Thermoacoustic Parameters Determination of Intermolecular Free-Length of 1-Butyl-2,3-dimethylimidazolium Chloride in Mixed Solvents at T = (298.15 to 313.15) K

Sailaja Muchipali[1], Ranjan Kumar Pradhan[2], Priyaranjan Mohapatra[1,*] and Braja B. Nanda[2,*]

[1]Department of Chemistry, Veer Surendra Sai University of Technology, Burla-768018, India
[2]P.G. Department of Chemistry, Vikram Deb Autonomous College, Jeypore-764001, India

*Corresponding authors: Email: priya_chem@vssut.ac.in; bbnanda.driems@gmail.com

The intermolecular free-length of 1-butyl-2,3-dimethylimidazolium chloride [bdmim]Cl in pure water as well as in tetra-*n*-butyl ammonium bromide (TBAB) + water at different concentrations of solute and at T = (298.15 to 313.15) K have been evaluated by making use of ultrasonic and thermoacoustical parameters followed by a comparative study. To accomplish this objective, thermoacoustical parameters for the above said solutions have been calculated. These parameters have been used to determine intermolecular free-length (L_f) for the solutions under study. The values of L_f obtained by thermoacoustical approach were tallied with the values obtained by well-known ultrasonic method (Schaaffs method). To the best of our understanding, this study is an innovative attempt in the determination of inter-molecular free-length present in the investigated solutions by making use of ultrasonic approach.

Keywords: Intermolecular free-length, Thermoacoustical parameter, 1-Butyl-2,3-dimethyl imidazolium chloride, Schaffs method.

INTRODUCTION

To study the intermolecular interactions and various thermodynamic properties present in ionic liquid mixtures available free volume is used [1]. The change of density and ultrasonic velocity are connected to thermal expansion coefficient and also shows the interactions among the molecules of studied solutions. A number of approaches are available in literature to evaluate thermoacoustical parameters for different ionic liquids [2-6]. Change in free energy and molecular orientation are effected by intermolecular interactions in ionic liquids which has impact on variation of thermodynamic properties [7]. To determine several thermoacoustical parameters in polymers, organic liquids and liquefied gases the data of expansivity was used [8,9]. Available volume is interconnected with another parameter which is inter molecular free length (L_f) due to which inter-molecular interactions can be studied in ionic liquid mixtures. The aim of this work is to investigate the inter-molecular free length in binary solutions of [bdmim]Cl in water as well as in ternary solutions like [bdmim]Cl + TBAB + water system by the help of thermoacoustical parameters and ultrasonic methods.

The applicability of these methods for the determination of available volume and inter molecular free length were checked and the values obtained were interpreted in terms of ion-solvent interactions exist in investigated solutions. Solute-solvent inter-actions are greatly affected by the addition of small amount of ionic solute in the aqueous solution. Tetra alkylammonium halides have been studied and aimed in different branches of chemistry [10-14]. The geometrical nature of water gets effec-ted by the addition of ionic liquids such as [bdmim]Cl and tetra-*n*-butyl ammonium bromide (TBAB). It is due to form-ation of clathrate like structure among the water molecules and ammonium ions of TBAB and imidazolium ion of [bdmim]Cl [15]. These ions contain hydrophilic and hydrophobic groups but do not form H-bonds. Aqueous solution of [bdmim]Cl shows many properties like high viscosity with temperature coeffi-cients [16], high apparent molar heat capacities [17,18], low surface charge densities, high apparent molar volume [19] which is usual. Large sized tetra alkylammonium halides have the ability to arrange with water molecules around themselves subject to their alkyl groups [20-23]. Tetra-*n*-butyl ammonium bromide (TBAB) is an aprotic solvent and commonly used as

a phase transfer catalyst. It is also used to prepare many other tetra butyl ammonium salts by metathesis reactions. In this article, the thermoacoustical parameters were determined by using the experimentally measured values of density and ultrasonic velocity of [bdmim]Cl + water and [bdmim]Cl + TBAB + water systems. The available volume and inter molecular free length at various temperatures, (298.15 to 313.15) K were determined from thermoacoustical parameters and Schaaffs method. The applicability of these two methods were checked and the data used for the interpretation of ion-solvent interactions as well as structure making or structure breaking capacity of the solute with solvents.

EXPERIMENTAL

1-Butyl-2,3-dimethyl imidazolium chloride ([bdmim]Cl) and tetra-*n*-butyl ammonium bromide (TBAB) with mass fraction purities ≥ 0.99 were brought from Sigma-Aldrich (U.S.A.). The chemicals were dried over night to remove moisture content under vacuum at 343.15 K. After Karl Fischer analysis, the water content was found to be 351 ppm. 1-Butyl-2,3-dimethyl imidazolium chloride ([bdmim]Cl) and TBAB was purified by recrystallization from acetone and all the required compounds were desiccated by keeping in vacuum desiccators over P_2O_5 for about 2-3 days earlier their use. The detailed information of the compounds taken in this study is presented in Table-1.

Electronic balance of model ABJ-220-4NM (KERN, Germany) was used to record the masses of solute and solvents with a precision of 10^{-4} g. The preparation of solutions of concentration 0.08, 0.10, and 0.12 mol dm^{-3} were done by weighing the required amount of electrolyte in a weighing bottle and then dissolving it in required amount of solvent in a 250 mL measuring flask. Rest of solutions of concentration 0.005, 0.0075, 0.01, 0.02, 0.04 and 0.06 mol dm^{-3} were prepared by dilution. The conversion of concentrations from molarity to molality was done by usual formula using density data at each concentration. For the preparation of solutions, we have used degassed triply distilled water having specific conductance value < 10^{-6} S cm^{-1} with uncertainty of molality found to be 2×10^{-5} kg mol^{-1}. The density (ρ) and ultrasonic velocity (u) of mixtures were determined simultaneously and mechanically with Anton Paar DSA 5000 (oscillating U-tube speed of sound and density analyzer) instrument. The temperature of the solution was controlled to $\pm 1 \times 10^{-3}$ K by keeping in thermostat. The instruments were calibrated with deionized degassed triply distilled water. The instrument sensitivity linked to precession in density and sound

speed were determined to be $\pm 1 \times 10^{-3}$ kg m^{-3} and $\pm 1 \times 10^{-2}$ m s^{-1}, respectively. The uncertainties of density (ρ) and ultrasonic velocity (u) measurements were $\pm 3 \times 10^{-6}$ g cm^{-3} and $\pm 1 \times 10^{-1}$ m s^{-1}, respectively.

Theory: For the determination of thermal expansion (α) at various temperatures T = (298.15 to 313.15) K, with the help of conventional thermodynamic relation by using the experimental values density (ρ) and ultrasonic velocity (u) of studied solutions [24].

$$\alpha = \frac{75.6 \times 10^{-3}}{T^{1/9} u^{1/2} \rho^{1/3}} \quad (1)$$

By knowing the value of thermal expansion (α) and temperature (T), Sharma parameter (S*), reduced molar volume ($\tilde{V}$) and Moelwyn-Hughes parameter (C$_1$) were determined as below:

Sharma parameter:

$$S^* = 1 + \frac{4\alpha T}{3} \quad (2)$$

Reduced molar volume:

$$\tilde{V} = \left(1 + \frac{\alpha T}{3(1 + \alpha T)}\right)^3 \quad (3)$$

Moelwyn-Hughes parameter:

$$C_1 = \frac{13}{3} + \frac{1}{\alpha T} + \frac{4\alpha T}{3} \quad (4)$$

By using the values of α, $\tilde{V}$ and C$_1$, the isochoric temperature coefficient of internal pressure (X) has been calculated from the following relation:

Isochoric temperature coefficient of internal pressure:

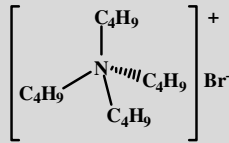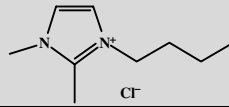$$X = \frac{-2(1 + 2\alpha T)}{\tilde{V} C_1} \quad (5)$$

Other expressions for isothermal (K′), isochoric (K″) and isobaric (K) acoustical parameters can be evaluated from α, X, T and S* as:

$$K = \frac{1}{2}\left(1 + \frac{S^*(1 + \alpha T)}{\alpha T}\right) \quad (6)$$

$$K' = \frac{1}{2}\left(3 + \frac{S^*(1 + \alpha T) + X}{\alpha T}\right) \quad (7)$$

$$K'' = 1 + \frac{X}{2\alpha T} \quad (8)$$

TABLE-1
SPECIFICATION OF CHEMICALS

Name of chemicals	Source	Purification method	Mass fraction purity	CAS number	Structure
Tetra-*n*-butyl ammonium bromide	Sigma-Aldrich	Vacuum drying	≥ 0.99	1643-19-2	
1-Butyl-2, 3-dimethylimidazolium chloride	Sigma-Aldrich	Vacuum drying	≥ 0.99[a]	1643-19-2	

[a]As declared by the supplier.

By using thermoacoustic parameters like K', K'' and K the available volume can be calculated:

$$V_a = \frac{V}{(K'+1)} = \frac{V}{(K''+K+1)} \qquad (9)$$

The value of V_a can be calculated as per Schaaffs method:

$$V_a = V\left(1 - \frac{u}{u_\infty}\right) \qquad (10)$$

where u_∞ and u are the ultrasonic velocity at 1600 m s^{-1} at temperature (T), respectively.

From the value of V_a, the inter molecular free length (L_f) can be determined by the relation:

$$L_f = \frac{2V_a}{Y} \qquad (11)$$

where Y is the surface area per mole of solution and V_a represents the available volume per mole and these are represented as:

$$V_a = (V - V_0) \qquad (12)$$

$$Y = (36\pi N_A V_0^2)^{1/3} \qquad (13)$$

where N_A is the Avogadro number and V_0 and V are the molar volume at zero temperature and at temperature T, respectively. Using eqns 9 and 10, the value of V_a can be calculated and is helpful to calculate intermolecular free length by the eqn. 11.

RESULTS AND DISCUSSION

The values of density (ρ) and ultrasonic velocity (u) for the solutions of [bdmim]Cl in pure water and TBAB-water at T = (298.15 to 313.15) K are reported in Table-2. The values of thermoacoustical parameters, available volume and intermolecular free-length for all the mentioned solutions obtained

from eqns. 9-11 have been reported in Tables 3 and 4, respectively. From the reported data (Table-2), it revealed that the density values of solutions increase with increase in mass fraction of [bdmim]Cl and decrease with increase of temperature. This trend is observed in all the systems irrespective the nature of solvents used in the solutions. The increase of density with increase in mass fraction of solute may be due to addition of solute to the interstitial space of solvent. The increase in ultrasonic speed in all the investigated solutions with increase in mass fraction of solute as well as temperature indicates the presence of strong solute-solvent interactions. With increase in mass fraction of solute, the interstitial space in solution decrease due to self-association and hence ultrasonic speed increases. But with increase in temperature, there occurs a structural rearrangement, as there is increase in molecular motion and decrease in intermolecular free-length at higher temperature, and leads the increase of ultrasonic speed. The values of available volume (V_a) as well as the intermolecular free-length (V_f) calculated by thermoacoustical method are almost increasing with increase in mass fractions of [bdmim]Cl in all the studied solutions as well as with increase in temperature. Whereas these values are decreasing with the same conditions when measured with ultrasonic method. A comparative study of these two methods has also been presented graphically in Figs. 1-4 for available volume (V_a) and Figs. 5-8 for intermolecular free length (L_f). As per data from Tables 3 and 4, it obviously elucidates a fairly good agreement in the values of intermolecular free-length, calculated by ultrasonic method (Figs. 7 and 8). The values of V_a and L_f obtained from ultrasonic method are decreasing with increase in mass fraction of [bdmim]-Cl as well as temperature, while, thermoacoustical approach displays the reverse trend. The variation of ultrasonic speed is

TABLE-2
DENSITY (ρ) AND ULTRASONIC VELOCITY OF 1-BUTYL-2,3-DIMETHYL IMIDAZOLIUM CHLORIDE IN
PURE WATER AS WELL AS IN AQUEOUS SOLUTIONS OF 0.0125 M TBAB, 0.025 M TBAB AND 0.05 M TBAB,
RESPECTIVELY AT TEMPERATURE = (298.15 to 313.15) K AND AT ATMOSPHERIC PRESSURE, $p = 0.1$ MPa

m_A (mol kg^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})				u (m s^{-1})			
	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
In pure water								
0.00000	0.99702	0.99555	0.99408	0.99240	1498.00	1507.00	1516.00	1526.00
0.00100	0.99703	0.99556	0.99409	0.99241	1498.28	1507.27	1516.30	1526.33
0.00502	0.99707	0.99560	0.99413	0.99245	1499.34	1508.39	1517.46	1527.54
0.01004	0.99711	0.99564	0.99417	0.99249	1500.65	1509.75	1518.90	1529.03
0.02013	0.99720	0.99574	0.99427	0.99259	1503.20	1512.42	1521.70	1531.95
0.04040	0.99739	0.99592	0.99445	0.99277	1508.05	1517.48	1527.00	1537.50
0.06082	0.99757	0.99610	0.99463	0.99296	1512.48	1522.20	1531.90	1542.70
0.08139	0.99775	0.99628	0.99481	0.99313	1516.60	1526.50	1536.45	1547.50
0.10211	0.99792	0.99645	0.99498	0.99331	1520.27	1530.48	1540.65	1551.90
0.12298	0.99809	0.99662	0.99515	0.99348	1523.70	1534.30	1544.60	1556.00
[bdmim]Cl in 0.0125 M TBAB + Water								
0.00000	0.99734	0.99593	0.99430	0.99247	1505.05	1516.93	1525.55	1533.99
0.00100	0.99734	0.99594	0.99431	0.99248	1506.40	1517.31	1526.70	1535.60
0.00502	0.99738	0.99597	0.99435	0.99252	1507.77	1518.27	1528.37	1536.87
0.01004	0.99743	0.99602	0.99439	0.99256	1509.35	1519.65	1529.85	1538.15
0.02013	0.99752	0.99611	0.99449	0.99266	1511.69	1522.19	1532.19	1540.49
0.04040	0.99770	0.99630	0.99467	0.99284	1516.82	1526.92	1537.12	1545.52
0.06082	0.99789	0.99648	0.99485	0.99302	1521.91	1532.20	1542.21	1551.31
0.08139	0.99806	0.99665	0.99503	0.99320	1526.76	1537.06	1547.46	1556.56
0.10211	0.99824	0.99683	0.99520	0.99337	1531.89	1541.86	1551.96	1561.96
0.12298	0.99841	0.99700	0.99537	0.99355	1536.86	1546.86	1556.96	1567.96

TABLE-3
VALUES OF AVAILABLE VOLUME (V_a) OF 1-BUTYL-2,3-DIMETHYL IMIDAZOLIUM CHLORIDE IN PURE WATER AND IN 0.0125 M
TBAB + WATER SOLUTIONS AT TEMPERATURE = (298.15 to 313.15) K AND AT ATMOSPHERIC PRESSURE, p = 0.1 MPa BY THER-
MOACOUSTICAL METHOD (eqn. 9) AS WELL AS BY ULTRASONIC METHOD (SCHAAFFS METHOD) (eqn. 10), RESPECTIVELY

m_A (mol kg^{-1})	$10^6 \times V_a$ (m^3 mol^{-1}) (eqn. 9) (Thermoacoustical method)				$10^6 \times V_a$ (m^3 mol^{-1}) (eqn. 10) (Schaaffs method)			
	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
In pure water								
0.00000	8.4586	8.4723	8.4861	8.5018	1.1509	1.0509	0.9506	0.8389
0.00100	8.4600	8.4737	8.4875	8.5032	1.1480	1.0480	0.9474	0.8352
0.00502	8.4657	8.4794	8.4932	8.5090	1.1367	1.0361	0.9349	0.8221
0.01004	8.4728	8.4866	8.5004	8.5163	1.1229	1.0215	0.9193	0.8058
0.02013	8.4871	8.5010	8.5149	8.5308	1.0958	0.9929	0.8890	0.7740
0.04040	8.5160	8.5301	8.5442	8.5602	1.0444	0.9387	0.8316	0.7132
0.06082	8.5453	8.5595	8.5738	8.5901	0.9974	0.8879	0.7784	0.6561
0.08139	8.5750	8.5894	8.6038	8.6203	0.9536	0.8417	0.7289	0.6032
0.10211	8.6050	8.6196	8.6342	8.6509	0.9148	0.7989	0.6831	0.5545
0.12298	8.6355	8.6503	8.6651	8.6819	0.8785	0.7576	0.6398	0.5091
[bdmim]Cl in 0.0125 M TBAB + Water								
0.00000	8.4895	8.5033	8.5184	8.5352	9.1723	1.0751	0.9420	0.8456
0.00100	8.4911	8.5047	8.5200	8.5369	9.1728	1.0600	0.9378	0.8327
0.00502	8.4969	8.5105	8.5258	8.5427	9.1751	1.0452	0.9275	0.8142
0.01004	8.5041	8.5177	8.5331	8.5500	9.1780	1.0281	0.9126	0.7981
0.02013	8.5185	8.5321	8.5476	8.5646	9.1838	1.0032	0.8852	0.7727
0.04040	8.5476	8.5614	8.5770	8.5941	9.1953	0.9481	0.8342	0.7189
0.06082	8.5772	8.5911	8.6069	8.6243	9.2069	0.8931	0.7765	0.6630
0.08139	8.6072	8.6212	8.6372	8.6548	9.2185	0.8405	0.7233	0.6048
0.10211	8.6377	8.6518	8.6679	8.6858	9.2301	0.7843	0.6705	0.5549
0.12298	8.6687	8.6829	8.6991	8.7173	9.2418	0.7296	0.6149	0.4989

TABLE-4
VALUES OF INTERMOLECULAR FREE-LENGTH (L_f) OF 1-BUTYL-2, 3-DIMETHYL IMIDAZOLIUM CHLORIDE IN PURE WATER
AND IN 0.0125 M TBAB + WATER SOLUTIONS AT TEMPERATURE = (298.15 to 313.15) K AND AT ATMOSPHERIC PRESSURE,
p = 0.1 MPa BY THERMOACOUSTICAL METHOD (eqn. 9) AS WELL AS BY ULTRASONIC METHODS (eqn. 10) RESPECTIVELY

m_A (mol kg^{-1})	$10^{11} \times L_f$ (m) (eqn. 9) (Thermoacoustical method)				$10^{11} \times L_f$ (m) (eqn. 10) (Schaaffs method)			
	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
In pure water								
0.00000	9.1723	9.1789	9.1855	9.1931	0.4278	0.3887	0.3499	0.3070
0.00100	9.1728	9.1795	9.1861	9.1936	0.4266	0.3876	0.3486	0.3056
0.00502	9.1751	9.1818	9.1885	9.1960	0.4221	0.3828	0.3437	0.3005
0.01004	9.1780	9.1847	9.1914	9.1990	0.4164	0.3770	0.3375	0.2942
0.02013	9.1838	9.1905	9.1973	9.2049	0.4055	0.3656	0.3257	0.2819
0.04040	9.1953	9.2021	9.2090	9.2167	0.3848	0.3441	0.3033	0.2586
0.06082	9.2069	9.2138	9.2207	9.2286	0.3659	0.3241	0.2826	0.2368
0.08139	9.2185	9.2255	9.2325	9.2405	0.3485	0.3059	0.2635	0.2168
0.10211	9.2301	9.2372	9.2444	9.2524	0.3330	0.2892	0.2459	0.1985
0.12298	9.2418	9.2491	9.2563	9.2644	0.3186	0.2732	0.2294	0.1814
[bdmim]Cl in 0.0125 M TBAB + Water								
0.00000	9.1723	9.1924	9.1994	9.2069	0.3975	0.3461	0.3092	0.2733
0.00100	9.1728	9.1930	9.2002	9.2078	0.3916	0.3445	0.3043	0.2664
0.00502	9.1751	9.1953	9.2027	9.2102	0.3857	0.3404	0.2972	0.2611
0.01004	9.1780	9.1982	9.2056	9.2131	0.3790	0.3345	0.2909	0.2557
0.02013	9.1838	9.2040	9.2114	9.2189	0.3690	0.3238	0.2811	0.2460
0.04040	9.1953	9.2156	9.2231	9.2306	0.3472	0.3038	0.2604	0.2249
0.06082	9.2069	9.2274	9.2349	9.2427	0.3256	0.2815	0.2391	0.2007
0.08139	9.2185	9.2393	9.2469	9.2548	0.3050	0.2611	0.2171	0.1789
0.10211	9.2301	9.2513	9.2589	9.2670	0.2834	0.2410	0.1983	0.1565
0.12298	9.2418	9.2635	9.2711	9.2795	0.2624	0.2200	0.1775	0.1316

interrelated to free-length. The increase in ultrasonic speed and corresponding decrease in free-length for all the systems under study, resembles the idea proposed by Eyring and Kincaid [25], according to which the ultrasonic speed increases with decrease in intermolecular free-length (L_f) and *vice-versa*. The decrease in intermolecular free-length and increase in ultrasonic speed in the studied solutions with increase in mass fraction of solute indicates the presence of solute-solvent interaction between the contributing molecules [26]. The ultrasonic speed also increases due to compactness and smaller intermolecular
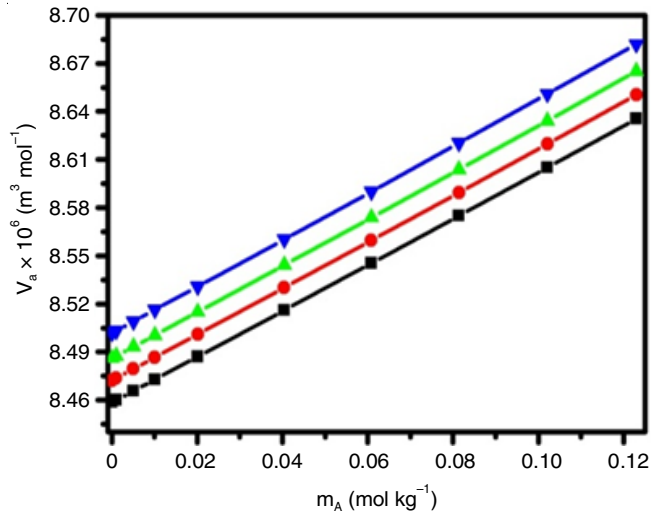
Fig. 1.   Plot of V_a vs. m_A of [bdmim]Cl in pure water by thermo acoustic method at different temperatures: ■ 298.15 K, ● 303.15 K, ▲ 308.15 K, ▼ 313.15 K
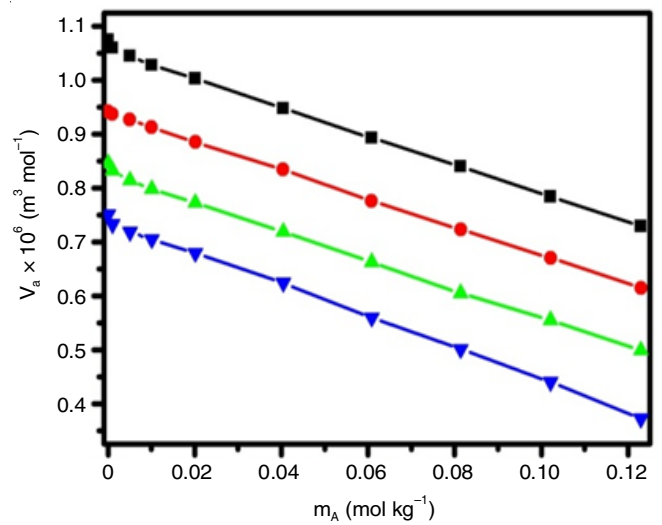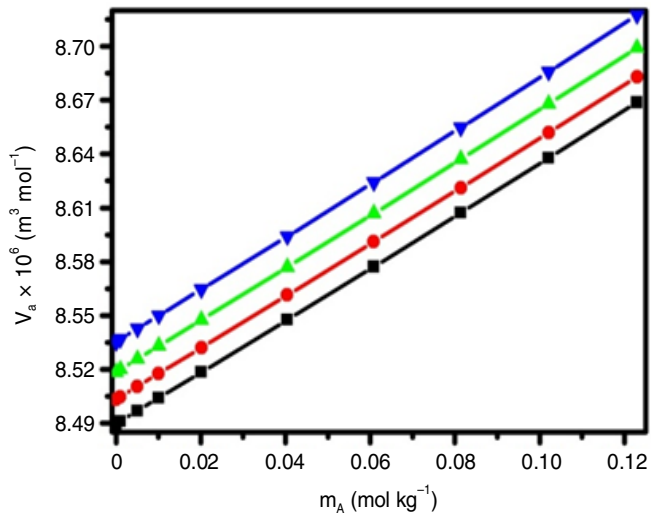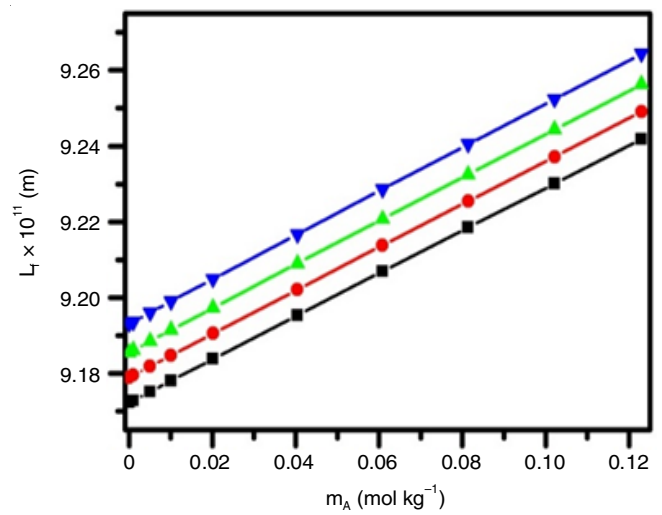

Fig. 4.   Plot of V_a vs. m_A of [bdmim]Cl in 0.0125 M TBAB + water by ultrasonic method at different temperatures: ■ 298.15 K, ● 303.15 K, ▲ 308.15 K, ▼ 313.15 K
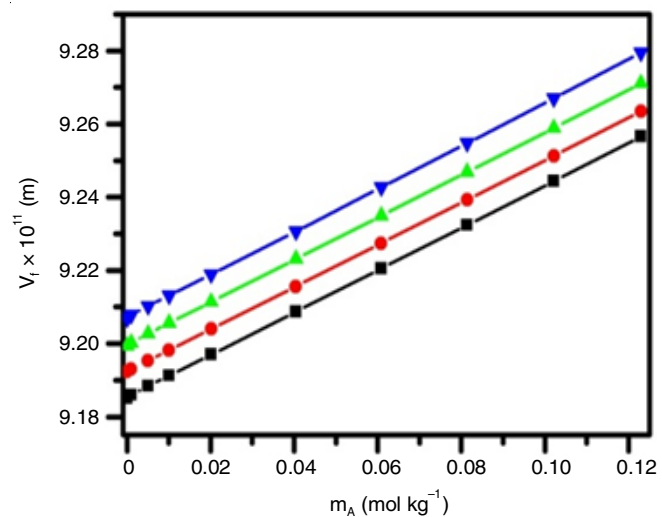

Fig. 2.   Plot of V_a vs. m_A of [bdmim]Cl in 0.0125 M TBAB + water by thermo acoustic method at different temperatures: ■ 298.15 K, ● 303.15 K, ▲ 308.15 K, ▼ 313.15 K

Fig. 5.   Plot of L_f vs. m_A of [bdmim]Cl in pure water by thermo acoustic method at different temperatures: ■ 298.15 K, ● 303.15 K, ▲ 308.15 K, ▼ 313.15 K
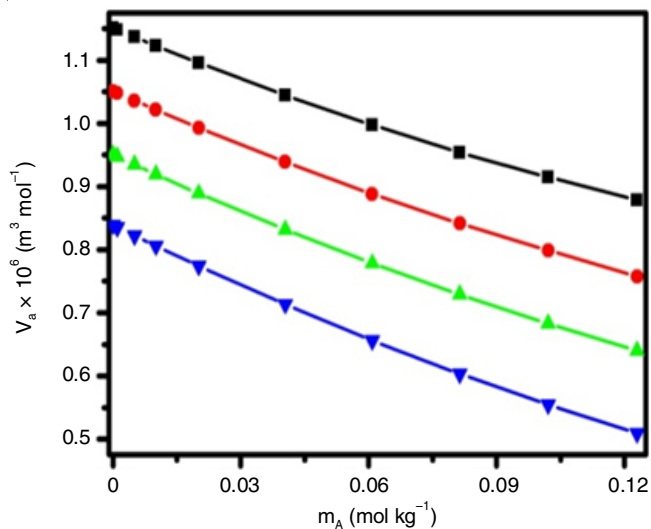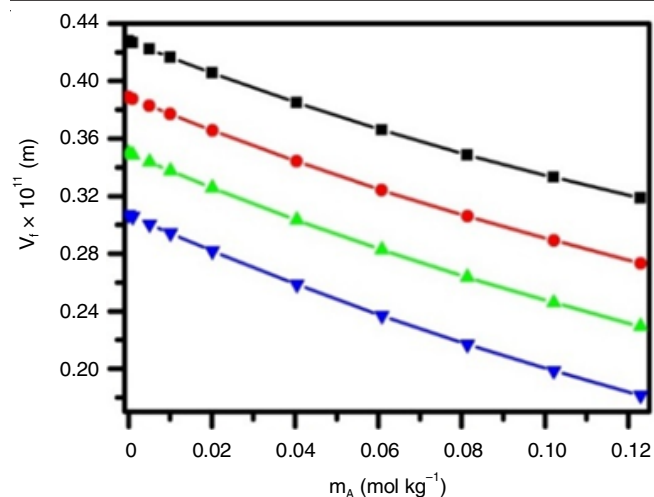

Fig. 3.   Plot of V_a vs. m_A of [bdmim]Cl in pure water by ultrasonic method at different temperatures: ■ 298.15 K, ● 303.15 K, ▲ 308.15 K, ▼ 313.15 K

Fig. 6.   Plot of L_f vs. m_A of [bdmim]Cl in 0.0125 M TBAB + water by thermo acoustic method at different temperatures: ■ 298.15 K, ● 303.15 K, ▲ 308.15 K, ▼ 313.15 K

Fig. 7.   Plot of L_f *vs.* m_A of [bdmim]Cl in pure water by ultrasonic method at different temperatures: ■— 298.15 K, ●— 303.15 K, ▲— 308.15 K, ▼— 313.15 K
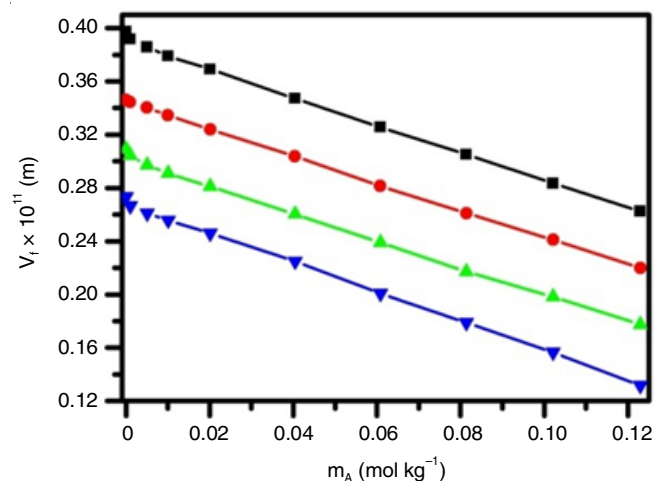

Fig. 8.   Plot of L_f *vs.* m_A of [bdmim]Cl in 0.0125 M TBAB + water by ultrasonic method at different temperatures: ■— 298.15 K, ●— 303.15 K, ▲— 308.15 K, ▼— 313.15 K

length. Therefore, it is concluded that the ultrasonic method (Schaaffs method) is the appropriate one for measuring the values of V_a and L_f whereas, thermoacoustical method is not appropriate to determine available volume as well as the intermolecular free-length for the solutions under study.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. P.S. Nikam, V.M. Kapade and M. Hasan, *J. Pure Appl. Ultrason.*, **22**, 16 (2000).
2. B. Nanda, *Indian J. Pure Appl. Phys.*, **54**, 471 (2016).
3. J.D. Pandey, B.D. Bhatt and R. Dey, *PhysChemComm*, **5**, 37 (2002); https://doi.org/10.1039/B109599D.
4. J.D. Pandey, R. Dey and J. Chhabra, *PhysChemComm*, **6**, 55 (2003); https://doi.org/10.1039/b307435h.
5. J.D. Pandey, V. Sanguri, M.K. Yadev and A. Singh, *Indian. J. Chem.*, **47A**, 1020 (2008).
6. V.A. Tabhane, S. Agarwal and M. Kalidoss, *PhysChemLiq.*, **40**, 39 (2002).
7. G.V. Ramarao, A.V. Sarma, D. Ramachandran and C. Rambabu, *Indian J. Pure Appl. Phys.*, **43**, 602 (2005).
8. K. Narendra, Ch. Srinivasu, S. Fakruddin and P. Narayanamurthy, *J. Chem. Thermodyn.*, **43**, 1604 (2011); https://doi.org/10.1016/j.jct.2011.05.018.
9. B.K. Sharma, *J. Acoust. Soc. Am.*, **73**, 106 (1983); https://doi.org/10.1121/1.388842.
10. V. Korolev, N.L. Smirnova and A.V. Kustov, *Thermochim. Acta*, **427**, 43 (2005); https://doi.org/10.1016/j.tca.2004.08.012.
11. D.V. Batov and D.V. Batov, *Russ. Chem. Bull.*, **58**, 765 (2009); https://doi.org/10.1007/s11172-009-0092-5.
12. S. Jain and J.C. Ahluwalia, *Thermochim. Acta*, **302**, 17 (1997); https://doi.org/10.1016/S0040-6031(97)00149-4.
13. J. Mata, D. Varade, G. Ghosh and P. Bahadur, *Colloids Surf. A Physicochem. Eng. Asp.*, **245**, 69 (2004); https://doi.org/10.1016/j.colsurfa.2004.07.009.
14. G.R. Behbehani, *J. Solution Chem.*, **36**, 939 (2007); https://doi.org/10.1007/s10953-007-9164-z.
15. W.Y. Wen, Water and Aqueous Solutions, Wiley: New York (1972).
16. E.R. Nightingale Jr., *J. Phys. Chem.*, **66**, 894 (1962); https://doi.org/10.1021/j100811a032.
17. H.S. Frank and W.Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957); https://doi.org/10.1039/df9572400133.
18. H. Rueterjans, F. Schreiner, U. Sage and T. Ackermann, *J. Phys. Chem.*, **73**, 986 (1969); https://doi.org/10.1021/j100724a038.
19. W.Y. Wen and S. Saito, *J. Phys. Chem.*, **68**, 2639 (1964); https://doi.org/10.1021/j100791a042.
20. Y. Nagano, M. Sakiyama, T. Fujiwara and Y. Kondo, *J. Phys. Chem.*, **92**, 5823 (1988); https://doi.org/10.1021/j100331a054.
21. S. Fukushima, H. Ogoshi and H. Ida, *NKK Tech Rep.*, **166**, 65 (1999) (In Japanese).
22. H. Hooshyar and B. Khezri, *Phys. Chem. Liq.*, **54**, 663 (2016); https://doi.org/10.1080/00319104.2016.1140762.
23. R.A. Daignault and E.L. Eliel, *Org. Synth.*, **5**, 303 (1973).
24. J.D. Pandey, G.P. Dubey, R. Dey and S.N. Dubey, *Acust. Acta Acust.*, **83**, 90 (1997).
25. B.B. Nanda, *Rev. Pharm. Appl. Sci.*, **6**, 1290 (2016).
26. B.B. Nanda, B. Nanda and P.C. Mohanty, *J. Mol. Liq.*, **171**, 50 (2012); https://doi.org/10.1016/j.molliq.2012.03.011.
27. S.R. Kanhekar, P. Pawar and G.K. Bichile, *Indian J. Pure Appl. Phys.*, **48**, 95 (2010).
28. H.S. Frank and M.W. Evans, *J. Chem. Phys.*, **13**, 507 (1945); https://doi.org/10.1063/1.1723985.

free length which decreases the value of α. This decrease in values of α causes a decrease in the available volume, which is reflected in present study. Further the solute which causes to increase the ultrasonic speed is a structure maker [27]. Moreover, a decrease in the value of α with increase in concentration of [bdmim]Cl in pure water as well as in TBAB-water solutions is due to the fact that a large portion of water molecules is electrostricted and the amount of bulk water decreases causing the thermal expansion to decrease. According to Frank and Evan [28], ionic solutes promote water in the surroundings and increase hydrogen bond network of water due to ion solvent interactions. Consequently, the water molecules rearranges themselves towards the formation of a local cage like structures surrounding each solute molecule and decrease the available volume. This indicates the presence of ion-solvent interactions as well as the structure making capacity of [bdmim]Cl. Again the addition of another co solute *i.e.* TBAB to water increases the ion solvent interaction between solute [bdmim]Cl and solvent molecules due to its structure making ability thereby decreasing the available volume and hence intermolecular free-