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Thermodynamic studies of ionic interactions in aqueous solutions of N-butyl-pyridinium bromide at 298.15 K



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ABSTRACT

Density and osmotic coefficient measurements for aqueous solutions of N-butyl-pyridinium bromide [Bpy] [Br] in concentration range ~0.019 to ~0.39 mol·kg⁻¹ at 298.15 K are reported. The density data are used to obtain apparent molar volume (ϕ_V), partial molar volume of solute and solvent (\overline{V}_2 and \overline{V}_1) respectively as well the limiting partial molar volume ($\overline{\phi}_V^0 = \overline{V}_2^0$) of the solute [Bpy][Br] (by appropriate extrapolation). The experimental osmotic coefficient (ϕ) data are used to determine the activity and mean ionic activity coefficients of solute and solvent respectively. Experimental activity coefficient data are compared with those obtained from Debye–Hückel and Pitzer models. The activity data have been further processed to obtain the Gibbs free energy change due to mixing (ΔG_m) and excess Gibbs free energy change (ΔG^E). The aggregation number (n) and critical micelle concentration (*cmc*) are obtained for ionic salt in solution phase by applying pseudo-phase separation model to ϕ and ϕ_V data respectively. Application of McMillan–Mayer theory of solutions to the data is made. The results have been interpreted on the basis of structural characteristic of salt, ion–solvent and ion–ion interactions.

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1. Introduction

lonic liquids (ILs) have attracted much attention over the past decade due to their large variety of applications in industry and applied chemistry [1,2]. The journey of ionic liquids started from molten salts or fused salts which are composed entirely of ions; their conductivity is considerable and higher than that of water [3,4]. Ionic liquids are termed room-temperature ionic liquids (RTILs) if they are composed of a salt that is liquid at room temperature. ILs almost always contain an organic ion as either the cation or the anion. These neoteric materials provide a feasibility of changing ion either cation or anion in accordance with the conditions. Such designing ability is the key reason as these materials are popular solvents for organic reactions [5].

Reliable knowledge of thermodynamic and thermophysical properties for both the pure ILs and their mixtures is a prerequisite for the design and optimization of different processes. Most of the ILs have negligibly low vapor pressures, high thermal decomposition temperatures, wide liquid temperature ranges and excellent stability in air and water. These features make ILs suitable for the application of IL + water mixtures as heat transfer fluids [4].

The ionic liquids mainly consist of ammonium, sulfonium and phosphonium cations. Furthermore, the applications of imidazolium and pyridinium-based ionic liquids are increased by many folds in recent years; large number of research articles, reviews, books and

* Corresponding author. E-mail address: patilkesharsingh@hotmail.com (K.J. Patil). monograph are now available [6–9]. To date, a number of researchers have studied the thermophysical properties of aqueous solutions of imidazolium-based ionic liquids. The thermodynamic studies (density, speed of sound and osmotic coefficient) of ionic interactions in aqueous solutions of 1-ethyl-3-methylimidazolium bromide and 1-butyl-3methylimidazolium chloride at 298.15 K are reported [10]. Similarly, the measurements for speed of sound and density of aqueous solutions of imidazolium chloride, 1-methyl imidazolium chloride and 1-butyl-3-methylimidazolium chloride at 298.15 K are reported and discussed in terms of hydrophobic hydration, hydrophobic interactions, and water structural changes in aqueous medium [11]. The electrical conductivity was measured for aqueous solutions of long-chain imidazolium ionic liquids (1-alkyl-methylimidazolium bromides) with C12-C16 chains and further the data were used for the determination of aggregation number, critical micelle concentration and degree of counter ion binding [12]. For the systems involving imidazolium based ionic liquids and water, the measurements of density, refractive index, viscosity, specific conductance and surface tension have been studied [13]. Osteryoung et al. pioneered the first room temperature pure electrolyte of pyridine family in 1975 [14,15]. Thereafter very few research articles which deal with the physical properties of pyridinium-based ionic liquids have been reported [16-19].

Our literature survey revealed that N-butyl pyridinium bromide salt has different freezing and melting points [20]. As such the salt exists at room temperature in a glassy state of which properties are difficult to determine. It is also known in literature [21,22] that pyridinium salts exert water structure breaking effect in aqueous

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solutions as well some have reported micellization when the nonpolar residues are substituted on the pyridinium nitrogen center [23]. Considering these aspects, in order to study the effects due to hydrophobic substituent such as N-butyl group, we focused our attention on N-butyl pyridinium bromide salt.

Recently, we have developed a rapid and simple method for the synthesis of the substituted imidazolium ionic liquids. Considering the applications for the devised method, we undertook the work of synthesis of N-butyl pyridinium bromide [Bpy][Br]. We could synthesize the compound successfully, however its identification was biased because of differing freezing and melting behavior (as well its highly hygroscopic nature). Therefore, a program was embarked to investigate the structural properties of aqueous pyridinium-based ionic liquid solutions, for the studies of hydrophobic interaction amongst pyridinium-based ionic liquids, their hydration properties i.e. ionic liquid-water interactions and water structural effects (structure making and breaking effect). For this the knowledge of partial volumes, free-energy and entropy changes at infinite as well as at finite concentrations is essential. It is suspected that ionic liquid depending upon the hydrophobic moieties may exhibit micelle type or aggregation equilibria in solution phase. To probe such an equilibria in solution phase, the measurements of density and osmotic coefficient properties of [Bpy][Br] in aqueous solutions at 298.15 K were carried-out. The results are being reported below and discussed in terms of water structural effects and presence of micellar type of equilibria in solution phase.

2. Experimental procedure

Synthesis of N-butyl-pyridinium bromide [BPy][Br] was carried-out by a simple and efficient method, previously reported by us [24]. It consists of reacting alkyl-halide and pyridine in appropriate amounts in the presence of molten-tetra-butyl-ammonium-bromide for about half an hour. On cooling the reaction mixture, the white product obtained was separated and purified with the help of tetrahydrofuran. The product [BPy][Br] was dried in vacuum-oven and identified by mass and spectral analysis [24–26]. It was stored in vacuum. However, it was found that the salt is very much hygroscopic (absorbs water), making the measurements of weight etc. difficult. Therefore, it was decided to determine the water content of the stored salt by Karl Fischer (KF) and Thermo-Gravimetric Analysis (TGA) and also estimating with the osmometry (to be discussed later). The structure of the studied ionic liquid is shown in Fig. 1. The salt NaCl of AR grade (Merck) was dried under vacuum at 393 K for 24 h before use.

All the solutions were prepared on molality basis using quartz doubly distilled water and were converted to molarity scale whenever required with the help of density data at 298.15 K. A Shimadzu AUW220D balance having a readability of 0.01 mg was used for weighing. The density measurements were made using an Anton Paar



Fig. 1. Molecular structure of the compound studied.

Digital Densitometer (Model: DMA-5000) at 298.15 \pm 0.001 K. After applying the humidity and lab pressure corrections, the uncertainty in the density measurements was found to be $\pm 5 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$. The details about the density measurements have been reported earlier [27]. The reliability of the density data was ascertained by making the measurements of binary aqueous solutions of alkali halides (NaCl and KCl) at 298.15 K and comparing the data with literature [28]. Also, the limiting apparent molar volumes (ϕ_V^0) for these standards are in good agreement with the literature data [29].

The osmotic coefficients (ϕ) of aqueous ionic salt solutions were measured using a Knauer Vapor Pressure Osmometer (Model: K-7000) at 298.15 \pm 0.001 K. The instrument was calibrated using aqueous NaCl solutions taking water as a reference. The required osmotic coefficient data for aqueous NaCl solutions were taken from literature [30]. The uncertainty in ϕ measurements was found to be $\pm 1 \cdot 10^{-3}$ at the lowest concentration studied. The details about the calibration, measurements and error analysis of vapor pressure osmometer were described earlier [31–33].

3. Results

3.1. Molecular weight determination of [Bpy][Br] by vapor pressure osmometry

We have used aqueous NaCl solutions of known osmolality for the calibration and hence determined the instrumental constant (K_{calib}). The K_{calib} is represented by the slope of the regression curve (measurement value as a function of osmolality of aqueous NaCl solutions) passing through origin and is represented by the equation:

$$K_{\text{calib}} = measurement \, value / known \, osmolality.$$
 (1)

The osmolality of the sample solution can be calculated with the following equation:

$$osmolality = measurement \, value/K_{calib}.$$
(2)

The osmotic pressure (π) is calculated by the following equation:

$$\pi(atm) = osmolality\left(m \, osmol \cdot kg^{-1}\right) \cdot 0.082056\left(L \cdot atm \cdot K^{-1} \cdot mol^{-1}\right) \cdot 298.15(K).$$
(3)

The concentration c in $(g \cdot cm^{-3})$ is calculated with the help of density and weight fraction data.

The values of parameter (π /cRT) are estimated with help of the following equation:

$$\pi/cRT(mol \cdot g^{-1}) = \pi(atm) / \left[c(g \cdot cm^{-3}) \cdot 82.056(cm^{3} \cdot atm \cdot K^{-1} \cdot mol^{-1}) \cdot 298.15(K) \right].$$
(4)

In Fig. 2, parameter π/cRT is plotted as a function of concentration (*c* in g·cm⁻³) for the studied compound. The intercept of the said plot yielded the value of reciprocal of molecular weight while the slope value gave the measure of osmotic second virial coefficient. The intercept of the plot reveals that the molecular weight of studied compound is 283.53 g·mol⁻¹. The theoretical molecular weight of the compound is 216.12 g·mol⁻¹. Therefore, we concluded that the salt contains four water molecules as water of hydration. This conclusion is also supported by our KF titrimetry and TGA analysis [25]. The calculated molecular weight was used to correct the molalities and reported in Table 1 as well as in Table 3.

3.2. Volumetric properties

The density (d) data as a function of concentration of ionic salt molecule in aqueous solutions at 298.15 K are reported in Table 1.



Fig. 2. The plot of parameter (π /cRT) against concentration (gm·cc⁻¹) of [Bpy][Br] in aqueous [Bpy][Br] solutions at 298.15 K.

The apparent molar volume (ϕ_V) as a function of molality of the ionic salt molecules was calculated by using the following equation:

$$\phi_V = \frac{1000(d_0 - d)}{mdd_0} + \frac{M_2}{d} \tag{5}$$

where *m* is the molality of ionic salt molecules in aqueous solution $(mol \cdot kg^{-1})$, *d* and *d*₀ are the densities of solution and solvent respectively in kg·m⁻³ and *M*₂ is the molar mass of the solute $(kg \cdot mol^{-1})$.

The ϕ_V data can also be expressed as [29,34,35]

$$\phi_V = \phi_V^0 + A_V c^{1/2} + B_V c \tag{6}$$

where ϕ_V^0 is the apparent molar volume of the salt at infinite dilution, A_V is the Debye–Hückel limiting law coefficient (1.868 for 1:1 electrolyte solutions at 298.15 K), B_V is the deviation parameter and c is the concentration of the salt on molarity scale. The variation of $(\phi_V - 1.868c^{1/2})$ parameter as a function of concentration of ionic salt $(c/\text{mol}\cdot\text{dm}^{-3})$ in aqueous solutions at 298.15 K is shown in Fig. 3. When $(\phi_V - 1.868c^{1/2})$ values are extrapolated to infinite dilution, they yield limiting apparent molar volumes (ϕ_V^0) of ionic salt. The values of ϕ_V^0 and B_V parameter of Eq. (6) are collected in Table 2.



Fig. 3. Variation of $(\phi_V - 1.868c^{1/2})$ as a function of concentration $(c/mol \cdot dm^{-3})$ of [Bpy][Br] in aqueous solutions at 298.15 K.

The partial molar volume of the ionic salt (\overline{V}_2) has been computed from ϕ_V data by using the following equation [36]

$$\overline{V}_{2} = \left[\phi_{V} + \frac{1000 - c \phi_{V}}{2000 + c \sqrt{c} \cdot \frac{d\phi_{V}}{d\sqrt{c}}}\right] \sqrt{c} \cdot \frac{d\phi_{V}}{d\sqrt{c}}.$$
(7)

The partial molar volume of solvent (\overline{V}_1) is calculated using equation

$$\overline{V}_1 = \left[\frac{M_1}{\left(d - c \cdot \frac{\delta d}{\delta c}\right)}\right] \tag{8}$$

where M_1 is the molecular weight of the solvent and c is the concentration in mol·dm⁻³.

The data of ϕ_V , \overline{V}_2 and \overline{V}_1 for aqueous solutions of [Bpy][Br] at 298.15 K are reported in Table 1.

Vikingstad et al. [37] have calculated the volume of the surfactant in the micellar state (V_m) directly from the apparent molal volume by using the following equation:

$$\phi_V = \frac{cmc}{m} V_s + \frac{m - cmc}{m} V_m \tag{9}$$

where V_s is the molar volume of the surfactant in the dispersed state and V_m is the molar volume of drugs in the micellar state. The data of ϕ_V are plotted against 1/*m* as suggested by Taboada et al. [38] (Fig. 4). Using Eq. (9) and the data shown in Fig. 4, we estimated the values of aggregation number (*n*) and *cmc* value as 6 and 0.17 mol·kg⁻¹

Table 1

Molality (*m*), density (*d*), concentration (*c*), apparent molar volume (ϕ_V), partial molar volumes of solute and solvent (\overline{V}_2 and \overline{V}_1) for Aqueous solutions of [Bpy][Br] at 298.15 K.

$m^a/mol \cdot kg^{-1}$	$d^b/\mathrm{kg}\cdot\mathrm{m}^{-3}$	c/mol⋅dm ⁻³	$10^3 \cdot \phi_V^c/\mathrm{mm}^3 \cdot \mathrm{mol}^{-1}$	$10^3 \cdot \overline{V}_2 / \text{mm}^3 \cdot \text{mol}^{-1}$	$10^3 \cdot \overline{V}_1 / \text{mm}^3 \cdot \text{mol}^{-1}$
0.00000	0997.043	0.00000	162.03 ^ª	162.03 ^a	18.068
0.01984	0998.117	0.01972	162.14	161.96	18.068
0.02735	0998.523	0.02715	162.07	161.82	18.069
0.04333	0999.388	0.04290	161.93	161.54	18.069
0.05223	0999.870	0.05164	161.85	161.38	18.069
0.06294	1000.450	0.06212	161.76	161.19	18.069
0.07738	1001.231	0.07620	161.63	160.93	18.069
0.09862	1002.381	0.09679	161.45	160.57	18.070
0.12224	1003.659	0.11653	161.24	160.16	18.071
0.16454	1005.949	0.15984	160.88	159.46	18.073
0.23438	1009.729	0.22525	160.27	158.33	18.077
0.31217	1013.394	0.29652	159.61	157.13	18.083
0.39501	1018.424	0.37065	158.90	155.90	18.092

a) The uncertainty in molality m is of the order of $\pm 5 \cdot 10^{-5}$ mol·kg⁻¹.

b) The error involved in density determination at lowest concentration is of the order of $\pm 5 \cdot 10^{-3}$ kg·m⁻³.

c) The errors in ϕ_V were obtained using the method of propagation of errors and found to be $\pm 0.25 \cdot 10^3$ mm³·mol⁻¹ at the lowest concentration studied.

^a Extrapolated value at infinitely dilute solution of [Bpy][Br] at 298.15 K.

Table 2

The limiting partial molar volume (\overline{V}_2^0) , deviation parameter (B_v) , critical micelle concentration (cmc), molar volume of the ionic salt in the dispersed state (V_s) and aggregation number (n) data for [Bpy][Br] in aqueous solutions at 298.15 K.

$\frac{10^3 \cdot \overline{V}_2^0}{\text{mm}^3 \cdot \text{mol}^{-1}}$	$10^3 \cdot B_v/$ mm ⁶ ·mol ⁻²	$cmc/mol \cdot kg^{-1}$	$10^3 \cdot V_s/$ mm ³ ·mol ⁻¹	п
162.03 ± 0.25	-11.64	0.17 ± 0.01	940	6

respectively and these are collected in Table 2. The calculation details of *n* and *cmc* were described earlier [27].

3.3. Osmotic and activity coefficients

The osmotic coefficient (ϕ) values of N-butyl-pyridinium bromide [Bpy][Br] in aqueous solutions were determined over the concentration range of ~0.019 to ~0.39 mol·kg⁻¹ at 298.15 K.

Using the osmotic coefficient (ϕ) values obtained for aqueous binary electrolyte solutions, the water activity (a_w) values have been calculated using the equation

$$\ln a_{w} = -\phi \left(\frac{x_{2}}{x_{1}}\right) \tag{10}$$

where x_1 and x_2 are the mole fractions of water and the salt in the aqueous solutions respectively.

Further the (a_w) data were utilized to calculate the solvent activity coefficient (γ_1) using the equation:

$$\gamma_1 = \frac{a_w}{x_1}.\tag{11}$$

The data of ϕ and a_w are collected in Table 3. The variation of ϕ as a function of square root of solute molality is shown in Fig. 5.

The experimental osmotic coefficient data for 1:1 type electrolyte has been expressed as [34]

$$\phi = 1 + \frac{1}{3} \ln \gamma_{\pm} \tag{12}$$

where γ_{\pm} represents the mean molal activity coefficient of solute.

According to Debye–Hückel limiting law, the solute activity coefficient (γ_+) is given as:

$$\ln\gamma_{+} = 2.303 \log\gamma_{+} = -2.303 A_{\gamma} z_{+} z_{-} \sqrt{m}.$$
(13)



Fig. 4. Variation of apparent molar volumes (ϕ_V) as a function of reciprocal of molality (1/*m*) of [Bpy][Br] in aqueous solutions at 298.15 K.

Substituting Eq. (13) into Eq. (12) and considering higher order interaction terms A_i , which are expected to be appreciable at higher concentrations, one can write Eq. (12) as [37]

$$\phi = 1 - \frac{2.303}{3} A_{\gamma} z_{+} z_{-} \sqrt{m} + \sum_{i=2}^{n} A_{i} m^{i/2}$$
(14)

where A_{γ} is the Debye–Hückel limiting slope for aqueous solutions and its value is 0.5115 at 298.15 K.

Eq. (14) can be written as

$$\phi = 1 + \sum_{i=1}^{n} A_i m^{i/2} \tag{15}$$

where A_1 is the Debye–Hückel constant equal to -0.3927 for 1:1 electrolyte at 298.15 K. The coefficient A_1 represents the term $[(-2.303 A_{\gamma}z_+z_-)/3]$, assuming the ionic salt studied as 1:1 electrolytes ($z_+ = z_- = 1$), and $A_{\gamma} = 0.5115$ at 298.15 K.

The experimentally observed osmotic coefficient values were fitted according to Eq. (15) and the corresponding values of A_i coefficients have been determined by least square fit method. The A_i coefficients in Eq. (15) are collected in Table 4.

For further processing, we applied the pseudo-phase separation model to ϕ data as suggested by Desnoyers et al. [39]. When ϕ values are plotted against 1/m (Fig. 6) it leads to the simultaneous determination of aggregation number n (by linear extrapolation in the high concentration region) and critical micelle concentration *cmc* according to equation [39,40]

$$\phi = \frac{1}{n} + \left(1 - \frac{1}{n}\right) \frac{cmc}{m}.$$
(16)

Using Eq. (16) and the data shown in Fig. 6, we calculated the values of *n* and *cmc* values as 1.4 and 0.15 mol·kg⁻¹ for [Bpy][Br] in aqueous solutions at 298.15 K respectively.

The mean molal activity coefficient of the solute (γ_{\pm}) in binary aqueous solutions can be expressed in terms of osmotic coefficient using the equation [36]

$$\ln\gamma_{\pm} = (\phi - 1) + 2\int_{0}^{\sqrt{m}} \frac{(\phi - 1)}{\sqrt{m}} d\sqrt{m}$$
(17)

This equation can be processed as:

$$b-1 = \sum_{i=1}^{n} A_i m^{i/2}$$
 (From Eq. (15))

Substituting $m^{1/2} = x$

1

$$\phi - 1 = \sum_{i=1}^{n} A_i x^i.$$
(18)

Solving the right hand side integral of Eq. (17) and using Eq. (18), one can write [36]

$$n\gamma_{\pm} = \sum_{i=1}^{n} \frac{2+i}{i} A_i m^{i/2}.$$
(19)

The mean molal activity coefficient (γ_{\pm}) values are calculated using Eq. (19) and the data are collected in the Table 3. The variation of ln γ_{\pm} as a function of square root of ionic liquid concentration is shown in Fig. 7. The calculation details can be obtained from our earlier reported studies [41–44].

Table 3

Molality (*m*), mole fraction (x_2), osmotic coefficient (ϕ), water activity (a_w), solvent activity coefficient (γ_1), activity coefficient (γ_{\pm}), free energy change due to mixing (ΔG_m) and excess Gibbs free energy change (ΔG^E) data for aqueous solutions of [Bpy][Br] at 298.15 K.

$m/mol \cdot kg^{-1}$	<i>x</i> ₂	ϕ^a	a _w ^b	γ^b_1	γ_{\pm}	$\Delta G_m^d/J \cdot mol^{-1}$	$\Delta G^{Ed}/J \cdot mol^{-1}$
0.00000	0.00000	1.0000	1.0000	1.0000	1.0000	0.00	0.00
0.01984	0.00071	0.9772	0.9993	1.0000	0.9093	- 14.72	-0.13
0.02735	0.00098	0.9759	0.9990	1.0000	0.9014	- 19.53	-0.39
0.04333	0.00156	0.9726	0.9985	1.0000	0.8879	-29.19	-0.70
0.05223	0.00188	0.9702	0.9982	1.0000	0.8811	-34.32	-0.89
0.06294	0.00226	0.9667	0.9978	1.0001	0.8729	-40.33	-1.14
0.07738	0.00278	0.9611	0.9973	1.0001	0.8616	-48.19	-1.50
0.09862	0.00354	0.9513	0.9966	1.0002	0.8442	- 59.33	-2.09
0.12224	0.00438	0.9387	0.9959	1.0003	0.8239	-71.28	-2.83
0.16454	0.00589	0.9140	0.9946	1.0005	0.7867	-91.77	-4.41
0.23438	0.00837	0.8738	0.9926	1.0010	0.7280	- 123.82	-7.76
0.31217	0.00111	0.8363	0.9906	1.0018	0.6727	- 157.71	-12.52
0.39501	0.00140	0.8037	0.9886	1.0027	0.6242	- 192.26	-18.64

a) The uncertainty in ϕ values at the lowest concentration is of the order $\pm 1 \cdot 10^{-3}$.

b) The uncertainty in the water activity (a_w) and solvent activity coefficient (γ_1) are of the order of $\pm 1 \cdot 10^{-4}$.

c) The mean ionic activity coefficient (γ_{\pm}) of the [Bpy][Br] at the lowest concentration studied are accurate up to $\pm 1 \cdot 10^{-3}$.

d) The errors in ΔG_m and ΔG^E are estimated to be of the order of $\pm 0.05 \text{ }\text{J} \cdot \text{mol}^{-1}$.

The activity coefficient data which have been converted to mole fraction scale and were used to calculate the Gibbs free energy change due to mixing (ΔG_m) and excess Gibbs free energy change (ΔG^E) of binary aqueous drug solutions at 298.15 K using equations

$$\Delta G_m = RT \sum_{i=1}^{2} x_i \ln a_i \tag{20}$$

$$\Delta G^{E} = RT \sum_{i=1}^{2} x_{i} \ln \gamma_{i}$$
(21)

where x_i , a_i and γ_i are the mole fraction, activity and activity coefficient of *i*th component.

The values for ΔG_m and ΔG^E parameters are collected in Table 3. The variation of ΔG_m and ΔG^E as a function of square root of ionic liquid concentration is shown in Fig. 8. The corrections to $\ln \gamma_{\pm}$, ΔG_m and ΔG^E data due to hydrolysis in low concentration region are assumed to be negligible.

Taking into the account the hydration effect, the mean molal activity coefficient γ_{\pm} for aqueous 1:1 electrolyte solutions then can be expressed as [30,36]

$$\log \gamma_{\pm} = -\frac{A_{\gamma}\sqrt{m}}{1+0.3286a\sqrt{m}} - \frac{h}{v}\log a_{w} - \log[1-0.018 \ (h-v)m]$$
(22)



Fig. 5. Variation of experimental osmotic coefficient (ϕ) as a function of square root of molality of ionic salt in aqueous ionic salt solutions at 298.15 K: $-\Phi-\Phi-$, [Bpy][Br]; - - -, Debye–Hückel limiting law.

where, a is the distance of the closest approach of oppositely charged ions and h is the hydration number of the electrolyte.

Our attempt to obtain hydration number values were hampered by the difficulty in choosing the value of *a*, the distance of the closest approach of oppositely charged ions. The standard value of 3.6 Å for closest ion approach yields a value of 5.4 for hydration number; however this does not reproduce the activity coefficient data, meaning in addition to ion–solvent interaction, other types of interactions i.e. hydrophobic cation–cation, stacking micellar type all are contributing to the deviation from Debye–Hückel limiting law for 1:1 electrolyte.

4. Discussion

4.1. Volumetric properties

It is observed from Table 1 and Fig. 3 that the apparent molar volume (ϕ_V) of [Bpy][Br] in aqueous solutions decreases as concentration of salt increases. The value of limiting partial molar volumes (\overline{V}_2^0) is found to be 162.03 \cdot 10³ mm³·mol⁻¹. The deviation parameter (B_V) is negative $(-11.64 \cdot 10^3 \text{ mm}^6 \cdot \text{mol}^{-2})$ for [Bpy][Br]. In general for structure making ions, B_V is negative due to overlap of cosphere effect. The calculations of partial molar volumes of solute and solvent $(\overline{V}_2 \text{ and } \overline{V}_1)$ respectively have been made and are reported in Table 1. The aggregation number (n) and critical micelle concentration (cmc) are found to be 6 and 0.17 mol·kg⁻¹ respectively for the studied ionic liquid by applying pseudo-phase separation model to ϕ_V data (Fig. 4). The negative values of the slope of $\overline{V}_2 - 2.802\sqrt{c}$ against concentration $(c \text{ in mol·dm}^{-3})$, suggest solute–solute (solvent induced)

Coefficients A_i in Eq. (15).
A_1	-0.3927
A_2	2.5709
A ₃	-7.1211
A4	2.9719
A ₅	3.8835
A ₆	1.3611
A ₇	-0.8042
A ₈	-1.8019
A ₉	-1.9113
A ₁₀	-1.5594
A_{11}^{a}	-1.0505

^a We stopped up to the coefficient A_{11} , since the experimental data gets well fitted within the experimental uncertainties and requires no higher order terms.



Fig. 6. Variation of experimental osmotic coefficient (ϕ) as a function of reciprocal of molality (1/*m*) of [Bpy][Br] in aqueous [Bpy][Br] solutions at 298.15 K.

interactions as has been observed for aqueous solutions of tetraalkylammonium halides [45].

The apparent molar volume behavior for various substituents on pyridine ring and substituents on nitrogen up to methyl group has been reported [21,22] and discussed in terms of electrostriction and water structure breaking properties of pyridinium salt. However, in present case of n-butyl group substitution on charged nitrogen centers, the volumetric behavior indicates negative magnitude for the limiting slope after Debye-Hückel correction meaning that the salt exerts a water structure making effect in solution. This is also similar to the volume behavior exhibited by 1-ethyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium chloride salts in water [10]. These salt ions have a very small hydration number and hence exhibit cation-cation interaction (hydrophobic in solution). The pyridinium salt is having four water molecules in its hydration sphere, still exhibit cation-cation (solvent induced) interaction, probably through the mechanism of solvent shared ion-pair formation [46].

4.2. Osmotic and activity coefficient

It is observed from Fig. 5 that the osmotic coefficient (ϕ) for aqueous [Bpy][Br] solutions, decreases as a function of the square root of concentration and ϕ data show the positive deviation from Debye–Hückel limiting law. We applied the pseudo-phase separation model to ϕ data. The ϕ varies linearly in lower concentration region and after a certain concentration shows a break with increase in concentration and the values of *n* and *cmc* are found to be 1.4 and 0.15 mol·kg⁻¹



Fig. 7. Variation of the mean activity coefficient of a ionic salt $(\ln \gamma_{\pm})$ as a function of square root of molality of ionic salt in aqueous ionic salt solutions at 298.15 K: $-\bullet-\bullet$, [Bpy][Br]; - - , Debye–Hückel limiting law.

respectively for the ionic liquid (Fig. 6). We note that the extrapolation at 1/m = 0 is difficult because of limited number of measurements in high concentration region. However, we are certain that, the *n* value signifies the formation of dimeric as well higher order aggregates in these solutions. Thus, the solution behavior is similar to that of systems exhibiting micellar type equilibria.

The variation of mean molal activity coefficient γ_{\pm} with concentration is shown in Fig. 7 and which shows the similar effect observed in the variation of ϕ data. The nature of the curve is similar to the variation observed in aqueous solutions of cationic surfactant solutions [38,47].

It is observed that the Gibbs free energy change due to mixing (ΔG_m) and excess Gibbs free energy change (ΔG^E) are negative over the studied concentration range. The ΔG_m and ΔG^E values decrease with increase in concentration of ionic liquid (Fig. 8). The excess free energy change values are small negative meaning in the solution process excess entropies are importantly contributing. However, due to the absence of excess enthalpy data, we could not able to do calculations of excess entropies.

4.3. Application of the McMillan-Mayer theory

An application of McMillan–Mayer theory of solutions to aqueous electrolytic solutions yields information about relative non-electrolytic contribution to the solute–solvent and solute–solute interactions. In dilute solutions of up to 0.1 mol·kg⁻¹, if the Debye–Hückel electrostatic contribution is subtracted from the thermodynamic parameter, i.e. from ln γ_{\pm} , then the remainder will be linear in the molality, similar to what is being observed for aqueous non-electrolyte solutions [48].

The mean molal activity coefficient of the solute (γ_{\pm}) in dilute concentration range can be represented as

$$\ln \gamma_{\pm} = -\alpha m^{1/2} \left(1 + b m^{1/2} \right)^{-1} + \omega m$$
(23)

where $\alpha = 1.173 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ at 25 °C and $b = 1.0 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ and ω is non-electrolyte solute–solute interaction parameter.

According to McMillan-Mayer [49],

$$\frac{\pi}{kT} = n + B_{22}^* n^2 + B_{222}^* n^3 + \dots$$
(24)

where *n* is number density of the solute and B_{22}^{*} and B_{222}^{*} are the osmotic second and third virial coefficients for solute–solute interaction.



Fig. 8. Variation of Gibbs free energy change due to mixing (ΔG_m) and excess Gibbs free energy change (ΔG^E) of ionic salt as a function of square root of molality of [Bpy][Br] in aqueous [Bpy][Br] solutions at 298.15 K: $-\blacksquare -\blacksquare -, \Delta G_m$: $\blacktriangle -\blacktriangle - \Delta G^E$.

The total Gibbs free energy of solution can be expressed as a function of mole ratio \overline{m} (ratio of moles of solute to solvent) using the equation

$$\frac{G}{n_1 k \mathrm{T}} = \frac{\mu_1^0}{k \mathrm{T}} + \frac{\mu_2^0}{k \mathrm{T}} \overline{m} - \overline{m} + \overline{m} \ln \overline{m} + \frac{1}{2} A_{22} \overline{m}^2 + \frac{1}{3} B_{222} \overline{m}^3 + \dots$$
(25)

where μ_1^0 and μ_2^0 are the chemical potential of pure solvent and solute respectively, whereas A_{22} and B_{222} are the pair and triplet interaction term for solute particles.

Hill [50,51] has shown that the coefficient A_{22} in the free energy expression (Eq. (25)), may be related to the coefficient B_{22}^{*} through the relation

$$A_{22}v_1^0 = 2B_{22}^{*0} - \overline{v}_2^0 + b_{11}^0 \tag{26}$$

where v_1^0 and \overline{v}_2^0 are the molecular volume of the pure solvent and partial molecular volume of the solute at infinite dilution respectively and $b_{11}^0 = (-B_{11}^{*0})$ is the solute–solvent cluster integral. The solute–solvent cluster integral b_{11}^0 is related to the partial molecular volume of the solute at infinite dilution by [52]

$$b_{11}^0 = -\overline{\nu}_2^0 + kT\kappa_T \tag{27}$$

where k is the Boltzmann constant, T is the absolute temperature, and κ_T is the isothermal compressibility coefficient for the pure solvent.

For a 1:1 electrolyte [48],

$$2\ln\gamma_2^* = A_{22}\overline{m} + B_{222}\overline{m}^2 \tag{28}$$

where γ_2^* is the nonelectrolyte contribution to the solute mean molal activity coefficient.

From Eqs. (23) and (28), $\omega = (A_{22} \cdot M_1) / 2$ (where M_1 is molar mass of solvent in kg·mol⁻¹).

Thus from Eqs. (26) and (27)

$$NB_{22}^{*0} = \frac{A_{22}V_1^0}{2} + \overline{V}_2^0 - \frac{RTk_T}{2}$$
(29)

where *N* is the Avogadro constant.

Using the Eq. (29), the value of solute–solute (osmotic second) virial coefficient (NB_{22}^{*0}) has been calculated for the studied ionic salt in aqueous solutions at 298.15 K and reported in Table 5 along with the corresponding values of ω and A_{22} . The NB_{22}^{*0} value (which is a measure of the solute cation–solute cation interactions) is large negative.

The value of solute–solvent (NB_{11}^{*0}) virial coefficient obtained using the McMillan–Mayer theory is also given in Table 5. We calculate the NB_{11}^{*0} value as $161 \cdot 10^3 \text{ mm}^3 \cdot \text{mol}^{-1}$ which is similar to that of ϕ_V^0 .

4.4. Application of the Pitzer model

According to the Pitzer model [53–55] the osmotic coefficient for 1:1 electrolyte can be expressed as

$$\phi - 1 = f^{\phi} + mB^{\phi} + m^2 C^{\phi} \tag{30}$$

where

$$f^{\phi} = -\frac{A_{\phi}\sqrt{l}}{1+b\sqrt{l}}.$$
(31)

Here, A_{ϕ} is the Debye–Hückel constant for the osmotic coefficient which is equal to 0.3927 for aqueous solutions at 298.15 K, b is an adjustable parameter having a value of 1.2 kg^{1/2}·mol^{-1/2}, and I = $[(1/2)\sum m_i \cdot z_i^2]$ is the ionic strength of solution. B^{ϕ} and C^{ϕ} are the second virial and third virial type coefficients for the osmotic coefficient.

The coefficient B^{ϕ} depends on concentration and is generally expressed as

$$B^{\phi} = \beta^{(0)} + \beta^{(1)} e^{-\alpha \sqrt{I}}$$
(32)

 $\beta^{(0)}$ and $\beta^{(1)}$ are the Pitzer ion interaction parameters, whereas α is the adjustable parameter having a value of 2.0 kg^{1/2}·mol^{-1/2}. With the help of the nonlinear least-squares fit method, the experimental osmotic coefficient data have been fitted using Eqs. (31)–(33) to obtain the Pitzer ion interaction parameters $\beta^{(0)}$ and $\beta^{(1)}$. The values obtained for $\beta^{(0)}$ and $\beta^{(1)}$ are included in Table 5. The standard deviation in osmotic coefficient obtained from the least-squares fit is also given in the last column of Table 5 and is calculated using the equation

$$\sigma(\phi) = \left[\frac{\sum \left(\phi^{\exp} - \phi^{\operatorname{cal}}\right)^2}{n - m}\right]^{1/2}.$$
(33)

We observe from Table 5 that when $\beta^{(0)}$ and $\beta^{(1)}$ values are compared with those reported by Pitzer and Mayorga [53] for 1:1 electrolytes, these are highly negative and highly positive for $\beta^{(0)}$ and $\beta^{(1)}$ respectively while the C^{ϕ} coefficient is also high. The positive value of 1.9639 for the parameter C^{ϕ} implies that there is a contribution to ln γ_{\pm} because of third virial coefficient. Thus, our interpretation of the presence of multiple cation–cation interaction equilibria is being supported. It is pleasing that these observations based upon the application of Pitzer approach are in close agreement with the results discussed earlier based on the application of MacMillan–Mayer theory. The ' ω ' parameter is negative and closely agrees with $\beta^{(0)}$. While the osmotic second virial coefficient NB_{22}^{*0} in solution is negative implying affinity between the solute–solute i.e. cation–cation interaction as well as having some additional cation–anion–cation affinity contribution in the form of third virial coefficient.

Earlier, we discussed the activity coefficient profiles as a function of concentration for few ionic liquids (imidazolium salts) in water [11]. We noted therein that the concentration dependence can be accounted for in terms of hydrophobic hydration of the ions similar to that of aqueous solutions of tetra-alkylammonium salts. The limiting properties however indicate a resemblance with aqueous solutions of simple alkali halide. We observe the similar type of interactions in water due to addition of ionic pyridyl salt.

When we compare the osmotic coefficient (ϕ) and mean molal activity coefficient (γ_{\pm}) behavior of studied pyridinium salt ions with imidazolium salt ions [10], it is noted that the former exhibits positive deviations from Debye–Hückel limiting law for both ϕ and γ_{\pm} as a function of concentration. In case of imidazolium salt ions, the Debye–Hückel limiting law is obeyed up to ~0.05 mol·kg⁻¹ and

Table 5

Nonelectrolyte solute–solute interaction parameter (ω), pair interaction terms for solute particles (A_{22}), solute–solute (osmotic second) virial coefficients (NB_{22}^{*0}) and solute–solvent virial coefficient (NB_{11}^{*0}) and Pitzer interactions parameters for [Bpy][Br] in aqueous solutions at 298.15 K.

$\omega/\text{kg}\cdot\text{mol}^{-1}$	A ₂₂	$10^3 \cdot NB_{22}^{*0}/mm^3 \cdot mol^{-1}$	$10^3 \cdot NB_{11}^*0/mm^3 \cdot mol^{-1}$	$\beta^{(0)}/\mathrm{kg}\!\cdot\mathrm{mol}^{-1}$	$\beta^{(1)}/\mathrm{kg}\cdot\mathrm{mol}^{-1}$	$\sigma(\phi)$
-2.09	-232.03	- 1935	161	-2.2085	4.5462	0.0008

thereafter the negative deviation from the limiting law for γ_{+} and positive deviation for ϕ has been observed. We feel that these are the important differences between hydration and hydrophobic effects exhibited by imidazolium and pyridinium salt ions. The positive deviation from the limiting law and negative virial coefficient observed for the studied salt indicates the aggregation (with limited number of solute molecule), similar to that of small sized micellar systems probably exhibiting stacking type equilibria in solution phase. The application of Pitzer model to the solution of pyridinium salt ions shows highly negative and highly positive $\beta^{(0)}$ and $\beta^{(1)}$ coefficients which suggest the predominance of cation-cation (hydrophobic interaction) in water resulting in the exhibition of positive deviation from Debye-Hückel limiting law for γ_{\pm} . The recent work on amino-acid ionic liquids in water revealed that $\beta^{(0)}$ and $\beta^{(1)}$ coefficients are having small positive and negative magnitudes respectively suggesting the presence of effects due to ionsolvent interactions along with solute-solute association [56].

The role of ion-aggregate formation in the calculation of physical properties of electrolyte solutions especially in water can be monitored by conductance, activity coefficient studies. The concept of aggregation cannot be studied with ease in non-aqueous solvent systems because of the low dielectric constants of the solvent. Still, in solvents of moderate dielectric constant (alcohols), the ionic properties have been probed with precise conductance, dielectric and vapor pressure techniques [57,58]. Also, now the theoretical avenues have been opened-up by making use of chemical models based on pair distribution functions (which include long and short-range interaction forces). The moderate to high concentration properties of aqueous as well as mixed aqueous and non-aqueous solutions of electrolytes can be analyzed by applying the Mean Spherical Approximation (MSA), the MSA-Mass Action Law (MAL) and the Associative MSA (AMSA) models permitting one to access to systems with ion aggregation and micellar equilibria [59–61]. In the present work, the inability to assess the closet distance parameter correctly and the knowledge about association constant, precluded us to apply mass action model to the activity data at different concentrations of [Bpy][Br] solutions in water. There is a need to study more systems of such type in aqueous solutions.

5. Conclusions

The apparent and partial molar volumes of [Bpy][Br] in aqueous solutions as a function of concentration at 298.15 K are studied. The osmotic coefficient behavior for aqueous [Bpy][Br] solutions is also reported. Osmotic coefficient data for the aqueous solution of ionic liquid molecule was used to study the variation of activity coefficient of the ionic liquid molecule. The cmc value of [Bpy][Br] obtained using volume data indicates the presence of solute-solute interactions in the form of multiple equilibria involving few cations and may be viewed as small sized micelle. The pyridinium salts without substituents at nitrogen center are water structure breakers. However, we observe the water structure making effect from ϕ_V and \overline{V}_2 profiles because of the substitution of n-butyl group at the pyridine nitrogen center. The mean ionic activity coefficient variation indicates positive deviation from Debye-Hückel limiting law similar to that exhibited by sodium-salts of higher fatty acids in water [46]. The application of Pitzer model and McMillan-Mayer theory of solutions reveals that the second virial coefficient is negative and the interactions are governed by cation-cation, cation-anion-cation interactions involving multiple equilibria.

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References

- [1] T. Welton, Chemical Reviews 99 (1999) 2071-2083.
- [2] P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley VCH, Weinheim, Germany, 2003.
- [3] P. Wasserscheid, W. Keim, Angewandte Chemie International Edition 39 (2000) 3772–3789.
- [4] V.I. Parvulescu, C. Hardacre, Chemical Reviews 107 (2007) 2615-2665.
- [5] N.V. Plechkova, K.R. Seddon, Chemical Society Reviews 37 (2008) 123–150.
- [6] H. Weingärtner, C. Cabrele, C. Herrmann, Physical Chemistry Chemical Physics 14 (2012) 415–426.
- M.C. Buzzeo, R.G. Evans, R.G. Compton, ChemPhysChem 5 (2004) 1106–1120.
 S.N. Baker, T.M. McCleskey, S. Pandey, G.A. Baker, Chemical Communications (2004) 940–941
- [9] K.R. Seddon, A. Stark, M.J. Torres, Pure and Applied Chemistry 72 (2000) 2275–2287.
- [10] R.L. Gardas, D.H. Dagade, J.A.P. Coutinho, K.J. Patil, The Journal of Physical Chemistry. B 112 (2008) 3380–3389.
- [11] R.L. Gardas, D.H. Dagade, S.S. Terdale, J.A.P. Coutinho, K.J. Patil, The Journal of Chemical Thermodynamics 40 (2008) 695–701.
- [12] T. Inoue, H. Ebina, B. Dong, L. Zheng, Journal of Colloid and Interface Science 314 (2007) 236–241.
- [13] W. Liu, L. Cheng, Y. Zhang, H. Wang, M. Yu, Journal of Molecular Liquids 140 (2008) 68-72.
- [14] H.L. Chum, V.R. Koch, LL. Miller, R.A. Osteryoung, Journal of the American Chemical Society 97 (1975) 3264–3265.
- [15] J. Robinson, R.A. Osteryoung, Journal of the American Chemical Society 101 (1979) 232–327.
- [16] M.E.V. Valkenburg, R.L. Vaughn, M. Williams, J.S. Wilkes, Thermochimica Acta 425 (2005) 181–188.
- [17] A. Noda, K. Hayamizu, M. Watanabe, The Journal of Physical Chemistry. B 105 (2001) 4603–4610.
- [18] K. Kim, B.K. Shin, H. Lee, F. Ziegler, Fluid Phase Equilibria 218 (2004) 215–220.
- [19] M. Yoshizawa, W. Xu, C.A. Angell, Journal of the American Chemical Society 125 (2003) 15411–15419.
- [20] J.M. Crosthwaite, M.L. Muldoon, J.K. Dixon, J.L. Anderson, J.F. Brennecke, The Journal of Chemical Thermodynamics 37 (2005) 559–568.
- [21] B.E. Conway, L.H. Laliberte, in: A.K. Covington, P. Jones (Eds.), Hydrogen Bonded Solvent Systems, Taylor and Francis Ltd., London, 1968.
- [22] L.H. Laliberte, B.E. Conway, Journal of Physical Chemistry 74 (1970) 4116–4125.
 [23] G.C. Kresheck, in: F. Franks (Ed.), Water–A Comprehensive Treatise, vol. IV,
- Plenum Press, New York, 1974. [24] G.R. Gupta, G.R. Chaudhari, P.A. Tomar, G.P. Waghulade, K.J. Patil, Asian Journal of
- Chemistry 24 (2012) 4675–4678. [25] G. Gupta, G. Chaudhari, P. Tomar, Y. Gaikwad, R. Azad, G. Pandya, G. Waghulade,
- K. Patil, European Journal of Chemistry 3 (2012) 475–479. [26] G. Gupta, G. Chaudhari, P. Tomar, Y. Gaikwad, R. Azad, G. Pandya, G. Waghulde, K.
- Patil, Asian Journal of Chemistry 25 (2013), (in press). [27] V.R. Shaikh, D.H. Dagade, D.G. Hundiwale, K.J. Patil, Journal of Molecular Liquids
- 164 (2011) 239–242. [28] J.L. Fortier, P.A. Leduce, J.E. Desnoyers, Journal of Solution Chemistry 3 (1974)
- 323–349.
 [29] F.J. Millero, in: R.A. Horne (Ed.), Water and Aqueous Solutions, Structure, Thermodynamics and Transport Processes, Wiley-Interscience, New York, 1972.
- [30] R.A. Robinson, R.H. Stokes, Electrolyte Solutions, second ed. Butterworths, London, 1959.
- [31] K. Patil, R. Pawar, D. Dagade, Journal of Physical Chemistry A 106 (2002) 9606–9611.
- [32] D.H. Dagade, K.J. Patil, Fluid Phase Equilibria 231 (2005) 44–52.
- [33] D.N. Kurhe, D.H. Dagade, J.P. Jadhav, S.P. Govindwar, K.J. Patil, Journal of Solution Chemistry 40 (2011) 1596–1617.
- [34] S. Glasstone, An Introduction to Electrochemistry, Litton Educational Publishing, Inc., 1942
- [35] O. Redlich, D.M. Meyer, Chemical Reviews 64 (1964) 221-227.
- [36] H.S. Harned, B.B. Owen, The Physical Chemistry of Electrolytic Solutions, third ed. Reinhold Publishing Corporation, New York, 1958.
- [37] E. Vikingstad, A. Skauge, H. Hoiland, Journal of Colloid and Interface Science 72 (1979) 59–67.
- [38] P. Taboada, D. Attwood, J.M. Ruso, M. Garcia, V. Mosquera, Langmuir 17 (2001) 173-177.
- [39] J.E. Desnoyers, G. Caron, R. Delisi, D. Roberts, A. Roux, G. Perron, Journal of Physical Chemistry 87 (1983) 1397–1406.
- [40] R. Coudert, S.M. Hajji, A. Cao, Journal of Colloid and Interface Science 155 (1993) 173–182.
- [41] V.R. Shaikh, D.H. Dagade, S.S. Terdale, D.G. Hundiwale, K.J. Patil, Journal of Chemical & Engineering Data 57 (2012) 3114–3122.
- [42] P.A. Tomar, R.R. Kolhapurkar, D.H. Dagade, K.J. Patil, Journal of Solution Chemistry 36 (2007) 193–209.
- [43] R.R. Kumbhar, D.H. Dagade, S.S. Terdale, K.J. Patil, Journal of Solution Chemistry 36 (2007) 259–273.
- [44] S. Terdale, D. Dagade, K. Patil, Journal of Chemical & Engineering Data 54 (2009) 294–300.

- [45] W.Y. Wen, S. Saito, Journal of Physical Chemistry 68 (1964) 2639–2644.
- [46] R.M. Diamond, Journal of Physical Chemistry 67 (1963) 2513–2517.
- [40] I.M. Durchfield, E.M. Woolley, Journal of Physical Chemistry 88 (1984) 2149–2155.
 [48] T.M. Harrington, E.L. Mole, Journal of the Chemical Society, Faraday Transactions I 78 (1982) 2095–2100.
- [49] W. McMillan, J. Mayer, Journal of Chemical Physics 13 (1945) 276–305.
- [50] T.L. Hill, Journal of the American Chemical Society 79 (1957) 4885–4890.
- [51] T.L. Hill, Journal of Chemical Physics 30 (1959) 93–97.
- [51] J.E. Garrod, T.M. Harrington, Journal of Physical Chemistry 74 (1970) 363–370.
 [53] K.S. Pitzer, G. Mayorga, Journal of Physical Chemistry 77 (1973) 2300–2308.
- [54] R.M. Pytkowicz, Activity Coefficients in Electrolyte Solutions, CRC Press, Boca Raton, FL, 1979.
- [55] K.S. Pitzer, Journal of Physical Chemistry 77 (1973) 268–277.

- [56] D.H. Dagade, K.R. Madkar, S.P. Shinde, S.S. Barge, The Journal of Physical Chemistry. B 117 (2013) 1031–1043.
- [57] J. Barthel, R. Neueder, G. Lauermann, Journal of Solution Chemistry 14 (1985) 621-633.
- [58] J. Barthel, G. Lauermann, R. Neueder, Journal of Solution Chemistry 15 (1986) 851-867.
- [59] J. Barthel, H. Krienke, R. Neueder, M.F. Holovko, Fluid Phase Equilibria 194–197 (2002) 107–122.
- [60] J.E. Desnoyers, R. DeLisi, G. Perron, Pure and Applied Chemistry 52 (1980) 433-444.
- [61] D. Attwood, P. Fletcher, E. Boitard, J.P. Dubes, H. Tachoire, Journal of Physical Chemistry 91 (1987) 2970–2975.