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Ultrasonic studies on temperature dependence of ion solvent interactions of ionic liquid 1-butyl-2,3- dimethylimidazolium chloride in aqueous solutions of tetra-n-butylammonium

bromide at T = (298.15 to 313.15) K

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ABSTRACT

The densities (ρ) , and ultrasonic velocities (u) of 1-Butyl-2, 3-dimethylimmidazolium chloride, [bdmim]Cl in aqueous solutions of Tetran-butyl ammonium bromide over the complete range of concentrations has been calculated at different temperatures T=(298.15 to 313)K. Experimentally obtained values of ρ and u were used to calculate the parameters like acoustic impedance (Z), isentropic compressibility (β_S) , molar sound velocity (Rao's constant) (R), molar compressibility (Wada's constant) (R), intermolecular free length (L_f) , co-efficient of thermal expansion (α) , heat capacity ratio (γ) , isothermal compressibility (β_T) and nonlinearity parameters (B/A). The final results obtained were analyzed to understand the ion-solvent and ion-ion interaction so taking place in the solutions. Further, the effect of temperature on the ion solvent interactions was discussed. Ion-solvent interactions are affected by the thermo acoustical properties and by nonlinear parameters.

Keywords: Ion-solvent interactions; Tetra-n-butyl ammonium bromide; 1-Butyl-2,3-dimethyl imidazolium chloride; Wada's constant; Rao's constant; ultrasonic velocity.

1. INTRODUCTION

Ionic liquids have a broad range of industrial properties, and research in the field of ILs endures to witness an astonishing period of remarkable growth. The importance of ionic liquids increases due to their use in synthesis as new solvents, as well as in the process of bio-catalysis, catalysis, chemical engineering and material science [1-5]. Nowdays, ultrasonic measurements have captured more importance in the field of industries, medical science engineering and agriculture. These studies are used to investigate different chemical processes; also play a very important role in the field of synthetic works [6]. The ultrasonic velocity of different electrolytic solutions has been determined at various concentrations and temperatures [7-10]. The knowledge of structure and thermo physical properties of Tetra-n-butyl ammonium bromide (TBAB) and 1-Butyl-2,3dimethylimmidazolium chloride [bdmim]Cl absolutely

necessary to study their intermolecular interactions. These observed properties are also providing knowledge about the nature of intermolecular interactions that can exist between TBAB and imidazolium based ionic liquid mixtures, and are dependent on the molecular geometry and charge distribution of the solvents [11]. The present research is an endeavor to study the intermolecular interactions as well as effects of the temperature on various physicochemical properties of the [bdmim]Cl in aqueous solutions of TBAB. Hereof, the speed of sound and densities for [bdmim]Cl in the aqueous solutions of TBAB at various concentrations and temperatures, T = (298.15-313.15) K were determined. A literature survey has been done and reveals that no reports are available for these investigated systems. These reports have a great deal to add in developing structure—property co-relationship as well as the molecular modelling.

2. MATERIALS AND METHODS

2.1 Materials.

The ionic liquid, 1-Butyl-2,3-dimethylimidazolium chloride, [bdmim]Cl, with mass fraction purity ≥ 0.985 , Tetra-nbutyl ammonium bromide, TBAB with mass fraction purity ≥ 0.99 were imported from Sigma-Aldrich (U.S.A.). The IL,[bdmim]Cl, was dried overnight to eliminate moisture content under vacuum at 343.15 K. Later than Karl Fischer analysis, the water content was found to be 351ppm. Tetra butyl ammonium bromide was purified by recrystallization from acetone, and all the required substances were desiccated by keeping in vacuum desiccators over P_2O_5 for

about 2-3 days before its application. The complete information of the compounds taken in this study is presented in Table 1.

2.2 Instruments and methods.

Electronic balance of model ABJ-220-4NM (KERN, Germany) was used to record the mass of solute and solvents with a precision of 10⁻⁴g. The solutions of concentration 0.08, 0.10, and 0.12mol dm⁻³ were prepared by weighing the required amount of electrolyte in a weighing bottle and then dissolving it in the required amount of solvent in a 250 mL measuring flask. Rest of the solutions of concentration 0.001, 0.005, 0.01, 0.02, 0.04, and 0.06 mol dm⁻³ were prepared by dilution. The conversion of

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concentrations from molarity to molality was done by using the usual formula and density data at each concentration. For the preparation of solutions, we used degassed double distilled water having specific conductance value in the range 2-3×10 ⁻⁶ S cm⁻¹ ¹with uncertainty of molality found to be 2×10^{-4} mol kg ⁻¹. The density (ρ) and the ultrasonic speed (u) of mixtures were determined simultaneously with a high precision digital density and sound velocity analyser-5000, (DSA-5000: oscillating U-tube speed of sound with frequency of 3MHz and density analyser), supplied by Anton Paar GmbH, Austria. The instrument has been calibrated periodically with two fluids i.e. dry air and distilled water over a temperature range (293.15-313.15) K. This two-inone instrument has been equipped with a density cell and a speed of sound cell; both the cells are thermally controlled by a built-in Peltier thermostat. The density and speed of sound measuring ranges are from (0 to 3) gcm⁻³ and from (1000 to 2000) m·s⁻¹. The uncertainties in the density measurements were found to lie well within 0.2 kg·m⁻³ while those in the speed of sound data were found to be better than 0.5 m·s⁻¹. The precision in temperature of the DSA-5000 was controlled to $\pm 1 \times 10^{-3}$ K.

2.3 Theory.

The density and ultrasonic velocities of the IL solutions have been measured at T = (298.15 to 313.15) K. From the experimentally determined values of density and ultrasonic velocities a number of thermo-acoustic parameters have been calculated by using the following relationships [12-19].

Isentropic compressibility (
$$\beta_S$$
) = $\frac{1}{\rho u^2}$

Isothermal compressibility
$$(\beta_T) = \frac{17.1 \times 10^{-4}}{T^{4/9} \rho^{4/3} u^2}$$
----(2)

Coefficient of thermal expansion,
$$(\alpha) = \frac{75.6 \times 10^{-3}}{T^{1/9} u^{1/3} \rho^{1/3}}$$
 -----(3)

Heat capacity ratio
$$(\gamma) = \frac{\beta_T}{\beta_S}$$
 -----(4)

Intermolecular free length
$$(L_f) = K_T \times \beta_s^{1/2}$$
 -----(5)

Acoustic Impedance (
$$Z$$
) = ρu -----(6)

Molar Sound Velocity
$$(R) = \left(\frac{M_z}{\rho}\right) u^{1/3}$$
----(7)

Molar compressibility
$$(W) = (\frac{\dot{M_z}}{\rho})\beta_s^{-1/7}$$
----(8)

Where K_T is the Jacobson's temperature dependent constant [20] and it is equal to $(93.875 + 0.375T) \times 10^{-8}$. And is equal to 207.5×10^{-8} at 303.15 K. M_z is the relative molar mass and T is temperature in Kelvin. R is known as Rao's constant and W is called as Wada's constant.

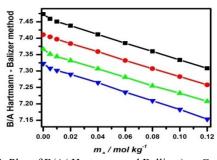


Figure 1. Plot of B/A(Hartmann and Ballizer)vs. Concentration of [bdmim]Cl in 0.0130mTBAB + Water solution at different temperatures:

— ▼—298.15K, — ▲—303.15 K, — ●—308.15K, and — ■—313.15 K respectively

Non linearity parameter, (B/A) which is due to Hartmann and Balizer is given by

$$\frac{B}{A} = -0.5 + (1.2 \times 10^4)/u$$
 -----(9)

And from the empirical relationship of Ballou employed by Hartmann, the values of non-linearity parameter can be given as:

$$\frac{B}{A} = 2 + \frac{0.98 \times 10^4}{v}$$
 -----(10)

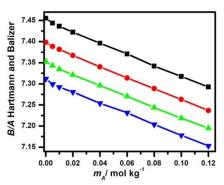


Figure 2. Plot of B/A(Hartmann and Ballizer)vs. Concentration of [bdmim]Cl in 0.02526mTBAB + Water solution at different temperatures:

— ▼—298.15K, — ▲—303.15 K, — ●—308.15K, and — ■—313.15 K respectively.

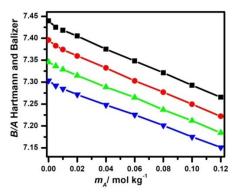


Figure 3. Plot of B/A(Hartmann and Ballizer)vs. Concentration of [bdmim]Cl in 0.0509mTBAB + Water solution at different temperatures:

—▼—298.15K, —▲—303.15 K, —●—308.15K, and —■—313.15 K respectively.

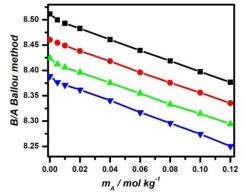


Figure 4. Plot of B/A(Ballou)vs. Concentration of [bdmim]Cl in 0.0130mTBAB + Water solution at different temperatures:

- V—298.15K, — △—303.15 K, — ●—308.15K, and — ■—313.15 K respectively.

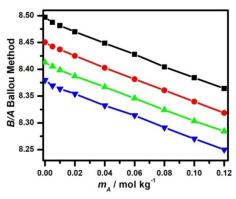


Figure 5. Plot of B/A(Ballou method)vs. Concentration of [bdmim]Cl in 0.02526mTBAB + Water solution at different temperatures:

—▼—298.15K, —▲—303.15 K, —●—308.15K, and —■—313.15 K respectively.

3. RESULTS

3.1. Effect of concentration and Temperature.

The ultrasonic velocity and density of [bdmim]Cl in aqueous solutions of 0.0130 mol kg-1 TBAB, 0.02526 mol kg-¹TBAB and in 0.05093 mol kg⁻¹ TBAB at various temperatures T = (298.15 - 313.15)K are presented in Table 2. Various thermoacoustic parameters like isothermal compressibility (β_T) , isentropic compressibility (β_s) , inter molecular free length (L_f) , acoustic impedance (Z), molar sound velocity(R), molar compressibility (W), heat capacity $ratio(\gamma)$ and coefficient of thermal expansion (a), were determined by using above mentioned formulae from equations (1-8). The nonlinear parameter values have been calculated at 3 MHz frequency by the empirical relation of Ballou and theoretically derived relation of Hartmann and Balizer from equation (9-10) at various temperatures 298.15K to 313.15K. The values of experimental data are mentioned in Table (2-5). From these values, it is observed that density of [bdmim]Cl rapidly increases by increasing the concentration of solute in the solvent. But the density decreases with an increase in temperature as the volume increases with it. An increase in density has a characteristic impact on ultrasonic velocity. Ultrasonic velocity increases with an increase in density are owing to the increase in the number of particles in a particular region with an increase in concentration, by which ultrasonic velocity gets transferred and therefore, ultrasonic velocity increases. This indicates that the greater association among the molecules of [bdmim]Cl solution due to effective solute-solvent interactions. As the interaction among the molecules of [bdmim]Cl in the solution is stronger. So the density and ultrasonic velocities are increased. The variation of ultrasonic velocity of the system with molality(m), of [bdmim]Cl in different concentrated TBAB solvent can be expressed in terms of density and adiabatic compressibility by the following expression;

$$\frac{du}{dm} = -\frac{u}{2} \left[\frac{1}{\rho} \frac{d\rho}{dm} + \frac{1}{\beta_T} \frac{d\beta_T}{dm} \right] \tag{11}$$

The sign and magnitude of du/dc and $d\beta_T/dc$ indicate that the H-bonded structure of water is disrupted by the addition of [bdmim]Cl. The ultrasonic velocity of the stock solutions increases with a rise in temperature and with an increase in concentration [21-23]. So it suggests that there is some interaction between the [bdmim]Cl particles with TBAB solvent at different concentration and at different temperatures. The solute particles

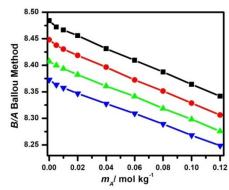


Figure 6. Plot of B/A(Ballou method)vs. Concentration of [bdmim]Cl in 0.0509mTBAB + Water solution at different temperatures:

—▼—298.15K, —▲—303.15 K, —●—308.15K, and —■—313.15 K respectively.

tend to occupy interstitial space of water + TBAB solvent and disturbed the orderly arrangement of water particles with TBAB. This is due to self-association of solute particles with solvent particles. The solute particles are causing electrostriction leads to a decrease in the compressibility of the solution [24-25].

Isentropic compressibility, β_S , is defined as the volume change that takes place due to a change in pressure at constant entropy. The same change at constant temperature is termed as isothermal compressibility, β_T . That means isentropic compressibility has a characteristic impact on the volume change of the solution. The isentropic values decrease with an increase in concentration of the solute as well as with an increase in temperature (Table 3) which is due to an increase in acoustic impedance (Z) [26-27]. The impedance offered by the components of the mixture to the sound wave is called acoustic impedance (Z).

It is well known that with an increase in ultrasonic velocity, acoustic impedance (Z) increases and decreases by the increase isothermal compressibility, β_T and isentropic compressibility, β_S . From the experimentally determined values of acoustic impedance, (Z), it is observed that this value increases with an increase in concentration and temperature, which is due to the presence of strong ion solvent interactions among solute [bdmim]Cl and solvent in TBAB + Water .

From Table-3 we can observe that there is reduction in intermolecular free length (L_f) with gradual increase in concentration of solute and increases with the rise of temperature gives an idea that there is some observable interactions exist between the solute [bdmim]Cl and solvent in TBAB + Water and also portentous the structure making behavior of [bdmim]Cl in TBAB + Water at different concentrations and temperatures [28]. The relation between L_f has been extracted from Eyring and Kincaid equation [29].

From the Table 3, the observable fall in coefficient of thermal expansion (α) by the rise of concentration of the solute i.e. [bdmim]Cl in solvent TBAB + Water and with temperature indicates that the increase in concentration of solute causes more ion-solvent interaction due to increase in values of density. But it also reduces with an increase in temperature. Hence the increase in ultrasonic velocity is due to compactness and small intermolecular free length. By these combined effects α also decreases in a solution. The decrease in isentropic compressibility and isothermal

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compressibility was caused due to a decrease in coefficient of thermal expansion which is due to a decrease in density [30-31]. From Table 3, the heat capacity ratio decreases to a lesser extent by increasing concentration but with rise of temperature notable fall of heat capacity ratio can be observed from the graph. Rao's constant (R) i.e. molar sound velocity increases with an increase in concentration and temperature suggesting the strong interaction among the particles of solute and solvent molecules. The knowledge of tight packing of solute particles inside the solvent can be withdrawn from the increase in values of "W" with a rise in temperature and concentration (Table 5). Hence inter molecular interaction among the solute and solvent increases from the above experimental measurements. The values of nonlinear parameter of [bdmim]Cl in solvent TBAB + Water at various concentrations and temperature regions have been determined with the help of two methods, empirical relation of Ballou and theoretically derived relation of Hartmann and Balizer from equation (9-10) are given Table 5. From Table 5 it is noticed that the Non linearity parameters (B/A) are decreased (Fig. 1-6) with the increase in concentration of [bdmim]Cl in solvent TBAB + Water and with the rise of temperature due to solute-solvent interactions.

In different concentrations of solvent, such as 0.0130 mol kg-1 TBAB, 0.02526 mol kg-1TBAB and in 0.05093 mol kg-1 TBAB the above mentioned thermo acoustic parameters have an observable effect. It is noticed that the values of isothermal compressibility, isentropic compressibility, heat capacity ratio, coefficient of thermal expansion, intermolecular free length of [bdmim]Cl in TBAB at various concentration decreases in the order 0.05093m TBAB>0.02526m TBAB >0.0130m TBAB. The greater β values due to molecular association is more in 0.05093m TBAB as compared to 0.02526m TBAB and 0.0130m TBAB. Hence, [bdmim]Cl molecules exist in ionic form in TBAB+Water solvent and have strong interaction between the surrounding solvent molecules. Large TBAB+Water around the ions produced by [bdmim]C1 [32]. A decrease in β_s and β_T and association of solvents leading to compression is due to negative variation of above discussed thermo acoustic parameters. We now focus on ionic interaction due to H-bonding. The H-bonding in 0.05093m TBAB>0.02526m TBAB >0.0130m TBAB. Due to greater Hbonding, the solvent becomes denser. Therefore the ultrasonic velocity is more in 0.05093m TBAB. So the interactions of solutesolvent follows the order 0.05093m TBAB >0.02526m TBAB >0.0130m TBAB.

Table 1. Provenance and mass fraction purity of the materials studied.

Chemical Name	Source	CAS number	Purification method	Initial mass fraction purity
1-Butyl-2,3-	Sigma-Aldrich	1643-19-2	Vacuum drying	Assay>0.98
dimethylimmidazoliumchloride				
Tetra-n-butylammonium bromide	Merck	1643-19-2	Vacuum drying	Assay> 0.99

As declared by supplier.

Table 2. Experimentally determined density, ρ , ultrasonic velocity, u, and of isentropic compressibility, β_s of [bdmim]Cl in TBAB +Water solutions at T= (298.15 to 313.15)K.

m_A		ρ/ k	gm ⁻³			u	ms ⁻¹		$ m eta_S imes 10^{10}/m^2 N^{-1}$				
mol	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15K	298.15 K	303.15 K	308.15 K	313.15 K	
kg ⁻													
						$m_B = 0.0130$							
0.000	997.33	995.92	994.30	992.47	1505.1	1516.9	1525.6	1534.0	4.426	4.364	4.321	4.282	
0.005	997.38	995.97	994.35	992.52	1507.8	1518.3	1528.4	1536.9	4.410	4.356	4.305	4.266	
0.010	997.43	996.02	994.39	992.56	1509.4	1519.7	1529.9	1538.2	4.401	4.348	4.297	4.258	
0.020	997.52	996.11	994.49	992.66	1511.7	1522.2	1532.2	1540.5	4.387	4.333	4.283	4.245	
0.040	997.70	996.30	994.67	992.84	1516.8	1526.9	1537.1	1545.5	4.356	4.305	4.255	4.217	
0.060	997.89	996.48	994.85	993.02	1521.9	1532.2	1542.2	1551.3	4.327	4.275	4.226	4.185	
0.080	998.06	996.65	995.03	993.20	1526.8	1537.1	1547.5	1556.6	4.298	4.247	4.197	4.156	
0.100	998.24	996.83	995.20	993.37	1531.9	1541.9	1552.0	1562.0	4.269	4.220	4.172	4.126	
0.120	998.41	997.00	995.37	993.55	1536.9	1546.9	1557.0	1568.0	4.241	4.192	4.144	4.094	
	TBAB ($m_B = 0.02526 \text{ mol kg}^{-1}$)+ Water												
0.000	997.63	996.20	994.56	992.71	1508.4	1519.3	1528.2	1536.1	4.406	4.349	4.306	4.269	
0.005	997.67	996.25	994.60	992.75	1510.6	1521.2	1530.0	1538.6	4.393	4.338	4.295	4.255	
0.010	997.72	996.29	994.65	992.79	1512.0	1522.5	1531.6	1540.0	4.384	4.330	4.286	4.247	
0.020	997.81	996.38	994.73	992.88	1514.7	1525.3	1534.3	1542.3	4.368	4.314	4.271	4.234	
0.040	997.99	996.56	994.90	993.04	1519.7	1530.6	1539.2	1547.6	4.339	4.283	4.243	4.205	
0.060	998.17	996.73	995.06	993.20	1524.6	1535.7	1544.3	1552.1	4.310	4.254	4.214	4.179	
0.080	998.34	996.90	995.22	993.35	1530.2	1540.7	1549.6	1557.7	4.278	4.226	4.185	4.149	
0.100	998.51	997.06	995.38	993.50	1535.0	1545.8	1554.7	1562.9	4.250	4.197	4.156	4.121	
0.120	998.68	997.22	995.54	993.65	1539.9	1551.0	1559.4	1568.0	4.222	4.169	4.131	4.093	
					TBAB ($m_B = 0.05093$	mol kg ⁻¹)+	Water					
0.000	997.90	996.70	995.05	993.19	1511.4	1519.8	1529.5	1537.8	4.387	4.344	4.296	4.258	
0.005	997.94	996.74	995.08	993.22	1514.2	1522.3	1531.3	1540.1	4.371	4.330	4.286	4.245	
0.010	997.98	996.77	995.12	993.25	1515.5	1524.0	1532.8	1541.5	4.363	4.319	4.277	4.237	
0.020	998.05	996.84	995.18	993.31	1518.0	1526.8	1535.5	1544.1	4.348	4.303	4.262	4.222	
0.040	998.20	996.98	995.31	993.44	1523.8	1532.1	1540.7	1548.8	4.314	4.273	4.233	4.196	
0.060	998.34	997.12	995.44	993.56	1529.0	1537.9	1545.4	1553.3	4.285	4.240	4.206	4.171	
0.080	998.48	997.25	995.57	993.68	1534.3	1543.0	1551.0	1558.2	4.254	4.212	4.175	4.145	
0.100	998.62	997.38	995.69	993.80	1539.9	1548.5	1556.0	1563.5	4.223	4.181	4.148	4.116	
0.120	998.75	997.51	995.81	993.91	1545.3	1554.0	1561.6	1568.4	4.193	4.152	4.118	4.090	

Ultrasonic studies on temperature dependence of ion solvent interactions of ionic liquid 1-butyl-2,3- dimethylimidazolium chloride in aqueous solutions of tetra-n-butylammonium bromide at T = (298.15 to 313.15) K

Table 3. Calculated values of isothermal compressibility, β_T , Co-efficient of thermal expansion, α , and heat capacity ratio, γ , of [bdmim]Cl in TBAB + Water solutions at T= (298.15 to 313.15)K.

m_A $\beta_T \times 10^{15} \text{/m}^2 \text{N}^{-1}$ $\alpha \times 10^4 / \text{K}^{-1}$ $\gamma \times 10^5$												
m _{A'}		$p_T \sim 10^{-71}$				u^10	/10			<i>/</i> ^.	10	
kg ⁻	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15K	298.15 K	303.15 K	308.15 K	313.15 K
TBAB ($m_B = 0.0130$ mol kg ⁻¹)+ Water												
0.000	6.021	5.895	5.799	5.708	1.036	1.030	1.026	1.022	1.360	1.351	1.342	1.333
0.005	5.999	5.884	5.777	5.687	1.035	1.030	1.025	1.021	1.360	1.351	1.342	1.333
0.010	5.986	5.873	5.766	5.677	1.034	1.029	1.024	1.020	1.360	1.351	1.342	1.333
0.020	5.967	5.853	5.747	5.659	1.033	1.028	1.024	1.020	1.360	1.351	1.342	1.333
0.040	5.925	5.815	5.709	5.621	1.031	1.027	1.022	1.018	1.360	1.351	1.342	1.333
0.060	5.884	5.774	5.670	5.577	1.030	1.025	1.020	1.016	1.360	1.351	1.342	1.333
0.080	5.846	5.736	5.630	5.539	1.028	1.023	1.018	1.014	1.360	1.351	1.342	1.333
0.100	5.805	5.699	5.596	5.499	1.026	1.021	1.017	1.012	1.360	1.351	1.341	1.333
0.120	5.766	5.661	5.559	5.456	1.024	1.020	1.015	1.010	1.360	1.350	1.341	1.333
	TBAB ($m_B = 0.02526 \text{ mol kg}^{-1}$)+ Water											
0.000	5.993	5.875	5.777	5.691	1.034	1.029	1.025	1.021	1.360	1.351	1.342	1.333
0.005	5.975	5.860	5.763	5.672	1.034	1.029	1.024	1.020	1.360	1.351	1.342	1.333
0.010	5.963	5.849	5.751	5.661	1.033	1.028	1.024	1.020	1.360	1.351	1.342	1.333
0.020	5.941	5.827	5.730	5.644	1.032	1.027	1.023	1.019	1.360	1.351	1.342	1.333
0.040	5.900	5.785	5.692	5.604	1.030	1.025	1.021	1.017	1.360	1.351	1.342	1.333
0.060	5.861	5.746	5.653	5.570	1.029	1.024	1.019	1.016	1.360	1.351	1.342	1.333
0.080	5.817	5.707	5.613	5.529	1.027	1.022	1.018	1.014	1.360	1.350	1.341	1.333
0.100	5.780	5.668	5.575	5.492	1.025	1.020	1.016	1.012	1.360	1.350	1.341	1.333
0.120	5.741	5.629	5.541	5.455	1.023	1.018	1.014	1.010	1.360	1.350	1.341	1.333
				T	$BAB (m_B =$	0.05093 mol	kg-1)+ Water	r				
0.000	5.966	5.867	5.763	5.675	1.033	1.029	1.024	1.020	1.360	1.351	1.342	1.333
0.005	5.944	5.847	5.749	5.658	1.032	1.028	1.024	1.020	1.360	1.351	1.342	1.333
0.010	5.933	5.834	5.738	5.647	1.032	1.027	1.023	1.019	1.360	1.351	1.341	1.333
0.020	5.914	5.812	5.717	5.627	1.031	1.026	1.022	1.018	1.360	1.351	1.341	1.333
0.040	5.867	5.771	5.678	5.592	1.029	1.025	1.021	1.017	1.360	1.350	1.341	1.333
0.060	5.826	5.726	5.642	5.559	1.027	1.023	1.019	1.015	1.360	1.350	1.341	1.333
0.080	5.785	5.687	5.600	5.523	1.025	1.021	1.017	1.013	1.360	1.350	1.341	1.333
0.100	5.742	5.646	5.563	5.485	1.023	1.019	1.015	1.012	1.360	1.350	1.341	1.333
0.120	5.701	5.605	5.523	5.450	1.022	1.017	1.013	1.010	1.360	1.350	1.341	1.332

Table 4. Calculated values of Intermolecular Free length, L_f , Acoustic impedance, Z, and Molar sound velocity, R, of [bdmim]Cl in TBAB + Water solutions at T=(298.15 to 313.15)K.

m_{A} $L_{\rm f} \times 10^{11}/{\rm m}$ $Z \times 10^{-6} / {\rm kg m^2 sec^{-1}}$ $R \times 10^4 / ({\rm m^3/mol}) ({\rm m/s})^{1/3}$													
m_A		$L_{\rm f} \times 10^{\circ}$	''/m			Z×10 ⁻⁰ / k	g m ^{-z} sec ⁻¹			$R \times 10^4 / (m^3/mol)(m/s)^{1/3}$			
mol kg ⁻	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15K	298.15 K	303.15 K	308.15 K	313.15 K	
TBAB ($m_B = 0.0130 \text{ mol kg}^{-1}$)+ Water													
0.000	4.327	4.336	4.354	4.373	1.501	1.511	1.517	1.522	2.0762	2.0847	2.0920	2.0997	
0.005	4.319	4.332	4.346	4.364	1.504	1.512	1.52	1.525	2.0772	2.0851	2.0929	2.1008	
0.010	4.315	4.328	4.341	4.360	1.505	1.514	1.521	1.527	2.0792	2.0869	2.0950	2.1028	
0.020	4.308	4.320	4.334	4.354	1.508	1.516	1.524	1.529	2.0816	2.0893	2.0974	2.1051	
0.040	4.293	4.307	4.320	4.339	1.513	1.521	1.529	1.534	2.0861	2.0939	2.1019	2.1096	
0.060	4.278	4.291	4.305	4.322	1.519	1.527	1.534	1.54	2.0952	2.1029	2.1110	2.1188	
0.080	4.264	4.277	4.290	4.308	1.524	1.532	1.54	1.546	2.1045	2.1122	2.1203	2.1285	
0.100	4.250	4.264	4.278	4.292	1.529	1.537	1.545	1.552	2.1137	2.1215	2.1298	2.1379	
0.120	4.236	4.250	4.264	4.275	1.534	1.542	1.55	1.558	2.1231	2.1307	2.1389	2.1475	
TBAB (m _B = 0.02526 mol kg ⁻¹)+ Water													
0.000	4.317	4.328	4.346	4.366	1.505	1.513	1.52	1.525	2.0851	2.0931	2.1007	2.1083	
0.005	4.311	4.323	4.340	4.359	1.507	1.515	1.522	1.527	2.0702	2.0781	2.0856	2.0931	
0.010	4.307	4.319	4.336	4.355	1.509	1.517	1.523	1.529	2.0878	2.0957	2.1033	2.1112	
0.020	4.299	4.311	4.328	4.348	1.511	1.52	1.526	1.531	2.0902	2.0981	2.1057	2.1136	
0.040	4.284	4.296	4.314	4.333	1.517	1.525	1.531	1.537	2.0949	2.1028	2.1104	2.1181	
0.060	4.270	4.281	4.299	4.320	1.522	1.531	1.537	1.542	2.1041	2.1122	2.1197	2.1276	
0.080	4.254	4.267	4.284	4.304	1.528	1.536	1.542	1.547	2.1133	2.1215	2.1291	2.1368	
0.100	4.240	4.252	4.270	4.290	1.533	1.541	1.548	1.553	2.1229	2.1309	2.1386	2.1465	
0.120	4.226	4.238	4.257	4.275	1.538	1.547	1.552	1.558	2.1322	2.1404	2.1482	2.1561	
							kg ⁻¹) + Wate						
0.000	4.308	4.326	4.341	4.360	1.508	1.515	1.522	1.527	2.1021	2.1085	2.1166	2.1244	
0.005	4.300	4.319	4.336	4.354	1.511	1.517	1.524	1.53	2.1029	2.1093	2.1172	2.1251	
0.010	4.296	4.314	4.331	4.349	1.512	1.519	1.525	1.531	2.1051	2.1114	2.1192	2.1273	
0.020	4.289	4.306	4.324	4.342	1.515	1.522	1.528	1.534	2.1075	2.1140	2.1217	2.1298	
0.040	4.272	4.291	4.309	4.329	1.521	1.527	1.533	1.539	2.1122	2.1189	2.1265	2.1345	
0.060	4.257	4.274	4.295	4.316	1.526	1.533	1.538	1.543	2.1219	2.1284	2.1360	2.1439	
0.080	4.242	4.260	4.279	4.302	1.532	1.539	1.544	1.548	2.1315	2.1383	2.1455	2.1533	
0.100	4.227	4.244	4.265	4.287	1.538	1.544	1.549	1.554	2.1412	2.1479	2.1554	2.1629	
0.120	4.212	4.229	4.250	4.274	1.543	1.55	1.555	1.559	2.1510	2.1578	2.1651	2.1728	

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Table 5. Calculated values of molar compressibility (W), nonlinear parameters by Hartmann - Balizer method and Ballou method in [bdmim]Cl in TBAB + Water solutions at T=(298.15 to 313.15)K.

m_A	,	$W \times 10^4 / (m^3/n$	nol)(N/m²) ^{1/7}			B/A (Hartma	nn – Balizer)		B/A(Ballou method)				
mol kg ⁻	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15K	298.15 K	303.15 K	308.15 K	313.15 K	
		•			TBAB (m _B	= 0.0130 mol	kg-1)+ Wate	r				•	
0.000	3.9298	3.9435	3.9554	3.9679	7.4732	7.4107	7.3660	7.3227	8.5114	8.4604	8.4239	8.3886	
0.005	3.9314	3.9443	3.9569	3.9697	7.4588	7.4037	7.3515	7.3081	8.4997	8.4547	8.4121	8.3766	
0.010	3.9350	3.9477	3.9607	3.9733	7.4504	7.3966	7.3439	7.3016	8.4929	8.4489	8.4059	8.3713	
0.020	3.9394	3.9519	3.9651	3.9775	7.4381	7.3834	7.3319	7.2897	8.4828	8.4381	8.3961	8.3616	
0.040	3.9477	3.9603	3.9733	3.9858	7.4113	7.3590	7.3068	7.2644	8.4609	8.4181	8.3756	8.3409	
0.060	3.9645	3.9769	3.9902	4.0028	7.3848	7.3319	7.2810	7.2354	8.4393	8.3960	8.3545	8.3172	
0.080	3.9815	3.9941	4.0072	4.0204	7.3598	7.3071	7.2546	7.2093	8.4188	8.3758	8.3330	8.2959	
0.100	3.9983	4.0110	4.0245	4.0377	7.3335	7.2828	7.2322	7.1827	8.3973	8.3560	8.3146	8.2742	
0.120	4.0155	4.0280	4.0413	4.0553	7.3081	7.2577	7.2073	7.1533	8.3766	8.3354	8.2943	8.2502	
TBAB ($m_B = 0.02526 \text{ mol kg}^{-1}$)+ Water													
0.000	3.9464	3.9594	3.9717	3.9839	7.4557	7.3986	7.3526	7.3122	8.4971	8.4505	8.4129	8.3800	
0.005	3.9180	3.9308	3.9429	3.9552	7.4440	7.3887	7.3430	7.2993	8.4876	8.4425	8.4051	8.3695	
0.010	3.9513	3.9641	3.9763	3.9891	7.4367	7.3817	7.3352	7.2922	8.4817	8.4368	8.3987	8.3636	
0.020	3.9556	3.9683	3.9808	3.9935	7.4224	7.3674	7.3214	7.2808	8.4699	8.4251	8.3875	8.3544	
0.040	3.9641	3.9770	3.9894	4.0018	7.3961	7.3400	7.2963	7.2539	8.4485	8.4026	8.3669	8.3324	
0.060	3.9810	3.9942	4.0064	4.0192	7.3708	7.3143	7.2705	7.2313	8.4278	8.3816	8.3459	8.3139	
0.080	3.9980	4.0113	4.0236	4.0360	7.3423	7.2886	7.2441	7.2036	8.4045	8.3607	8.3243	8.2912	
0.100	4.0155	4.0285	4.0411	4.0538	7.3176	7.2630	7.2185	7.1782	8.3844	8.3397	8.3035	8.2706	
0.120	4.0326	4.0459	4.0585	4.0714	7.2925	7.2370	7.1954	7.1532	8.3639	8.3185	8.2846	8.2501	
						0.05093 mo							
0.000	3.9783	3.9887	4.0018	4.0145	7.4395	7.3959	7.3459	7.3036	8.4839	8.4483	8.4075	8.3729	
0.005	3.9796	3.9901	4.0029	4.0158	7.4252	7.3830	7.3366	7.2919	8.4723	8.4378	8.3999	8.3634	
0.010	3.9837	3.9939	4.0065	4.0196	7.4180	7.3740	7.3288	7.2844	8.4664	8.4304	8.3935	8.3573	
0.020	3.9880	3.9986	4.0110	4.0241	7.4053	7.3595	7.3152	7.2716	8.4560	8.4186	8.3825	8.3468	
0.040	3.9966	4.0074	4.0198	4.0329	7.3750	7.3325	7.2889	7.2479	8.4313	8.3966	8.3610	8.3274	
0.060	4.0144	4.0249	4.0373	4.0501	7.3483	7.3030	7.2651	7.2253	8.4095	8.3725	8.3415	8.3090	
0.080	4.0319	4.0430	4.0546	4.0674	7.3210	7.2772	7.2369	7.2010	8.3871	8.3514	8.3185	8.2892	
0.100	4.0497	4.0606	4.0727	4.0850	7.2926	7.2494	7.2120	7.1751	8.3640	8.3287	8.2981	8.2680	
0.120	4.0677	4.0786	4.0905	4.1030	7.2655	7.2223	7.1845	7.1513	8.3418	8.3065	8.2756	8.2485	

4. CONCLUSIONS

The structure promotion behavior of [bdmim]Cl in solvent of TBAB+Water was successfully analyzed from the experimental results. From the experimental results, density and ultrasonic velocity obtained for IL, [bdmim]Clin 0.0130 mol kg⁻¹ TBAB, 0.02526 mol kg⁻¹ TBAB and in 0.05093 mol kg⁻¹ TBAB indicates that with an increase in concentration of [bdmim]Cl in the above solvents increases the density as well as ultrasonic velocity. But with an increase in temperature the density decreases. This information strongly supports the interaction among the molecules of solute and solvent. The electrolyte occupies the interstitial space of water and tends to break the actual structure of water, due to the interaction between molecules of solute and solvent. There

is a decrease in inter molecular free length with the rise of solute concentration. The compressibility in solution is caused due to a decrease in values of *Z*, *R* and *W* indicating the structure making behavior of [bdmim]Cl in TBAB. The isentropic and isothermal compressibility decrease with an increase in concentration of [bdmim]Cl in aqueous TBAB solutions. From the above the discussion it is concluded that ion-solvent interactions affected by the thermo acoustical properties and by nonlinear parameters, which are on the whole get not only affected by pressure but also with temperatures and concentration of [bdmim]Cl and the solvent used.

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