0.137	1.496	0.999	3.176	1.499	0.998	3.188	1.502	0.997	3.205	1.506	0.996	3.218

propane, the molar sound velocity (R) increases [27]. Relative association (R_A) [28] is used to study the ion-ion and ion-solvent interactions. The factors which affect the relative association are association of solution with solute particles that leads to increase in association and breaking of the associated solvent molecules on addition of solute tetra-*n*-butylammonium bromide that leads to decrease in relative association. During this study it is observed that the relative association (R_A) decreases with increase in concentration of tetra-*n*-butylammonium bromide. This indicates that by adding solute, the association of solvent molecules with solute decreases.

Free length, free volume and internal pressure: The values of free length (L_f), free volume (V_f) and internal pressure (π_i) of tetra-*n*-butylammonium bromide in aqueous solution of 1,3-dioxolane and 2,2-dimethoxypropane at 298.15-313.15 K were calculated (Table-5). The free volume (V_f) is nothing but the available volume around centre of the molecule in a liquid. To determine the structure of liquid, the strong repulsion which exists inside the liquid with relatively low cohesive forces providing the internal pressure responsible for attracting the liquid molecules together is known. It is found that the internal pressure (π_i) is sensitive towards attractive forces and the free volume towards repulsive forces [29]. The free volume increases regularly with increase in the concentration of tetra-*n*-butylammonium bromide in 1,3-dioxolane and 2,2-dimethoxypropane. But it is observed that π_i decreases with increase in concentration of tetra-*n*-butylammonium bromide and decreases with increase in temperature. The increase in V_f (Fig. 2) and decrease of π_i indicates the formation of less hard solvation

layer around the ammonium ion of tetra-*n*-butylammonium bromide which lead to decrease in free length (L_f). On the other hand it is known from the model proposed by Eyring and Kincaid [28] that sound speed will increase with decrease in intermolecular free length. This is found in the solutions of tetra-*n*-butylammonium bromide in 1,3-dioxolane and 2,2-dimethoxypropane. The ratio between free volumes to molar volume is a sign of crowdedness of the ions in solution. The frictional force formed due to various layers of liquid, increases with increase in ions and non-polar solvent content in solution. Due to this effect the ultrasonic absorption increases [30]. Suryanarayana *et al.* [31] expressed that the cohesive force and free energy of activation (ΔG) are almost equal to each other.

Conclusion

In this present work, the experimentally measured values of density, ultrasonic velocity and co-efficient of viscosity at temperatures from 298.15-315.15 K for mixtures of tetra-*n*-butylammonium bromide in 1,3-dioxolane and 2,2-dimethoxypropane were used to calculate the thermodynamic and thermo acoustic properties and the results obtained were analyzed to interpret the ion-ion and ion-solvent interactions occurring in the solutions. It has been observed that the values of density and ultrasonic velocity increase with increase in concentration of tetra-*n*-butylammonium bromide in solution. Except the ultrasonic velocity which increases with temperature, other two parameters such as density and viscosity decrease with temperature. This implies that the increase in ion solvent inter-

TABLE-5
INTERNAL PRESSURE (π_i), FREE LENGTH (L_F) AND FREE VOLUME (V_F) OF TETRA-*n*-BUTYLAMMONIUM
BROMIDE IN 10 % 1,3-DIOXOLANE + WATER AND 10 % 2, 2-DIMETHOXYPROPANE + WATER SOLUTIONS
AT DIFFERENT TEMPERATURES AND ATMOSPHERIC PRESSURE

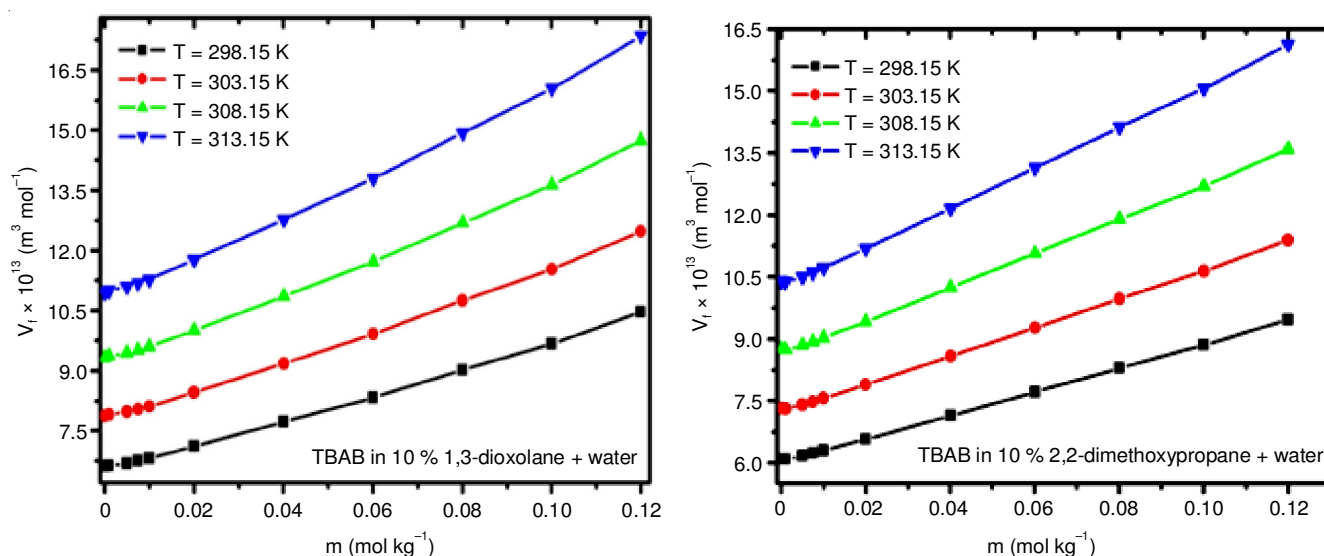| Conc. (mol kg^{-1})	298.15 K			303.15 K			308.15 K			313.15 K		
	$\pi_i \times 10^{-10}$ (Nm^{-2})	$L_f \times 10^{11}$ (m)	$V_f \times 10^{13}$ (m^3 mol^{-1})	$\pi_i \times 10^{-10}$ (Nm^{-2})	$L_f \times 10^{11}$ (m)	$V_f \times 10^{13}$ (m^3 mol^{-1})	$\pi_i \times 10^{-10}$ (Nm^{-2})	$L_f \times 10^{11}$ (m)	$V_f \times 10^{13}$ (m^3 mol^{-1})	$\pi_i \times 10^{-10}$ (Nm^{-2})	$L_f \times 10^{11}$ (m)	$V_f \times 10^{13}$ (m^3 mol^{-1})
Tetra-*n*-butylammonium bromide in 10 % 1,3-dioxolane + water												
0.000	7.880	4.168	6.609	7.554	4.196	7.872	7.252	4.220	9.320	6.976	4.248	10.954
0.001	7.855	4.165	6.634	7.530	4.193	7.902	7.228	4.217	9.357	6.954	4.246	10.993
0.005	7.772	4.156	6.683	7.444	4.184	7.981	7.146	4.209	9.447	6.876	4.238	11.097
0.008	7.709	4.154	6.746	7.388	4.182	8.040	7.094	4.207	9.513	6.825	4.236	11.175
0.010	7.644	4.153	6.814	7.331	4.181	8.107	7.039	4.206	9.593	6.770	4.232	11.277
0.021	7.386	4.144	7.114	7.085	4.173	8.455	6.803	4.199	10.002	6.542	4.223	11.768
0.042	6.913	4.137	7.721	6.630	4.167	9.178	6.366	4.194	10.851	6.122	4.218	12.768
0.064	6.493	4.130	8.327	6.223	4.160	9.917	5.977	4.185	11.718	5.746	4.207	13.792
0.087	6.101	4.120	9.016	5.845	4.150	10.749	5.615	4.175	12.686	5.399	4.198	14.929
0.110	5.760	4.112	9.669	5.518	4.142	11.530	5.298	4.169	13.631	5.093	4.193	16.042
0.133	5.430	4.100	10.463	5.201	4.131	12.476	4.995	4.158	14.748	4.802	4.184	17.348
Tetra-*n*-butylammonium bromide in 10 % 2,2-dimethoxypropane + water												
0.000	8.009	4.377	6.087	7.648	4.404	7.321	7.308	4.427	8.757	7.004	4.448	10.398
0.001	7.992	4.374	6.088	7.636	4.401	7.312	7.296	4.424	8.743	6.995	4.446	10.374
0.005	7.892	4.363	6.165	7.540	4.393	7.407	7.206	4.416	8.851	6.908	4.439	10.504
0.008	7.824	4.358	6.231	7.478	4.388	7.475	7.148	4.413	8.928	6.850	4.436	10.605
0.011	7.757	4.355	6.294	7.411	4.385	7.561	7.086	4.412	9.025	6.792	4.434	10.710
0.021	7.491	4.348	6.570	7.156	4.378	7.895	6.843	4.406	9.420	6.559	4.427	11.180
0.044	7.001	4.343	7.140	6.687	4.372	8.580	6.393	4.397	10.244	6.127	4.419	12.158
0.066	6.566	4.336	7.715	6.271	4.365	9.271	5.994	4.389	11.072	5.745	4.411	13.141
0.090	6.180	4.327	8.289	5.901	4.355	9.969	5.641	4.379	11.902	5.406	4.400	14.124
0.113	5.840	4.320	8.848	5.576	4.349	10.638	5.331	4.374	12.690	5.109	4.396	15.058
0.137	5.522	4.314	9.467	5.271	4.340	11.391	5.039	4.365	13.593	4.829	4.386	16.129

Fig. 2. Plot of free volume (V_f) *vs*. molality (m) of solutions of tetra-*n*-butylammonium bromide (a) in 10 % 1,3-dioxolane + water and (b) in 10 % 2,2-dimethoxypropane + water at 298.15-313.15 K

actions with increase in concentration and temperature. Further the decrease in compressibility (β_S and β_T) are expected due to the structure-making ability of tetra-*n*-butylammonium bromide. Bulkiness of tetra-*n*-butylammonium bromide decreases due to the insertion of co-solvents in the interstitial spaces of water, as the value of molar compressibility increases with increase in temperature.

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