Acoustic and volumetric properties of aqueous solutions of imidazolium based ionic liquids at 298.15 K

Ramesh L. Gardas [a,b], Dilip H. Dagade [a], Santosh S. Terdale [a],
João A.P. Coutinho [b], Kesharsingh J. Patil [a,*]

[a] *Department of Chemistry, Shivaji University, Kolhapur 416 004, India*
[b] *CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal*

Abstract

The experimental measurements of the speed of sound and density of aqueous solutions of imidazolium based ionic liquids (IL) in the concentration range of $0.05 \, \text{mol} \cdot \text{kg}^{-1}$ to $0.5 \, \text{mol} \cdot \text{kg}^{-1}$ at $T = 298.15$ K are reported. The data are used to obtain the isentropic compressibility (β_S) of solutions. The apparent molar volume (ϕ_V) and compressibility (ϕ_{K_S}) of ILs are evaluated at different concentrations. The data of limiting partial molar volume and compressibility of IL and their concentration variation are examined to evaluate the effect due to IL–water and IL–IL interactions. The results have been discussed in terms of hydrophobic hydration, hydrophobic interactions, and water structural changes in aqueous medium.
© 2007 Elsevier Ltd. All rights reserved.

1. Introduction

The rapid growth in the ionic liquid (IL) literature shows that they attract much attention of both industry and academia as negligible vapor pressure alternatives to traditional organic solvents, the ability to solubilize an enormous variety of compounds, a wide liquid range, and the possibility to tailor their chemical structure at will to better match a given target are particularly noteworthy. While applications of ILs in a diverse range of fields, such as electrochemistry, separation processes, synthesis, and catalysis, have begun to be explored, still much research is needed towards the understanding of molecular interactions of ILs with water. The most widely studied ILs are comprised of bulky, asymmetric N-containing organic cations (*e.g.*, imidazole, pyrrole, pyridine, etc.) in combination with any wide variety of anions, ranging from simple inorganic ions (*e.g.*, halides) to more complex organic species

(*e.g.*, triflate). The nature of the anion is considered to be primarily responsible for many of the physical properties of ionic liquids, such as their miscibility with conventional solvents and hygroscopicity [1]. Simple changes in the cation and anion combinations or the nature of the moieties attached to each ion allow the physical properties of ionic liquids such as hydrophobicity, viscosity, and density to be designed for specific applications [2].

While ILs cannot contribute to air pollution due to their negligible vapour pressures, they may hold a significant solubility in water and go into aqueous streams what leads to an environmental problem, besides the costs due to the ionic liquid loss and the additional separation and purification steps required. Furthermore, once in the environment, the IL ecotoxicity depends directly on their lipophilicity [3–6]. The knowledge of the ILs solubilities in water can thus be an accurate way to predict the IL toxicity in the overall ecosystem.

The knowledge of thermophysical properties of binary mixtures of water and hydrophilic ILs is required for the development of practical applications and design of processes

---

* Corresponding author. Tel.: +91 0231 2690571.
  E-mail address: patilkesharsingh@hotmail.com (K.J. Patil).

using (water + IL) systems. To date, a number of papers have studied the thermophysical properties of these binary systems: some of them report values for dilute aqueous solutions of ILs [7–11] or, in the other extreme, the effect of water content in "pure" ILs or binary mixtures with low fractions of water [12–18] whereas only few works present measurements covering the whole composition range [19–29].

In this work, the experimental measurements of the speed of sound and density of aqueous solutions of imidazolium chloride ([Im][Cl]), 1-methyl imidazolium chloride ([Mim][Cl]), and 1-butyl-3-methyl imidazolium chloride ([Bmim][Cl]) in the concentration range of $0.05 \; mol \cdot kg^{-1}$ to $0.5 \; mol \cdot kg^{-1}$ at 298.15 K are reported. The data are used to obtain the isentropic compressibility (β_S) of solutions. The apparent molar volume (ϕ_V) and compressibility (ϕ_{K_S}) of IL are evaluated at different concentrations. The data of limiting partial molar volume and compressibility of IL and their concentration variation are examined to study the effect due to IL–water and IL–IL interactions.

2. Experimental

[Im][Cl] and [Mim][Cl] were acquired from Solchemer with a purity greater than 98% and [Bmim][Cl] of purity >99% was obtained from Merck. The concentrations of the ILs solutions in water were prepared on a molality basis. The water used for the solutions was freshly prepared, doubly quartz distilled. The uncertainty in composition was found to be of the order of $\pm 1 \cdot 10^{-4} \; mol \cdot kg^{-1}$. The water content in the ILs was determined using a microprocessor based automatic Karl–Fischer Titrator, TKF-55, Chemito from the M/s Toshniwal company. Pyridine free Aquanil-5 Karl–Fischer reagent of Thomas Baker was used for analysis. The reagent was standardized with a solution of water in methanol. The instrument is able to detect the water content on the order of ± 2 ppm in organic solvents. The water content found for [Im][Cl], [Mim][Cl] and [Bmim][Cl] were of 3.06%, 1.24%, and 0.94% by mass, respectively. This water content in the ILs was taken into account during the preparation of the aqueous solutions of ILs.

The densities of aqueous solutions of [Im][Cl], [Mim][Cl], and [Bmim][Cl] were measured at $T = 298.15$ K using a high precision Anton PAAR (DMA 60/602) digital density meter. The temperature constancy of the vibrating tube was better than ± 0.02 K as it is maintained constant by circulating water through a Julabo cryostat having a temperature stability of ± 0.01 K. After applying humidity and laboratory pressure corrections the accuracy in the density values is found to be of the order of $\pm 5 \cdot 10^{-3} \; kg \cdot m^{-3}$. The reliability of the density data obtained is ascertained by making measurements of aqueous binary solutions of alkali halides and comparing the data with the literature [30] (figure 1). Similarly, the calculated apparent molar volume (ϕ_V) of NaCl or KCl in aqueous solutions at $T = 298.15$ K, plotted
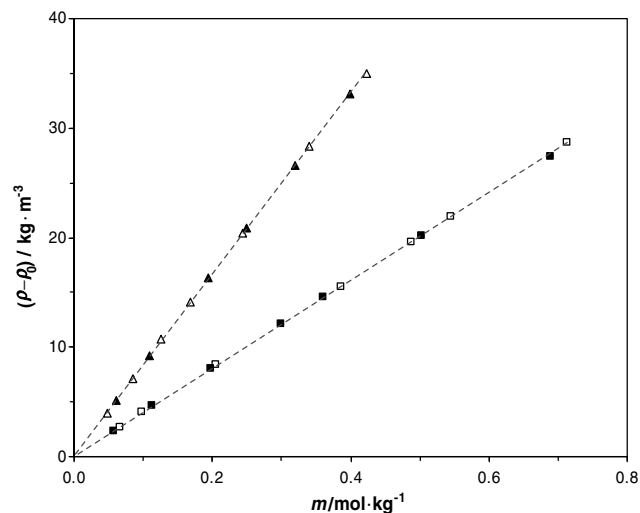

FIGURE 1. Comparison of experimental and the literature density data of aqueous binary solutions of alkali halides; NaCl: Exp., □; Fortier *et al.* [30], ■; KBr: Exp., △; Fortier *et al.* [30], ▲.

in the form of $\phi_V - 1.868\sqrt{c}$ against the concentration of salt (c) in $mol \cdot L^{-1}$, when extrapolated to infinite dilution yield limiting apparent molar volumes which are in excellent agreement with the literature data [31]. The concentration of IL in molality units are converted to molarity scale as and when required using density data.

The speed of sound measurements were carried out for aqueous solutions of [Im][Cl], [Mim][Cl], and [Bmim][Cl] at $T = 298.15 \pm 0.02$ K at a fixed frequency of 2 MHz (M/s Mittle Enterprises). Good quality thermostating (temperature inside the cell ± 0.05 K) to maintain constant temperature was achieved by circulating water by means of a Julabo thermostat having an accuracy of ± 0.02 K around the cell. The reliability of the measurements were checked by obtaining sound velocity data for water at $T = 298.15$ K (1497.6 $m \cdot s^{-1}$) which agree well with the reported literature data [32]. The standard deviation in speed of sound measurement values are found to be of the order of $\pm 0.3 \; m \cdot s^{-1}$ obtained after repeated measurements.

3. Results

The speed of sound and density data of aqueous solutions of [Im][Cl], [Mim][Cl], and [Bmim][Cl] in the concentration range of $0.05 \; mol \cdot kg^{-1}$ to $0.5 \; mol \cdot kg^{-1}$ at $T = 298.15$ K are reported in table 1. The variations of the speed of sound parameter ($\Delta u = u_{solution} - u_{solvent}$) as a function of the molality of ILs in water are shown in figure 2. Isentropic compressibility (β_s) of solvents and solutions were obtained using the Laplace equation $\beta_s = 1/(u^2\rho)$. The variations of β_s values with the molality of water are shown in figure 3. The uncertainty in $\beta_s(\delta\beta_s)$ values was obtained using method of propagation of errors and standard deviations obtained for the experimental parameters including concentration and density of pure solvent; the corresponding equation obtained as

TABLE 1
Density, speed of sound, compressibility, apparent, and partial molal properties of aqueous solutions of ionic liquids at $T = 298.15$ K

$m/$ (mol·kg^{-1})	$\rho/$ (kg·m^{-3})	$u/$ (m·s^{-1})	$10^{-3} \cdot \phi_V/$ (mm^3·mol^{-1})	$10^{-3} \cdot \overline{V}_2/$(mm^3·mol^{-1})	$10^{-3} \cdot \overline{V}_1/$(mm^3·mol^{-1})	$10^{11} \cdot \beta_S/$ Pa^{-1}	$\phi_{K_S}/$(mm^3·MPa^{-1}·mol^{-1})
				[Im][Cl] + Water			
0.00000	997.05	1497.6	104.40[a]	–	18.068	44.72	−13.8[a]
0.04296	998.24	1500.1	104.70	104.69	18.068	44.52	−13.0 ± 4.2
0.10274	999.89	1503.8	104.52	104.35	18.068	44.23	−14.3 ± 1.7
0.15300	1001.26	1507.0	104.38	104.05	18.069	43.98	−14.9 ± 1.2
0.19764	1002.47	1509.7	104.26	103.77	18.070	43.77	−14.5 ± 0.9
0.24165	1003.72	1512.4	104.13	103.48	18.071	43.56	−14.9 ± 0.7
0.29145	1004.65	1515.8	104.03	103.20	18.072	43.32	−14.3 ± 0.6
0.33998	1006.45	1517.9	103.84	102.83	18.074	43.12	−14.1 ± 0.5
0.38926	1007.62	1521.2	103.72	102.53	18.076	42.89	−14.3 ± 0.4
0.44952	1008.96	1525.2	103.59	102.16	18.080	42.61	−14.2 ± 0.4
0.50034	1010.31	1527.9	103.45	101.82	18.083	42.40	−13.8 ± 0.3
				[Mim][Cl] + Water			
0.00000	997.05	1497.6	118.46[a]	–	18.068	44.72	−14.9[a]
0.05234	998.29	1501.6	118.74	118.72	18.068	44.43	−14.1 ± 3.4
0.09548	999.30	1504.7	118.62	118.48	18.068	44.20	−12.7 ± 1.9
0.14703	1000.49	1508.5	118.48	118.17	18.069	43.92	−12.6 ± 1.2
0.19981	1001.69	1512.5	118.34	117.85	18.070	43.64	−12.7 ± 0.9
0.24717	1002.77	1516.0	118.21	117.56	18.071	43.39	−12.6 ± 0.7
0.30106	1003.97	1519.9	118.07	117.23	18.073	43.12	−12.3 ± 0.6
0.35550	1005.18	1523.9	117.93	116.88	18.075	42.84	−12.3 ± 0.5
0.39940	1006.13	1526.3	117.81	116.61	18.077	42.66	−11.0 ± 0.4
0.45507	1007.35	1530.5	117.67	116.25	18.080	42.38	−11.2 ± 0.4
0.51388	1008.62	1534.6	117.52	115.88	18.083	42.10	−11.1 ± 0.3
				[Bmim][Cl] + Water			
0.00000	997.05	1497.6	174.76[a]	–	18.068	44.72	−15.7[a]
0.05281	997.72	1504.8	175.06	175.05	18.068	44.26	−15.4 ± 3.4
0.09783	998.29	1510.5	174.96	174.85	18.068	43.91	−12.2 ± 1.8
0.14328	998.85	1516.7	174.86	174.63	18.069	43.52	−13.2 ± 1.2
0.19981	999.56	1524.4	174.73	174.33	18.069	43.05	−13.9 ± 0.9
0.24711	1000.15	1530.2	174.63	174.08	18.070	42.70	−12.7 ± 0.7
0.28987	1000.69	1535.5	174.54	173.85	18.072	42.39	−12.1 ± 0.6
0.31733	1001.04	1539.1	174.48	173.70	18.072	42.17	−12.3 ± 0.5
0.40515	1002.14	1549.9	174.29	173.22	18.076	41.54	−11.5 ± 0.4
0.42202	1002.35	1551.9	174.25	173.13	18.076	41.42	−11.4 ± 0.4
0.49947	1003.31	1562.2	174.08	172.70	18.080	40.84	−11.9 ± 0.3

[a] Extrapolated values to infinite dilution.
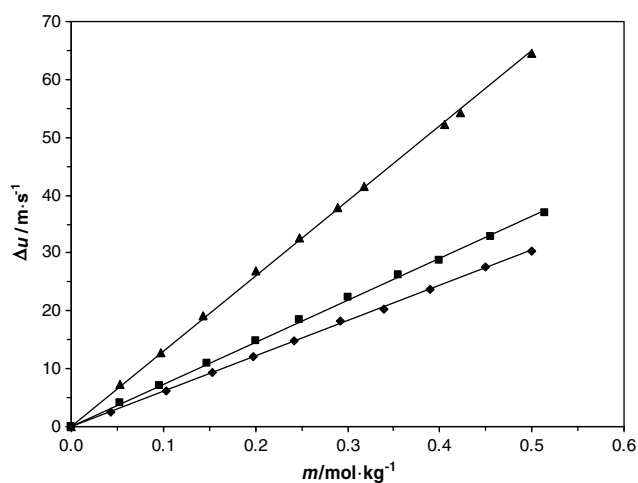
FIGURE 2. The variation of sound velocity parameter (Δu) as a function of molality of ionic liquids (m) at $T = 298.15$ K. [Im][Cl], ♦; [Mim][Cl], ■; [Bmim][Cl], ▲.

$$\delta \beta_S = \beta_S \left[\left(\frac{2\delta u}{u} \right)^2 + \left(\frac{\delta \rho}{\rho} \right)^2 \right]^{\frac{1}{2}} \qquad (1)$$

and were found to be of the order of $\pm 1.3 \cdot 10^{-13}$ Pa^{-1}.

The apparent molar volume (ϕ_V) and apparent molar isentropic compressibility (ϕ_{K_S}) of aqueous solutions of ILs as a function of molality of IL were calculated using equations (2) and (3):

$$\phi_V = \left(\frac{M_2}{\rho} \right) + \left[\frac{(\rho_0 - \rho)}{m\rho\rho_0} \right] \qquad (2)$$

$$\phi_{K_S} = \left(\frac{M_2 \beta_s}{\rho} \right) + \left[\frac{(\beta_s \rho_0 - \beta_s^0 \rho)}{m\rho\rho_0} \right] \qquad (3)$$

where M_2 is the molar mass of IL in kg·mol^{-1}, m is the molality in mol·kg^{-1} while β_S^0, ρ_0, and β_S, ρ represents the isentropic compressibility and density values for water and solution, respectively. The errors in ϕ_V and ϕ_{K_S} values

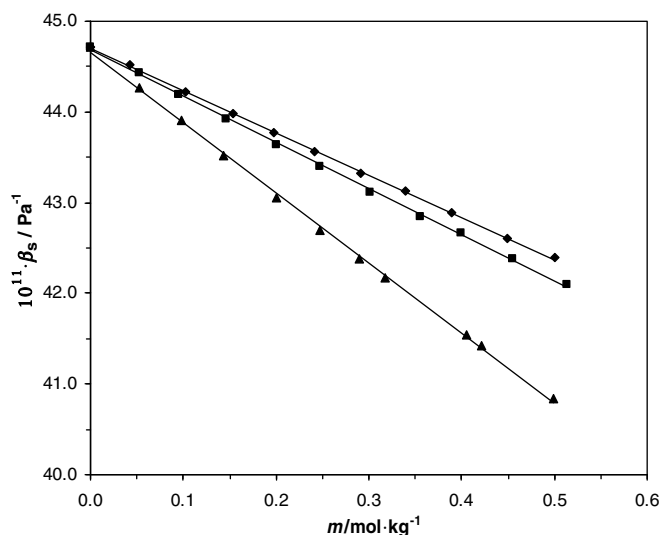FIGURE 3. The variation of isentropic compressibility (β_S) as a function of molality of ionic liquids (m) at $T = 298.15$ K. [Im][Cl], ♦; [Mim][Cl], ■; [Bmim][Cl], ▲.

were estimated using the same method used for estimation of the uncertainty in β_S. The data of ϕ_V and ϕ_{K_S} along with their uncertainties are shown in table 1. The uncertainties in the derived apparent quantities are estimated to be of the order of $\pm 0.23 \cdot 10^3$ mm$^3 \cdot$ mol^{-1} for ϕ_V and ± 4 mm$^3 \cdot$ MPa$^{-1} \cdot$ mol^{-1} for ϕ_{K_S} at the lowest concentration studied.

The ϕ_V and ϕ_{K_S} data of aqueous solutions of studied ILs as a function of IL molarity at $T = 298.15$ K are shown in figures 4 and 5, respectively. The ϕ_V and ϕ_{K_S} can also be expressed as

$$\phi_V = \phi_V^0 + S_V \sqrt{c} + B_V c \tag{4}$$
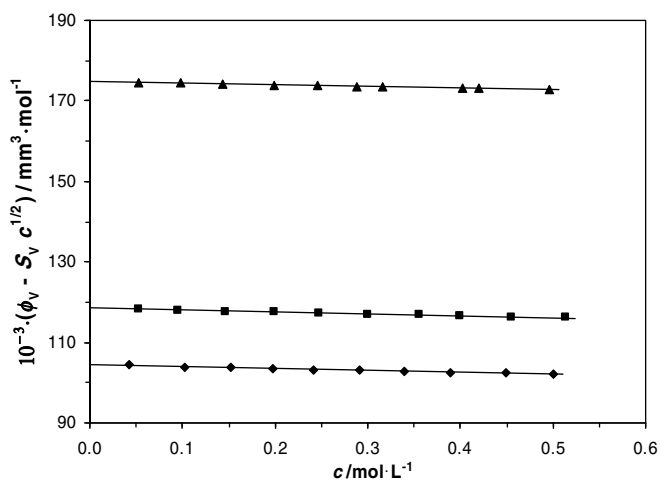
$$\phi_{K_S} = \phi_{K_S}^0 + S_K \sqrt{c} \tag{5}$$

FIGURE 4. The dependence of apparent molar volume (ϕ_V) as a function of concentration of ionic liquids (c) at $T = 298.15$ K. [Im][Cl], ♦; [Mim][Cl], ■; [Bmim][Cl], ▲.
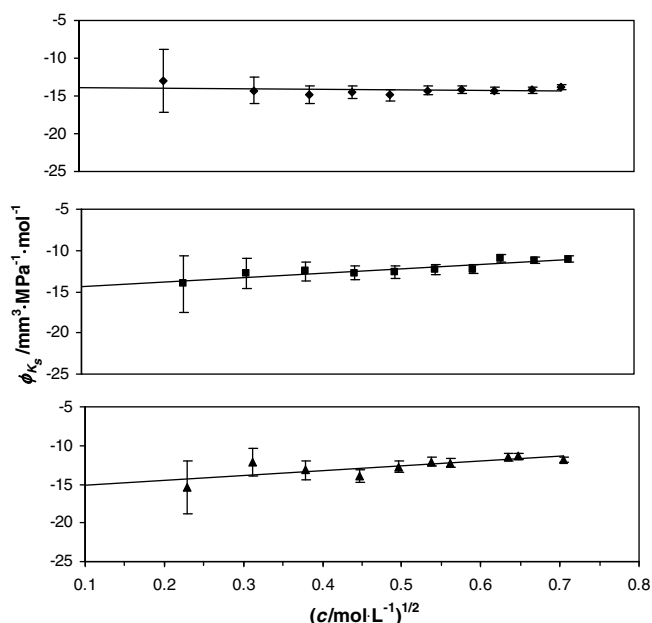
FIGURE 5. The dependence of apparent molar isentropic compressibility (ϕ_{K_S}) as a function of square root concentration of ionic liquids ($\sqrt{c}$) at $T = 298.15$ K. [Im][Cl], ♦; [Mim][Cl], ■; [Bmim][Cl], ▲.

where S_V is the Debye–Huckel limiting slope ($S_V = 1.868 \cdot 10^6$ (mol $\cdot$ mm^{-3})$^{-3/2}$ for aqueous solutions of 1:1 electrolytes at 298.15 K) and S_K is the experimental limiting slope whereas B_V is the deviation parameter. The smooth extrapolations of the ϕ_V and ϕ_{K_S} data to infinitely dilute solutions enabled us to obtain limiting apparent molar volume (ϕ_V°) and compressibility ($\phi_{K_S}^\circ$) of ILs as shown in figures 4 and 5. Experimental slopes of ϕ_{K_S} (S_K values) for aqueous solutions of [Im][Cl], [Mim][Cl], and [Bmim][Cl] are found to be $(-0.8 \pm 2.3) \cdot 10^3$, $(5.3 \pm 2.2) \cdot 10^3$, and $(6.2 \pm 2.4) \cdot 10^3$ in mm$^{9/2} \cdot$ MPa$^{-1} \cdot$ mol$^{-3/2}$, respectively. B_V values for aqueous solutions of [Im][Cl], [Mim][Cl], and [Bmim][Cl] are found to be $(-4.7 \pm 0.5) \cdot 10^3$, $(-4.6 \pm 0.4) \cdot 10^3$, and $(-4.1 \pm 0.5) \cdot 10^3$ in mm$^6 \cdot$ mol^{-2}, respectively. The data of ϕ_V were further used to calculate the partial molar volumes of solute ($\overline{V}_2$) and solvent ($\overline{V}_1$) using the standards equations [33] and that are reported in table 1. The dependence of partial molar volume of solute ($\overline{V}_2$) as a function of molality of IL is shown in figure 6. The partial molar volume of solute (Y) displays a very good linear relationship with the molality of IL (X) as equations (6)–(8), respectively, for aqueous solutions of [Im][Cl], [Mim][Cl], and [Bmim][Cl] at 95% level of confidence:

$$Y = (-6.3258 \pm 0.0524)X + (105.00 \pm 0.02) \quad (R^2 = 0.9995) \tag{6}$$

$$Y = (-6.1729 \pm 0.0356)X + (119.07 \pm 0.01) \quad (R^2 = 0.9997) \tag{7}$$

$$Y = (-5.3107 \pm 0.0500)X + (175.37 \pm 0.02) \quad (R^2 = 0.9993) \tag{8}$$

FIGURE 6. The dependence of partial molar volume of solute ($\overline{V}_2$) as a function of concentration of ionic liquids (m) at $T = 298.15$ K. [Im][Cl], $\blacklozenge$; [Mim][Cl], $\blacksquare$; [Bmim][Cl], $\blacktriangle$.
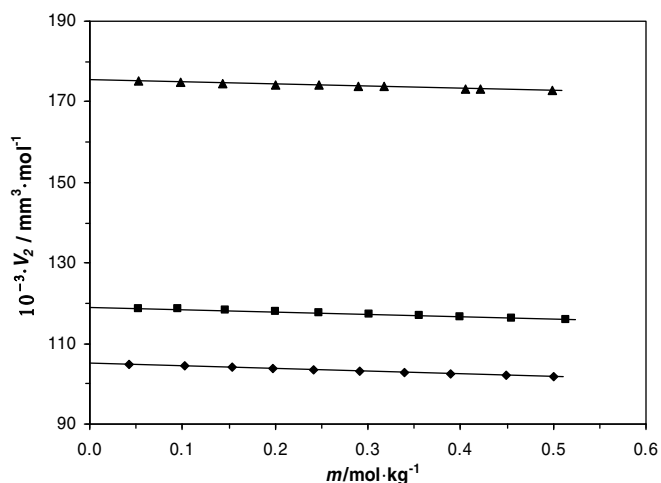
4. Discussion

It is observed from figure 2 that speed of sound increases as the imidazolium ring is substituted at the N centers by methylene groups and a butyl chain. This is also reflected in decrease of adiabatic compressibility as the salt concentration increases, the decrease is much more pronounced for the [Bmim][Cl]. Such behaviour has also been noted in case of aqueous solutions of amines [34].

The interest for the volumetric behaviour of aqueous solutions as a useful tool for elucidating local changes of solvent structure brought about by neutral or charged solute molecules has been illustrated previously [35–37]. Cabani et al. [38] have studied the volumetric properties of chloride salts of cyclic amines at 298.15 K and noted that apparent molar volume as a function of salt concentration exhibit negative deviation from the Debye–Huckel limiting law, the deviations increasing with the hydrocarbon portion of the molecule. Small negative deviations from limiting law are observed in figure 4 where $\phi_V - S_V\sqrt{c}$ is plotted against the IL concentration. The negative B_V values imply a solvent induced solute co-sphere over-lap effect, i.e., the increase of solute–solute interactions along with water structure making effect. We do not include here the effect of interaction of anions, since all the studied molecules have a common anion.

Examining the limiting partial molar volumes of the salts ($\overline{V}_2^0$), as reported in table 1, it is found that the increment in volume due to addition of –CH$_2$ group is of the order of $14.00 \cdot 10^3$ mm$^3 \cdot$ mol^{-1} in the case of first two salts while addition of four more –CH$_2$ groups causes a proportional increase. The additivity of partial molar volumes is coherent with that observed for molar volumes [39–42]. Since ϕ_V^0 values give information about solute–solvent interactions, the observed effect is in good agreement with the concept of volume increase in neutral or hydrophobic salt ion/molecules [43].

The calculations of $\overline{V}_2$ and $\overline{V}_1$, i.e., partial molar volumes of the salt molecules and water respectively, also exhibit a behavior analogous to that observed for ϕ_V. It is observed that these cations exhibit a water structuring effect similar to that of neutral solutes like alcohols, ethers (hydrophobic) and tetra-alkyl ammonium salts in water i.e., $\overline{V}_1$ increases in with IL concentration in dilute concentration region [44–46]. It is well known that the $\overline{V}_1$ increases in dilute concentration region marginally from a value of $18.068 \cdot 10^3$ mm $\cdot$ mol^{-1} (molar volume of pure water) if the solute causes a strengthening of water structure around it due to hydrophobic hydration. At higher concentrations of the solute, the breakdown of H-bonding amongst the water cluster around the solute or cation (structure breaking effect) leads to decrease in the value of $\overline{V}_1$ from that of pure water. The contribution of Cl$^-$ ion to volume is known ($17.83 \cdot 10^3$ mm$^3 \cdot$ mol^{-1} [47]). The estimation of partial molar volume of the ions [Im]$^+$, [Mim]$^+$, and [Bmim]$^+$ are $(86.57 \pm 0.64) \cdot 10^3$ mm$^3 \cdot$ mol^{-1}, $(100.63 \pm 0.69) \cdot 10^3$ mm$^3 \cdot$ mol^{-1} and $(156.93 \pm 1.10) \cdot 10^3$ mm$^3 \cdot$ mol^{-1}, respectively.

The isentropic compressibility ϕ_{K_S} is related to the second pressure differential of the partial molar free energy of the solute and has proved to be very sensitive to changes in solvation, H-bond and water structural changes in the aqueous medium. The limiting apparent molar compressibilities ($\phi_{K_S}^\circ$) are generally negative for electrolytes in aqueous solutions [48]. The magnitude depends upon the charges of cations (electrostriction). The negative values are attributed to hydration of cations (water loosing compressibility due to coloumbic attraction). The hydration number for the ions has been calculated by using Passynski's equation [49].

A distinction has also been made between compressibility changes due to electrostriction (high charge density) and similar changes which arise for large R$_4$N$^+$ ions [50] but for completely different reasons associated with hydrophobic structure promotion. Seen in this light, the limiting apparent molar compressibility (table 1) for the studied ILs are all negative but they are of much smaller magnitude than those for 1:1 electrolytes but similar to R$_4$N$^+$X solutes. Thus the $\phi_{K_S}^\circ$ values indicate that the imidazolium cations are solvated by hydrophobic hydration in water and the charge density of the hydrated sheath is small. Similarly, the small positive $\phi_{K_S}^\circ$ values for pyridinium salts have been reported by Conway and Laliberté [51] in aqueous solutions at 298.15 K. Assuming the ionic compressibility of Cl$^-$ ions $= -0.17$ mm$^3 \cdot$ MPa$^{-1} \cdot$ mol^{-1} [52], one can obtain the individual ionic compressibilities of the cations as (-13.6 ± 6.5) mm$^3 \cdot$ MPa$^{-1} \cdot$ mol^{-1}, (-14.8 ± 5.9) mm$^3 \cdot$ MPa$^{-1} \cdot$ mol^{-1} and (-15.6 ± 6.2) mm$^3 \cdot$ MPa$^{-1} \cdot$ mol^{-1} for [Im]$^+$, [Mim]$^+$, and [Bmim]$^+$, respectively. Thus the compressional properties of these ions are almost similar. These values indicate that the hydrophobically hydrated imidazolium cations are not compressible to a significant extent. The water structure around the N$^+$ centered cation is less compressible (ϕ_{K_S} value of water is $+8$ mm$^3 \cdot$ MPa$^{-1} \cdot$ mol^{-1})

due to less electrostriction and increased H-bonding amongst the water molecules in the water clusters around cation (structure making effect) resulting in very small negative $\phi_{K_S}^{\circ}$ values. The large negative $\phi_{K_S}^{\circ}$ values are observed in case of usual metal halides where the electrostriction is large and the hydration sheath around the cation is less compressible if the charge density is high [53]. It has also been questioned about the compressibility of the ions itself. However, it can be resolved if the compressibility of the salts are known in pure liquid state or in CCl$_4$ solutions [54].

The Debye–Huckel theory requires ϕ_{K_S} to be linear in $m^{1/2}$ (or $c^{1/2}$), so that equation (5) has a limiting slope S_K^0. The limiting slope S_K^0 is not known precisely as its calculation requires the dielectric constant data at different pressures. We observed from figure 5 that ϕ_{K_S} increases linearly with square root of concentration; giving small positive values of S_K parameter. We do not compare these with the literature values of S_K for variety of electrolytes, since our data are of limited accuracy and the concentration range is also above Debye–Huckel limiting region. However, the small positive values of S_K do indicate that the water structure around these imidazolium cations is affected by the pressure effect giving support to the hypothesis of soft and hydrophobic structures around the cations.

5. Conclusions

The variations of the speed of sound parameter ($\Delta u = u_{\text{solution}} - u_{\text{solvent}}$) as a function of the molality of studied ILs in water increases with the insertion of methylene groups or butyl chain at the N centers of ILs; and the reverse is observed in case of isentropic compressibility. For the studied systems, the solvent induced solute co-sphere over-lap effect (*i.e.*, increase of solute–solute interaction along with water structure making effect) is observed and the extent of the effect is more important in case of [Bmim][Cl]. Studied imidazolium cations are solvated by hydrophobic hydration in water and charge density of the hydrated sheath is small and they are not compressible to significant extent. The water structure around the imidazolium cation is less compressible due to less electrostriction and increased H-bonding amongst the water molecules in the water clusters around cation (structure making effect) resulting in the small negative $\phi_{K_S}^{\circ}$ values.

Acknowledgements

References

[1] P. Bonhote, A.-P. Dias, N. Papargeorgiou, K. Kalyanasundaram, M. Gratzel, Inorg. Chem. 35 (1996) 1168–1178.

[2] J.H. Davis Jr., Chem. Lett. 33 (2004) 1072–1077.

[3] K.M. Docherty, C.F. Kulpa, Green Chem. 7 (2005) 185–189.

[4] D.J. Couling, R.J. Bernot, K.M. Docherty, J.K. Dixon, E.J. Maggin, Green Chem. 8 (2006) 82–90.

[5] D. Zhao, Y. Liao, Z. Zhang, Clean 35 (2007) 42–48.

[6] J. Ranke, A. Müller, U. Bottin-Weber, F. Stock, S. Stolte, J. Arning, R. Störmann, B. Jastorff, Ecotoxicol. Environ. Safe. 67 (2006) 430–438.

[7] L. Gaillon, J. Sirieix-Plenet, P. Letellier, J. Solut. Chem. 33 (2004) 1333–1347.

[8] X.-M. Lu, W.-G. Xu, J.-S. Gui, H.-W. Li, J.-Z. Yang, J. Chem. Thermodyn. 37 (2005) 13–19.

[9] M.T. Zafarani-Moattar, H. Shekaari, J. Chem. Thermodyn. 37 (2005) 1029–1035.

[10] A.V. Orchillés, V. González-Alfaro, P.J. Miguel, E. Vercher, A. Martínez-Andreu, J. Chem. Thermodyn. 38 (2006) 1124–1129.

[11] W. Liu, T. Zhao, Y. Zhang, H. Wang, M. Yu, J. Solut. Chem. 35 (2006) 1337–1346.

[12] K.R. Seddon, A. Stark, M.J. Torres, Pure Appl. Chem. 72 (2000) 2275–2287.

[13] B.D. Fitchett, T.N. Knepp, J.C. Conboy, J. Electrochem. Soc. 151 (2004) E219–E225.

[14] S. Pandey, K.A. Fletcher, S.N. Baker, G.A. Baker, Analyst 129 (2004) 569–573.

[15] J.A. Widegren, A. Laesecke, J.W. Magee, Chem. Commun. (2005) 1610–1612.

[16] D. Chakrabarty, A. Chakraborty, D. Seth, N. Sarkar, J. Phys. Chem. A 109 (2005) 1764–1769.

[17] R.L. Gardas, M.G. Freire, P.J. Carvalho, I.M. Marrucho, I.M.A. Fonseca, A.G.M. Ferreira, J.A.P. Coutinho, J. Chem. Eng. Data 52 (2007) 80–88.

[18] M.G. Freire, P.J. Carvalho, A.M. Fernandes, I.M. Marrucho, A.J. Queimada, J.A.P. Coutinho, J. Colloid Interf. Sci. 314 (2007) 621–630.

[19] S. Zhang, X. Li, H. Chen, J. Wang, J. Zhang, M. Zhang, J. Chem. Eng. Data 49 (2004) 760–764.

[20] L.P.N. Rebelo, V. Najdanovic-Visak, Z.P. Visak, M. Nunes. da Ponte, J. Szydlowski, C.A. Cerdeirina, J. Troncoso, L. Romani, J.M.S.S. Esperancua, H.J.R. Guedes, H.C.A. de Sousa, Green Chem. 6 (2004) 369–381.

[21] H. Xu, D. Zhao, P. Xu, F. Liu, G. Gao, J. Chem. Eng. Data 50 (2005) 133–135.

[22] J.-Z. Yang, X.-M. Lu, J.-S. Gui, W.-G. Xu, H.-W. Li, J. Chem. Thermodyn. 37 (2005) 1250–1255.

[23] E. Gomez, B. Gonzalez, A. Dominguez, E. Tojo, J. Tojo, J. Chem. Eng. Data 51 (2006) 696–701.

[24] A. Jarosik, S.R. Krajewski, A. Lewandowski, P. Radzimski, J. Mol. Liq. 123 (2006) 43–50.

[25] Q. Zhou, L.-S. Wang, H.-P. Chen, J. Chem. Eng. Data 51 (2006) 905–908.

[26] E. Gomez, B. Gonzalez, N. Calvar, E. Tojo, A. Dominguez, J. Chem. Eng. Data 51 (2006) 2096–2102.

[27] H. Rodriguez, J.F. Brennecke, J. Chem. Eng. Data 51 (2006) 2145–2155.

[28] N. Calvar, B. Gonzalez, A. Dominguez, J. Tojo, J. Solut. Chem. 35 (2006) 1217–1225.

[29] E. Vercher, A.V. Orchillés, P.J. Miguel, A. Martinez-Andreu, J. Chem. Eng. Data 52 (2007) 1468–1482.

[30] J.-L. Fortier, P.-A. Leduc, J.E. Desnoyers, J. Solut. Chem. 3 (1974) 323–349.

[31] F.J. Millero, J. Phys. Chem. 74 (1970) 356–362.

[32] M. Greenspan, C.E. Tschiegg, J. Res. Natl. Bur. Std. 59 (1957) 249–258.

[33] H.S. Harned, B.B. Owen, The Physical Chemistry of Electrolyte Solutions, third ed., Reinhold Publishing Corporation, New York, 1958.

[34] M.V. Kaulgud, K.J. Patil, J. Phys. Chem. 78 (1974) 714–717.

[35] W.Y. Wen, S. Saito, J. Phys. Chem. 68 (1964) 2639–2644.

[36] M.E. Friedman, H.A. Scheraga, J. Phys. Chem. 69 (1965) 3795–3800.
[37] F. Franks, H.T. Smith, Trans. Faraday Soc. 63 (1967) 2586–2598.
[38] S. Cabani, G. Conti, L. Lepori, G. Leva, J. Phys. Chem. 76 (1972) 1343–1347.
[39] J.M.S.S. Esperança, Z.P. Visak, N.V. Plechkova, K.R. Seddon, H.J.R. Guedes, L.P.N. Rebelo, J. Chem. Eng. Data 51 (2006) 2009–2015.
[40] C. Ye, J.M. Shreeve, J. Phys. Chem. A 111 (2007) 1456–1461.
[41] R.L. Gardas, M.G. Freire, P.J. Carvalho, I.M. Marrucho, I.M.A. Fonseca, A.G.M. Ferreira, J.A.P. Coutinho, J. Chem. Eng. Data 52 (2007) 1881–1888.
[42] R.L. Gardas, J.A.P. Coutinho, Fluid Phase Equilibr. (2007), doi:10.1016/j.fluid.2007.09.016.
[43] F. Franks, in: F. Franks (Ed.), Water – A Comprehensive Treaties, vol. IV, Plenum Publication, New York, 1973.
[44] D.N. Glew, H.D. Mak, N.S. Rath, in: A.K. Covington, P. Jones (Eds.), Hydrogen Bonded Solvent Systems, Taylor & Francis, London, 1968.

[45] F. Franks, D.J.G. Ives, Quart. Rev. Chem. Soc. 20 (1966) 1.
[46] W.-Y. Wen, S. Saito, J. Phys. Chem. 69 (1965) 3569–3574.
[47] F.J. Millero, Chem. Rev. 71 (1971) 147–176.
[48] M.V. Kaulgud, Z. Phys. Chem. 47 (1965) 24–41.
[49] A. Passynski, Acta Physicochim. 8 (1938) 385–418.
[50] (a) B.E. Conway, R.E. Verrall, J. Phys. Chem. 70 (1966) 3952–3961;
(b) B.E. Conway, R.E. Verrall, J. Phys. Chem. 70 (1966) 3961–3969.
[51] B.E. Conway, L.H. Laliberte, J. Phys. Chem. 72 (1968) 4317–4320.
[52] J.G. Mathieson, B.E. Conway, J. Solut. Chem. 3 (1974) 455–477.
[53] F.J. Millero, G.K. Ward, F.K. Lepple, E.V. Hoff, J. Phys. Chem. 78 (1974) 1636–1643.
[54] R.R. Kolhapurkar, S.A. Jangam, D.H. Dagade, K.J. Patil, J. Chem. Thermodyn. 38 (2006) 830–835.

JCT 07-236