**Chemistry Europe**

**AWARD**

# Nominate a Worthy Chemist Chemistry Europe Award

**Subject:**
chemistry for sustainability, energy, materials, environment

**Consists of:**
prize money amounting to EUR 10,000, certificate

**Deadline:**
November 1, 2022

▶ **Click here for more info & nomination**

■ Electro, Physical & Theoretical Chemistry

# Studies of Viscosity Coefficient and Density Properties of Imidazolium Based Ionic Liquids in Aqueous Solutions at Different Temperatures

Pramod P. Patil,[a] Vasim R. Shaikh,[a] Gaurav R. Gupta,[b] Pankaj D. Patil,[a] Amulrao U. Borse,[a] and Kesharsingh J. Patil*[a]

The densities and viscosity coefficients for binary aqueous solutions of imidazolium based ionic liquids (IL's), namely 1-Butyl-3-Methylimidazolium Bromide (0.02281 to 0.17232 mol·kg$^{-1}$) and 1-Butyl-3-Methylimidazolium Chloride (0.01948 to 0.19816 mol·kg$^{-1}$) have been measured at 293.15, 298.15, and 303.15 K, and at atmospheric pressure, respectively. Using the density data, the apparent molar volumes ($V_\phi$) and partial molar volumes ($\overline{V}_2$) of solutes at finite concentrations and at infinitely dilute solutions ($V_\phi^0 = \overline{V}_2^0$) were estimated. The limiting partial molar volumes of the constituent ions are also reported. The viscosity A, B and D coefficients of Jones-Dole equation for the studied IL's are obtained by using viscosity coefficient data. It is observed that viscosity A and B coefficients are positive in magnitude for studied IL's while the temperature coefficient of B (dB/dT) is of negative, signifying that cations are water structure making ions. The application of Vand's equation to viscosity data and estimation of volume fractions of the solute enabled us to obtain Einstein-Simha factor and particle interaction coefficient for the ion-pairs. The analysis of the results indicates that imidazolium cations act as electrostrictive water structure making ions.

## 1. Introduction

In the current scenario the research on ionic liquids (IL's) is surging tremendously as these electrolytes act as green solvents and catalyst as well as they have significant solubility in water, non-flammability, negligible vapour pressure, low melting temperature, wide liquid temperature ranges and high thermal stability etc. Since the era of molten salts, scientific community is keenly interested to investigate the molecular interactions of IL's in solution phase. The thermophysical properties play an important role to study such interactions by understanding structural characteristics of IL's, IL-solvent and IL-IL interactions (ion-ion, cation-cation) in solution phase.[1–12] The utility of IL's as 1:1 electrolytes has not been yet tested fully. In literature, there are many studies regarding volumes, heat changes over entire concentration region of aqueous solutions and pure ionic liquids (0 to 1 mole fraction of IL). It is felt that to characterize, solute-solvent interaction and cation-cation or anion-anion interaction, the data of partial molar volumes, partial molar enthalpies and partial molar entropies are needed both in the limiting dilute concentration region as well at finite concentrations.

The Jones-Dole viscosity equation has been proved to yield information about structural changes in water in presence of electrolytes as well as for non-electrolytes like urea or sucrose. Traditionally, Li$^+$, F$^-$ are known to be electrostrictive water structure makers while Br$^-$, I$^-$, Cs$^+$ are known to be water structure breakers. This is based on the concept of Frank and Wens model of water structure around the cations.[13] In general the viscosity B coefficient of ions are negative and having positive dB/dT, indicating water structure breaking effect for normal 1:1 electrolytes. In such a case extent of -H bonding in the B zone of Frank-Wens water structure model decreases. While high positive viscosity B coefficient with negative dB/dT has been explained as water structure making ion, strengthening the -H bonding interactions in the B zone of Frank-Wens water model for electrolytic solutions. Kay have explained viscosity B coefficient for tetra-alkyl-ammonium ions based on this quite satisfactorily.[14] The significance of the ionic viscosity B coefficient lies primarily in the fact that it appears to characterize the solvated ion as a kinetic entity.[15,16] The ionic B coefficient is proportional to the partial molar entropy of hydration and a positive viscosity B coefficient is a measure of effective hydrodynamic volume or co-sphere of the hydrated ion.[17] However, the experimental data for viscosity measurements of IL's in water in limiting dilute concentration region having meaningful accuracy are not easily available. In recent years, Jenkins and Marcus[18] have written reviews on viscosity coefficient and water structure making/breaking effects; however, such information for imidazolium ions is not available and now reported for a first time.

In this communication, we report the experimentally obtained density and viscosity coefficient data for the ionic

[a] P. P. Patil, Dr. V. R. Shaikh, P. D. Patil, Prof. A. U. Borse, Prof. K. J. Patil
School of Chemical Sciences
North Maharashtra University
Jalgaon-425001 (M.S.), India
E-mail: patilkesharsingh@hotmail.com
[b] G. R. Gupta
Institute of Chemical Technology
Matunga, Mumbai-400019 (M.S.), India

**Table 1.** Limiting Apparent Molar Volumes $V_\phi^0$ and Deviation Parameter $B_V$ Data for aqueous solutions of [Bmim][Br] and [Bmim][Cl] at 293.15, 298.15, and 303.15 K and Limiting Apparent Molar Expansivity $E_\phi^0$ Data of [Bmim][Br] and [Bmim][Cl] at 298.15 K and at Ambient Pressure of 101.325 kPa

| | [Bmim][Br] | | | [Bmim][Cl] | | |
| --- | --- | --- | --- | --- | --- | --- |
| | 293.15 K | 298.15 K | 303.15 K | 293.15 K | 298.15 K | 303.15 K |
| $10^6 \cdot V_\phi^0 \, (= \overline{V}_2^0)$ /m3·mol-1 | 174.11±0.13<br>168.88c<br>169.19d | 174.22±0.13<br>170.86b<br>169.85c<br>169.75d<br>169.42e | 174.52±0.13<br>171.65b<br>170.82c<br>170.35d | 162.06±0.15 | 162.59±0.15<br>162.07a<br>163.32d<br>163.09e | 163.18±0.15<br>163.87d |
| $10^6 \cdot BV$ /m6·mol-2 | -10.7 | -11.1 | -11.3 | -7.7 | -6.3 | -6.1 |
| $10^6 \cdot E_\phi^0$ /m3·mol-1 | | 0.041 | | | 0.112 | |

$^a$Ref. (6), $^b$Ref. (10), $^c$Ref. (33), $^d$Ref. (31), $^e$Ref. (32)

liquids, namely 1-Butyl-3-Methylimidazolium Bromide [Bmim][Br] and 1-Butyl-3-Methylimidazolium Chloride [Bmim][Cl] in aqueous solutions at 293.15, 298.15, and 303.15 K. The density data have been used to calculate apparent molar volumes and partial molar volumes of both the IL's in aqueous solutions at studied temperatures. Using the density and viscosity coefficient data, viscosity A, B, and D coefficients for the studied IL's have been estimated. The processing of the data and results obtained are presented and discussed.

## 2. Results

### 2.1. Density and Apparent Molar Volume

The density ($\rho$) of aqueous solutions of [Bmim][Br] and [Bmim][Cl] at 293.15, 298.15, and 303.15 K are reported in Table S2 and Table S3, respectively (Supporting Information: Table S2-S3). The variation of $\rho$ data as a function of molality of [Bmim][Br] and [Bmim][Cl] in aqueous solutions at studied temperatures are shown in Figures S8-S13 (Supporting Information: Figures S8-S13).

The experimental $\rho$ data obtained were further used to calculate the apparent molar volumes ($V_\phi$) of ILs at finite concentration by using the equation:

$$V_\phi = \frac{(\rho_0 - \rho)}{m\rho\rho_0} + \frac{M}{\rho} \tag{1}$$

where $m$ is molality of solute molecule in aqueous solution (mol·kg-1), $\rho$ and $\rho_0$ are the densities of solution and solvent, respectively, (kg·m-3) and M is the molar mass of the solute (kg·mol-1).

The $V_\phi$ data for [Bmim][Br] and [Bmim][Cl] in aqueous solutions at studied temperatures are collected in Table S2 and Table S3, respectively (Supporting Information: Table S2 and Table S3). The error in $V_\phi$ values were calculated by considering error in density measurement ($\Delta\rho$) and error in molality ($\Delta m$). The combined error estimation for $V_\phi$ parameter is indicated in the form of $\Delta V_\phi$ in Table S2 and Table S3 (Supporting Information: Table S2 and Table S3). These are calculated using the expressions: $\Delta V_\phi = -\frac{1000}{m}\Delta\rho$ and $\Delta V_\phi = -\frac{1000}{m^2}\left(\frac{1}{\rho} - \frac{1}{\rho_0}\right)\Delta m$,

where $\Delta\rho$ and $\Delta m$ refers to uncertainty in density and molality parameters, respectively.

The $V_\phi$ data can also be expressed as[19,20]

$$V_\phi = V_\phi^0 + A_V c^{1/2} + B_V c \tag{2}$$

where $V_\phi^0$ is apparent molar volume of the solute at infinite dilution, $A_V$ is Debye-Hückel limiting law coefficient (1.782, 1.868, and 1.955·10-6 (mol·mm-3)-3/2 for 1:1 electrolyte solutions at 293.15, 298.15 K, and 303.15 K),[20] $B_V$ is a deviation parameter (m6·mol-2) indicating the deviations from Debye-Hückel limiting law which is a measure of ion-ion (cation-anion) electrostatic interactions and $c$ is the concentration of the solute (mol·dm-3), obtained through appropriate conversion of molalities to molarities.

On plotting a graphs of $(V_\phi - A_V c^{1/2})$ parameter as a function of concentration ($c$/mol·dm-3) of ILs in aqueous solutions (Supporting Information: Figure S14 and Figure S15), the intercept and slope of the lines results into the values of $V_\phi^0$ and $B_V$, respectively. The obtained values of $V_\phi^0$ and $B_V$ for [Bmim][Br] and [Bmim][Cl] in aqueous solutions at studied temperatures are given in Table 1.

The partial molar volume of solvent water ($\overline{V}_1$) and partial molar volumes of the IL's ($\overline{V}_2$) are calculated by using the equations:

$$\overline{V}_1 = \frac{M_1}{\rho - c\left(\frac{\partial\rho}{\partial c}\right)} \tag{3}$$

$$\overline{V}_2 = \phi_V + \left[\frac{1000 - c\phi_V}{2000 + c\sqrt{c}\frac{d\phi_V}{d\sqrt{c}}}\right]\sqrt{c}\frac{d\phi_V}{d\sqrt{c}} \tag{4}$$

The values of $\overline{V}_1$ and $\overline{V}_2$ for [Emim][Br] and [Bmim][Cl] in aqueous solutions at studied temperatures are collected in Table S2 and Table S3, respectively (Supporting Information: Tables S2 and Table S3).

The $\overline{V}_2$ data can also be expressed as:

$$\overline{V}_2 = \overline{V}_2^0 + 2.802\sqrt{c} \tag{5}$$

The variation $(\overline{V}_2 - 2.802\sqrt{c})$ parameter as a function of concentration of [Emim][Br] and [Bmim][Cl] in aqueous solutions at 298.15 K are shown in Figure 1 and extrapolating to
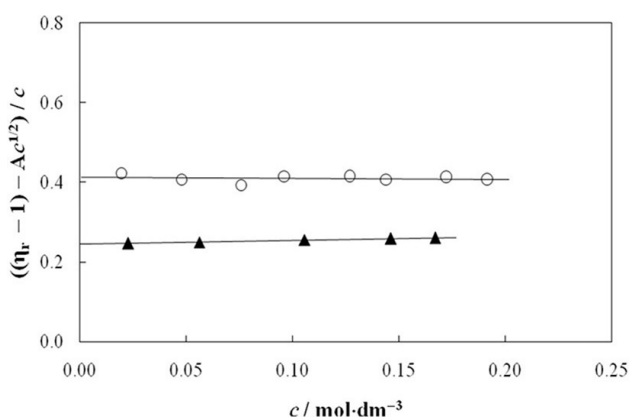


**Figure 1.** The variation of $(\overline{V}_2 - 2.802\sqrt{c})$ parameter as a function of concentration of studied IL's in aqueous solutions at 298.15 K: ▲, [Bmim][Br]; ◯, [Bmim][Cl].

the infinitely dilute solutions, yields the limiting partial molar volume $\overline{V}_2^0$ (= limiting apparent molar volume $V_\phi^0$).

## 2.2. Viscosity Measurements

The relative viscosity coefficients $\eta_r$ values for aqueous solutions of [Emim][Br], [Bmim][Br] and [Bmim][Cl] at 293.15, 298.15 and 303.15 K were calculated by using expression:

$$\eta_r = \frac{\eta}{\eta_0} = \left(\frac{t\rho}{t_0\rho_0}\right)K \tag{6}$$

where $\eta$, $t$, and $\rho$ are the viscosity, time of flow, and density of the solution, respectively, $\eta_0$, $t_0$, and $\rho_0$ are the viscosity, time of flow, and density of the solvent, respectively and $K$ is kinetic energy correction factor.

The kinetic energy correction factor ($K$) was calculated by making time of flow measurements for water at 293.15, 298.15 and 303.15 K respectively (having time of flow equal to 547.3, 487.1 and 437.6 ± 0.1 s, respectively) and using the expression:

$$\nu = Mt - \frac{N}{t} \tag{7}$$

where $\nu$ is the kinematic viscosity (= $\eta$ / $\rho$, where $\eta$ is absolute

viscosity and $\rho$ is density) $M$ and $N$ are the instrumental constants.

The equation (7) can be written as:

$$\nu = Mt - \frac{K}{t^n} \tag{8}$$

where $n$ is Reynolds number and $K$ is kinetic energy correction factor. The correction due to this is found to be negligible and therefore the $K$ in equation (6) is taken as unity.

The relative viscosity coefficients $\eta_r$ values of studied IL's in aqueous solutions at 293.15, 298.15 and 303.15 K are reported in Table 2. The estimated error in $\eta_r$ values is of the order of ± 0.0005. The variation of $\eta_r$ as a function of square root of concentration of [Bmim][Br] and [Bmim][Cl] at 293.15 K, 298.15 K and 303.15 K are depicted in Figure S16-S18 (Supporting Information: Figures S16-S18).

The variation of $\eta_r$ with the concentration ($c$/mol·dm$^{-3}$) can be represented by the Jones-Dole equation:[21]

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc \tag{9}$$

where $\eta$ and $\eta_0$ are the viscosity coefficient of the solution and solvent respectively, $A$ is a constant characterizing ion-ion interactions and B is an adjustable parameter which is related to the size of the ions, proportional to the partial molar entropies of the ions and is additive.

The $\eta_r$ data were used to determine the viscosity A and B coefficients with the help of the plot of $(\eta_r - 1)/c^{1/2}$ against $c^{1/2}$. The values of viscosity A and B coefficients of [Bmim][Br] and [Bmim][Cl] in aqueous solutions at studied temperatures are given in Table 3.

The Jones-Dole equation is limited to very low concentrations of electrolytes ($< 0.1$ mol·kg$^{-1}$) while for little higher concentrations, additional parameter can be added[22]

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc + Dc^2 \tag{10}$$

where D is generally positive, its significance is obscure but probably related to solute-solute association effects.

By using the value of viscosity A coefficient of equation (9), viscosity B and D coefficients have been estimated with the help of the plot of $\left((\eta_r - 1) - Ac^{1/2}\right)/c$ against $c$ of [Bmim][Br] and [Bmim][Cl] at studied temperatures (Figures 2-4). The values of viscosity B and D coefficients of [Bmim][Br] and [Bmim][Cl] in aqueous solutions at studied temperatures are given in Table 3. The accuracy in determination of B coefficient value is of the order of ± 0.01 dm$^3$·mol$^{-1}$.

The $\eta_r$ as a function of concentration can be expressed as a power series of volume fraction $\phi_2$:[23,24]

$$\frac{\eta}{\eta_0} = 1 + \nu_1\phi_2 + \nu_2\phi_2^2 \tag{11}$$

The values of $\nu_1$ and $\nu_2$ coefficients were $\nu_1 = 2.5$ due to Einstein and $\nu_2 = 10.05$ due to Thomas.[23,24] However, we

**Table 2.** Molality $m$, Concentration $c$, Relative Viscosity Coefficient $\eta_r$, $((\eta_r-1)-Ac^{1/2})/c$, Volume Fraction $\phi_2$ Data for Aqueous Solutions of [Bmim][Br] and [Bmim][Cl] at 293.15, 298.15, and 303.15 K and at Ambient Pressure of 101.325 kPa*

| | 293.15 K | | | | 298.15 K | | | | 303.15 K | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $m^o$/mol·kg⁻¹ | $c$/mol·dm⁻³ | $\eta_r^a$ | $\frac{((\eta_r-1)-Ac^{1/2})}{c}$ | $\phi_2$ | $c$/mol·dm⁻³ | $\eta_r^a$ | $\frac{((\eta_r-1)-Ac^{1/2})}{c}$ | $\phi_2$ | $c$/mol·dm⁻³ | $\eta_r^a$ | $\frac{((\eta_r-1)-Ac^{1/2})}{c}$ | $\phi_2$ |
| **[Bmim][Br]** | | | | | | | | | | | | |
| 0.00000 | 0.00000 | 1.0000 | | | | 1.0000 | | | | 1.0000 | | |
| 0.02281 | 0.02268 | 1.0057 | 0.2466 | 0.0039 | 0.02265 | 1.0051 | 0.2194 | 0.0039 | 0.02262 | 1.0044 | 0.1891 | 0.0039 |
| 0.05680 | 0.05615 | 1.0142 | 0.2495 | 0.0098 | 0.05608 | 1.0126 | 0.2213 | 0.0097 | 0.05601 | 1.0110 | 0.1930 | 0.0097 |
| 0.10777 | 0.10561 | 1.0273 | 0.2557 | 0.0182 | 0.10549 | 1.0240 | 0.2242 | 0.0182 | 0.10534 | 1.0210 | 0.1962 | 0.0183 |
| 0.15020 | 0.14613 | 1.0382 | 0.2588 | 0.0252 | 0.14596 | 1.0334 | 0.2264 | 0.0252 | 0.14576 | 1.0293 | 0.1984 | 0.0252 |
| 0.17232 | 0.16704 | 1.0439 | 0.2605 | 0.0288 | 0.16685 | 1.0384 | 0.2275 | 0.0287 | 0.16662 | 1.0337 | 0.1996 | 0.0288 |
| **[Bmim][Cl]** | | | | | | | | | | | | |
| 0.00000 | 0.00000 | 1.0000 | | | | 1.0000 | | | | 1.0000 | | |
| 0.01948 | 0.01938 | 1.0120 | 0.4233 | 0.0031 | 0.01936 | 1.0117 | 0.4484 | 0.0031 | 0.01933 | 1.0039 | 0.1942 | 0.0032 |
| 0.04809 | 0.04763 | 1.0253 | 0.4079 | 0.0077 | 0.04758 | 1.0230 | 0.3825 | 0.0077 | 0.04751 | 1.0168 | 0.3495 | 0.0077 |
| 0.07678 | 0.07570 | 1.0372 | 0.3935 | 0.0122 | 0.07561 | 1.0347 | 0.3783 | 0.0123 | 0.07550 | 1.0284 | 0.3721 | 0.0123 |
| 0.09781 | 0.09611 | 1.0483 | 0.4153 | 0.0155 | 0.09600 | 1.0425 | 0.3721 | 0.0156 | 0.09586 | 1.0373 | 0.3862 | 0.0156 |
| 0.12965 | 0.12677 | 1.0621 | 0.4140 | 0.0204 | 0.12661 | 1.0573 | 0.3911 | 0.0205 | 0.12642 | 1.0489 | 0.3843 | 0.0206 |
| 0.14784 | 0.14414 | 1.0689 | 0.4071 | 0.0232 | 0.14396 | 1.0658 | 0.3992 | 0.0233 | 0.14375 | 1.0554 | 0.3824 | 0.0234 |
| 0.17773 | 0.17247 | 1.0824 | 0.4125 | 0.0278 | 0.17225 | 1.0779 | 0.3995 | 0.0279 | 0.17199 | 1.0672 | 0.3882 | 0.0280 |
| 0.19816 | 0.19168 | 1.0898 | 0.4067 | 0.0308 | 0.19143 | 1.0864 | 0.4013 | 0.0310 | 0.19115 | 1.0752 | 0.3913 | 0.0311 |

*Standard uncertainties u are u (T) = 0.01 K; u (p) = 10 kPa [a] Standard uncertainties u are u (m) = 0.00005 mol·kg⁻¹; u ($\eta_r$) = 0.0001
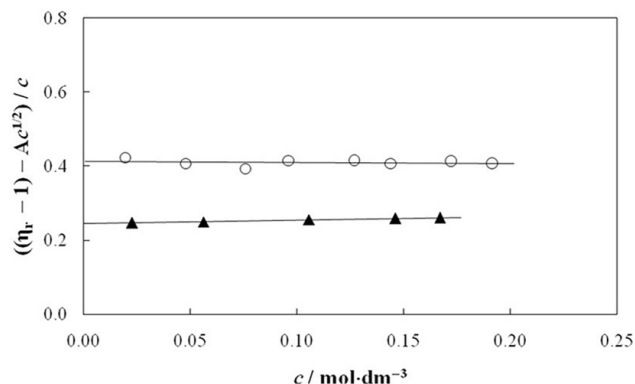


**Figure 2.** Variation of $((\eta_r-1)-Ac^{1/2})/c$ parameter as a function of concentration of studied IL's in aqueous solutions at 293.15 K: ▲, [Bmim][Br]; ○, [Bmim][Cl].
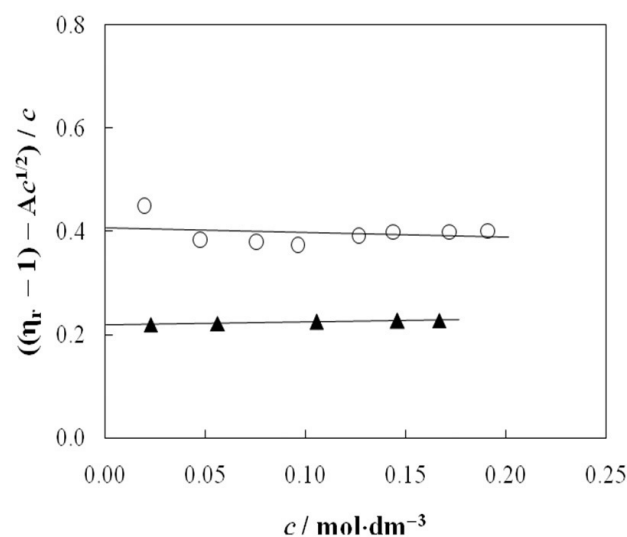


**Figure 3.** Variation of $((\eta_r-1)-Ac^{1/2})/c$ parameter as a function of concentration of studied IL's in aqueous solutions at 298.15 K: ▲, [Bmim][Br]; ○, [Bmim][Cl].
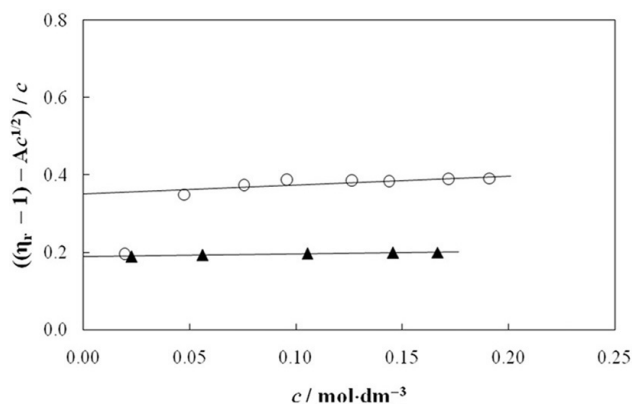


**Figure 4.** Variation of $((\eta_r-1)-Ac^{1/2})/c$ parameter as a function of concentration of studied IL's in aqueous solutions at 303.15 K: ▲, [Bmim][Br]; ○, [Bmim][Cl].

**Table 3.** Viscosity A coefficient, Viscosity B Coefficient, Viscosity D Coefficient, Temperature Coefficient of B (dB/dT), Einstein-Simha factor $\nu_1$, Particle Interaction Coefficient Q and Hydration Number $h$ Data for Aqueous Solutions of [Bmim][Br] and [Bmim][Cl] at 293.15, 298.15, and 303.15 K and at Ambient Pressure of 101.325 kPa

| T / K | $A^a$ / dm$^{3/2}$·mol$^{-1/2}$ | B Coefficient$^a$ / dm$^3$·mol$^{-1}$ | B Coefficient$^b$ / dm$^3$·mol$^{-1}$ | D Coefficient$^b$ / dm$^6$·mol$^{-2}$ | dB/dT | $\nu$ (Experimental) | $\nu$ (Calculated) $=\frac{1000B}{\overline{V}_2}$ | Q | h |
|---|---|---|---|---|---|---|---|---|---|
| **[Bmim][Br]** | | | | | | | | | |
| 293.15 | 0.001 | 0.257 | 0.244 | 0.098 | | 1.44 | 1.40 | 1.22 | -0.26 |
| 298.15 | 0.001 | 0.225 | 0.218 | 0.056 | -0.006 | 1.29 | 1.25 | 0.48 | -0.29 |
| 303.15 | 0.001 | 0.197 | 0.188 | 0.069 | | 1.12 | 1.08 | 1.04 | -0.37 |
| **[Bmim][Cl]** | | | | | | | | | |
| 293.15 | 0.027 | 0.407 | 0.413 | -0.028 | | 3.33 | 2.55 | -6.45 | -2.11 |
| 298.15 | 0.022 | 0.391 | 0.406 | -0.090 | -0.006 | 2.78 | 2.50 | -1.19 | -0.92 |
| 303.15 | 0.001 | 0.383 | 0.351 | 0.230 | | 2.19 | 2.15 | 2.35 | 0.16 |

[a] The values of A and B coefficients are calculated by using equation (9). [b] The values of B and D coefficients are calculated by using equation (10).

obtained these values by fitting the relative viscosity data as a function of volume fraction ($\phi_2$). The experimental calculated values of $\nu_1$ and $\nu_2$ coefficients of equation (11) for [Bmim][Br] and [Bmim][Cl] in aqueous solutions at studied temperatures are given in Table 4.

**Table 4.** $\nu_1$ and $\nu_2$ coefficients of equation (11) for [Bmim][Br] and [Bmim][Cl] in Aqueous Solutions at 293.15, 298.15, and 303.15 K and at Ambient Pressure of 101.325 kPa.

| | | 293.15 K | 298.15 K | 303.15 K |
|---|---|---|---|---|
| [Bmim][Br] | $\nu_1$ | 1.48 | 1.30 | 1.14 |
| | $\nu_2$ | 1.01 | 1.01 | 1.00 |
| [Bmim][Cl] | $\nu_1$ | 2.96 | 2.77 | 2.36 |
| | $\nu_2$ | 1.05 | 1.04 | 1.03 |

The volume fraction ($\phi_2$) values were estimated by using equation:

$$\phi_2 = \frac{x_2\overline{V}_2}{x_2\overline{V}_2 + x_1\overline{V}_1} \tag{12}$$

where, $x_1$ and $x_2$ represent the mole fraction of the IL's and solvent water, respectively, while $\overline{V}_2$ and $\overline{V}_1$ are the partial molar volumes of IL's and solvent water, respectively.

In calculating the mole-fractions of electrolyte, proper method suggested by Stoke's[16] was used. The $\phi_2$ values are collected in Table 2.

If Vand theory of viscosity[24,25] is applied to relative viscosity coefficient data, which is in the form:

$$\ln \eta_r = \frac{\nu\phi_2}{1 - Q\phi_2} \tag{13}$$

where $\nu$ is the Einstein-Simha factor and $Q$ is termed as a particle interaction coefficient.

By appropriate rearrangement, equation (13) can be written in the form

$$\frac{\ln \eta_r}{\phi_2} = \nu + Q \cdot \ln \eta_r \tag{14}$$

Following Eagland and Pilling[26] as well as Patil and Thakare,[27] by plotting graph of $\frac{\ln \eta_r}{\phi_2}$ against $\ln \eta_r$, the values of Einstein-Simha factor ($\nu$) and particle interaction coefficient ($Q$) have been determined and are collected in Table 3. In this approach, we assumed that the studied ionic liquids exist as ion-pairs, since it is difficult to have estimation of single ionic volumes.

## 3. Discussion

The variation of density data as a function of molality of [Bmim][Br] and [Bmim][Cl] in aqueous solutions at studied 293.15, 298.15 and 303.15 K are shown in Figures S5a-S5f (Supporting Information: Figures S8-S13). An examination of Figures S11-S13 (Supporting Information: Figures S11-S13) reveals that, the experimental densities obtained for [Bmim][Cl] in aqueous solutions at 293.15 K, 298.15 K and 303.15 K show very good agreement with the reported literature values.[6,28,29] However, our density data for [Bmim][Br] in aqueous solutions at all studied temperatures show little lower values than literature data[10,30] (Supporting Information: Figures S8-S10).

The variation of ($V_\phi - A_V c^{1/2}$) with concentration ($c$/mol·dm$^{-3}$) for [Bmim][Br] and [Bmim][Cl] in aqueous solutions at 293.15 K, 298.15 K and 303.15 K are shown in Figure S14 and Figure S15 (Supporting Information: Figure S14 and Figure S15). It is observed from Table S2 and Table S3 (Supporting Information: Table S2 and Table S3) and Figure S14 and Figure S15 (Supporting Information: Figure S14 and Figure S15) that the apparent molar volume of studied imidazolium salts in aqueous solutions at 293.15, 298.15 and 303.15 K decreases as the concentration of IL's increases. The values of $V_\phi^0$ for studied IL's

The particle interaction coefficient ($Q$) values (Table 3) are negative which increase with increase in temperature in case of [Bmim][Cl], signifying the presence of cation-cation association effect in solution phase. The calculated values of hydration number $h$ ($B = \nu_1(\overline{V}_2^0 + h\overline{V}_1^0)$) for studied IL's at studied temperatures are reported in Table 3. We observed that, $h$ values are very small for [Bmim][Br].

## 4 Conclusions

The apparent molar volume and partial molar volume of [Bmim][Br] and [Bmim][Cl] in aqueous solutions as a function of concentration at different temperatures have been reported. We observed that the deviation parameters $B_V$ of Debye-Hückel theory for volumes are negative for studied IL's indicating water structure making effect due to overlap of solvent cosphere effect. The $E_\phi^0$ of studied IL's in water has been calculated at 298.15 K. The single ion partial molar volume of the cation [Bmim]$^+$ is also estimated. The main objective of this work is the experimental determination of viscosity A, B and D coefficients at different temperatures in limiting concentration range ($\sim 0.019$ to $\sim 0.2$ mol·kg$^{-1}$) of [Bmim][Br] and [Bmim][Cl] in aqueous solutions. It is observed that the Jones-Dole viscosity A and B coefficients are positive in magnitude. The viscosity A coefficient values decreases with increase in temperature for [Bmim][Cl]. These results indicate that the studied IL's act similar to that of 1:1 electrolyte and exhibit water structure making effect (i.e., H-bonding amongst water molecules surrounding the cations get increased) in aqueous solutions. An application of Vand's equation enabled us to obtain the values of $\nu_1$ Einstein-Simha factor and $Q$ particle interaction coefficient. We observed that, for [Bmim][Cl] the $\nu_1$ values are greater than 2.5 indicating deviation from a spherical shape of the molecule, along with a contribution due to hydrophobic interactions with the solvent, while $\nu_1$ values are smaller than 2.5 in case of [Bmim][Br] indicating more hydrophobicity for such salt favouring more cation-solvent-cation interactions. It has been suggested by Ludwig et al.[33] that tuning thermodynamical and transport properties of IL's is of great importance for their application in science and technology. The present results of volumes and viscosity A and B coefficients for three studied IL's in water support the said conjecture strongly.

## Acknowledgment

## Conflict of Interest

The authors declare no conflict of interest.

[1] T. Kavitha, P. Attri, P. Venkatesu, R. S. Rama Devi, T. Hofman, *J. Phys. Chem. B* **2012**, *116*, 4561–4574.

[2] R. Umapathi, P. Attri, P. Venkatesu, *J. Phys. Chem. B* **2014**, *118*, 5971–5982.

[3] I. J. Warke, K. J. Patil, S. S. Terdale, *J. Chem. Thermodyn.* **2016**, *93*, 101–114.

[4] M. A. R. Martins, C. M. S. S. Neves, K. A. Kurnia, P. J. Carvalho, M. A. A. Rocha, L. M. N. B. F. Santos, S. P. Pinho, M. G. Freire, *Fluid Phase Equilib.* **2016**, *407*, 188–196.

[5] D. H. Dagade, S. P. Shinde, K. R. Madkar, S. S. Barge, *J. Chem. Thermodyn.* **2014**, *79*, 192–204.

[6] R. L. Gardas, D. H. Dagade, S. S. Terdale, J. A. P. Coutinho, K. J. Patil, *J. Chem. Thermodyn.* **2008**, *40*, 695–701.

[7] R. L. Gardas, D. H. Dagade, S. S. Terdale, J. A. P. Coutinho, K. J. Patil, *J. Phys. Chem. B* **2008**, *112*, 3380–3389.

[8] V. R. Shaikh, S. S, Terdale, G. R. Gupta, D. G. Hundiwale, K. J. Patil, *J. Mol. Liq.* **2013**, *186*, 14–22.

[9] R. L. Gardas, H. F. Costa, 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* **2008**, *53*, 805–811.

[10] M. T. Zafarani-Moattar, H. Shekaari, *J. Chem. Thermodyn.* **2005**, *37*, 1029–1035.

[11] E. Gómez, B. González, Á. Domínguez, E. Tojo, J. Tojo, *J. Chem. Eng. Data* **2006**, *51*, 696–701.

[12] T. Chen, M. Chidambaram, Z. Liu, B. Smit, A. T. Bell, *J. Phys. Chem. B* **2010**, *114*, 5790–5794.

[13] H. S. Frank, W. Y. Wen, *Discuss. Faraday Soc.* **1957**, *24*, 133–140.

[14] R. L. Kay in *Water-A Comprehensive Treatise, Vol. 3* (Ed.: F. Franks), Plenum Press, New York, **1973**.

[15] E. R. Nightingale, in *Chemical Physics of Ionic Solutions*, (Eds.: B. E. Conway, R. G. Barradas), John Wiley, New York, **1965**.

[16] R. A. Robinson, R. H. Stokes, *Electrolyte Solutions, 2$^{nd}$ Ed.*, Butterworths, London, **1959**.

[17] R. H. Stokes, R. Mills, *Viscosity of Electrolytes and Related Properties, International Encyclopedia of Physical Chemistry and Chemical Physics*, Pergamon Press, New York, **1965**.

[18] H. Donald, B. Jenkins, Y. Marcus, *Chem. Rev.* **1995**, *95*, 2695–2724.

[19] H. S. Harned, B. B. Owen, *The Physical Chemistry of Electrolytic Solutions, 3$^{rd}$ Ed.*; Reinhold Publishing Corporation, New York, **1958**.

[20] O. Redlich, D. M. Meyer, *Chem. Rev.* **1964**, *64*, 221–227.

[21] G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, *51*, 2950–2964.

[22] J. E. Desnoyers, G. Perron, *J. Solution Chem.* **1972**, *1*, 199–212.

[23] B. R. Breslau, I. F. Miller, *J. Phys. Chem.* **1970**, *74*, 1056–1061.

[24] D. G. Thomas, *J. Colloid. Sci.* **1965**, *20*, 267–277.

[25] V. Vand, *J. Phys. Chem.* **1948**, *52*, 277–299.

[26] D. Eagland, G. Pilling, *J. Phys. Chem.* **1972**, *76*, 1902–1906.

[27] K. J. Patil, O. B. Thakare, *Indian J. Pure Appl. Phys.* **1981**, *19,* 497–499.

[28] B. Lal, M. Sahin, E. Ayranci, *J. Chem. Thermodyn.* **2012**, *54*, 142–147.

[29] H. Shekaari, M. T. Zafarani-Moattar, A. Kazempour, Z. Ghasedi-Khajeh, *J. Chem. Eng. Data* **2015**, *60*, 1750–1755.

[30] R. Sadeghi, R. Golabiazar, H. Shekaari, *J. Chem. Thermodyn.* **2010**, *42*, 441–453.

[31] H. L. Friedman, C. V. Krishnan in *Water-A Comprehensive Treatise, Vol. 3* (Ed.: F. Franks), Plenum Press, New York, **1973**.

[32] T. T. Herskovits, T. M. Kelly, *J. Phys. Chem.* **1973**, *77*, 381–388.

[33] A. Wulf, K. Fumino, R. Ludwig, *Angew. Chem. Int. Ed.* **2010**, *49*, 449–453.