

## Densimetric, acoustic and viscometric behaviour of sucrose solutions in aqueous 1-butyl-3-methylimidazolium hexafluorophosphate at different temperatures and ambient pressure

Tanu Sharma, Taniya Sharma, Ashwani Kumar & Rajinder K Bamezai\*

Department of Chemistry, University of Jammu, Jammu 180 006, India

Email: rkb10@rediffmail.com

Received 15 January 2019; revised and accepted 20 December 2019

The thermophysical properties like density, speed of sound and viscosity have been measured for different molalities of sucrose in aqueous and different concentrations of aqueous solutions of an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, at different temperatures and atmospheric pressure. The results are explained in terms of acoustic parameters like apparent molar volume, apparent molar isentropic compressibility, limiting apparent molar volume, limiting apparent molar isentropic compressibility, limiting apparent molar transfer volume, limiting apparent molar transfer compressibility, hydration number, etc. Further, pair and triplet interaction coefficients, solvation number, viscosity *B*-coefficients and activation parameters have also been evaluated. The results demonstrate that solute-solvent interactions exist in the ternary system which increases with an increase in ionic liquid concentration.

**Keywords:** 1-Butyl-3-methylimidazolium hexafluorophosphate, Sucrose, Apparent molar volume, Transport properties

Ionic liquids (ILs), formed by the combination of positive and negative ions, are molten salts with melting point less than 100 °C. The ordinary salts like sodium chloride, potassium chloride, etc. need some solvent to dissociate into respective ions, whereas ILs are self dissociated and hence do not need a solvent to dissociate into cations and anions. Ionic liquids are fast emerging as a field of interest for the researchers. Its wide applicability in numerous fields has proved it as a 'solvent of choice' for research purposes<sup>1-3</sup>. Being non-volatile in nature, ILs are best suited for room temperature experiments. Compatibility of ILs with different type of ions makes them suitable for various combinations and hence can be subjected to create a number of possibilities by even a small change in their anionic as well as cationic part. The most extensively studied class of ILs is based on imidazolium cation. Since the use of imidazolium based IL for the dissolution of cellulose by Swatoski *et al.*,<sup>4</sup> a great interest has been shown for the use of ILs, especially imidazolium based ILs, for the biomass dissolution and conversion of biomass to biocompatible or biodegradable materials<sup>5-8</sup>.

Biomacromolecules which constitute an essential class of compounds, such as proteins, glycolipids, nucleic acids, etc., are largely made up of

carbohydrates (saccharides). Of all these biomacromolecules, saccharides are widely distributed in various forms of life as essential moieties. Their solution properties are of considerable interest for the various aspects of basic research and in many applications as well. In order to understand the effect of ILs on biomacromolecule dissolution, studies have been conducted on low molecular weight saccharides<sup>9,10</sup>.

The application of ILs in carbohydrate chemistry can bring about new methodologies and enhanced procedures for solution processing of lignocellulosic materials (carbohydrate polymers and an aromatic polymer). The solution properties of saccharides in general and sucrose in particular in some ionic liquids have been reported in the literature. Jin and Chen<sup>11</sup> reported volumetric properties of (1-allyl-3-methylimidazolium chloride + sucrose + water) solutions. The volumetric and conductivities of (1-butyl-3-methylimidazolium tetrafluoroborate + sucrose + water) solutions have been studied by Wu *et al.*<sup>12</sup> The influence of imidazolium based ionic liquid on the thermodynamic properties of aqueous sucrose solutions at different temperatures was also investigated by Zafarani-Moattar *et al.*<sup>13</sup>.

The thermophysical and spectroscopic studies of titled IL, 1-butyl-3-methylimidazolium hexafluorophosphate

[BMIM][PF<sub>6</sub>], and its binary formulations with Triton X-45 and Triton X-100 over the entire composition range at different temperatures were studied by Chaudhary *et al.*<sup>14</sup>. The excess thermodynamic and deviation parameters along with spectroscopic properties were analyzed to understand the interaction behaviour. Prior to it, the density behaviour of [BMIM][PF<sub>6</sub>] in aqueous medium was analyzed by Ali *et al.*,<sup>15</sup> Jacquemin *et al.*,<sup>16</sup> and later by Wang *et al.*<sup>17</sup>. The thermodynamic and viscosity data of the likewise systems containing 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF<sub>6</sub>] have also been investigated by some authors<sup>17-21</sup>. However, there appears to be no report available about volumetric as well as compressibility in conjunction with transport properties of sucrose in aqueous solutions of ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate. Hence, in this work a combination of ternary, [BMIM][PF<sub>6</sub>]-sucrose-water system, has been undertaken, at temperatures ranging from 293.15 K to 313.15 K and atmospheric pressure (0.1009 MPa), to evaluate various thermodynamic parameters in understanding the nature of solute-solvent interactions in the system.

### Materials and Methods

1-Butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF<sub>6</sub>] and sucrose (SUC) were obtained from Sigma Aldrich. The reported mass fraction purity of 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF<sub>6</sub>] and sucrose (SUC) was found to be  $\geq 0.970$  and  $\geq 0.995$ , respectively. Prior to making the solutions, the samples were stored over P<sub>2</sub>O<sub>5</sub> in desiccator. No further purification was performed

before the analysis. Properties of materials used are mentioned in Table 1. The triply distilled deionized water with specific conductivity less than 1  $\mu\text{S cm}^{-1}$  at room temperature was used for preparation of solutions.

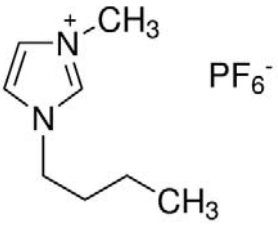
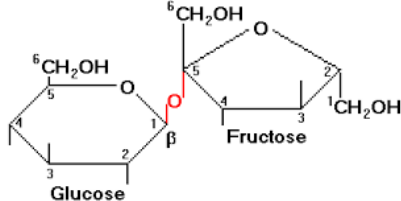
### Apparatus and methods

The aqueous solutions of IL (0.0105, 0.0303, 0.0496 and 0.0698) mol kg<sup>-1</sup> were used as a solvent to prepare SUC solutions of five different molal concentrations. An analytical balance (Mettler AE-240) with a precision of  $\pm 0.01$  mg was used to measure the mass. The water content of IL only was determined by Karl Fischer titration method. The mass fraction of water in [BMIM][PF<sub>6</sub>] was found to be 0.0028. The water content in the IL was considered for molality correction of the stock solution (water + IL).

The uncertainty in molality of solute was  $\pm 2.0 \times 10^{-5}$  mol kg<sup>-1</sup>, while in case of solvent it was  $\pm 1.0 \times 10^{-4}$  mol kg<sup>-1</sup>. All the solutions were prepared with precaution and stored in special air tight bottles to minimize evaporation and contamination. The density of solutions was measured using a vibrating tube densimeter (DMA 5000 M, Anton Paar) at temperatures, T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. The temperature was automatically controlled within  $\pm 1.0 \times 10^{-3}$  K by the Peltier technique built in the densimeter. The experimental uncertainty of density measurement was  $\pm 5.0 \times 10^{-3}$  kg m<sup>-3</sup>. The instrument was calibrated with doubly distilled, degassed and deionized water and dry air in frequent intervals of time.

The speed of sound of solutions was measured using a single-crystal variable-path multi-frequency ultrasonic interferometer (M-82, Mittal Enterprises,

Table 1 — Materials used

| Chemical name  | Source               | Molecular weight (g mol <sup>-1</sup> ) | Mass fraction purity | Structure   |
|--|----------------------|---|----------------------|---|
| 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF <sub>6</sub> ] | Sigma Aldrich, India | 284.18                                  | $\geq 0.970$         |  |
| Sucrose (SUC)  | Sigma Aldrich, India | 342.30                                  | $\geq 0.995$         |  |

India) having stainless steel sample cell (with a digital micrometer) with gold plating at its bottom operating at a frequency of 5 MHz. The uncertainty in speed of sound measurements was found to be  $0.1 \text{ ms}^{-1}$ . The viscosity measurements were carried out with a suspended level Ubbelohde type capillary viscometer, mounted in water thermostat (Model: TIC-4000 N, Thermotech, India) which was calibrated with triply distilled water at the studied temperatures. The viscometer containing the test liquid was allowed to stand for about 30 min in a thermostatic water bath so as to minimize the thermal fluctuations in viscometer. The flow rate of a constant volume of liquid through capillary was measured using an electronic stop watch with a resolution of 0.01 s. An average of at least four readings of flow time with variation not exceeding  $\pm 0.1 \text{ s}$  was taken for each solution. The uncertainty in viscosity measurements was  $\pm 1.0 \times 10^{-6} \text{ Pa s}$ . The temperature of thermostat bath was also maintained within  $\pm 0.01 \text{ K}$ . The same water bath was simultaneously used for speed of sound measurements.

## Results and Discussion

### Apparent molar volume and apparent molar isentropic compressibility

The influence of solute molecules on the solvent or vice versa forms the base of some important interaction parameters. The interaction of SUC (solute) in aqueous as well as aqueous solutions of [BMIM][PF<sub>6</sub>] (solvent) can be explained by the two important interaction parameters, apparent molar volume ( $V_\phi$ ) and apparent molar isentropic compressibility ( $K_{\phi,s}$ ). These parameters can be calculated from the experimental values of density and speed of sound by using the following equations:

$$V_\phi = (M/d) - [(d - d_o)/mdd_o] \quad \dots (1)$$

$$K_{\phi,s} = (MK_s/d) - [(K_s^o d - K_s d_o)/mdd_o] \quad \dots (2)$$

Where  $M$  is the molar mass and  $m$  is the molality of the solute,  $d_o$ ,  $K_s^o$  and  $d$ ,  $K_s$  are densities and isentropic compressibilities of solvent (water or water + IL) and solution (solute + water + IL), respectively. Further, the isentropic compressibility is evaluated by using the following relations:

$$K_s = 1/(u^2 d) \text{ or } K_s^o = 1/(u_o^2 d_o) \quad \dots (3)$$

Where  $u$  and  $u_o$  are speeds of sound of solution and solvent, respectively.

The density and speed of sound of SUC in aqueous as also in aqueous solutions of [BMIM][PF<sub>6</sub>] as a

function of concentration and temperature is reported in Table 2. It may be pointed out here that our concentrations and the concentrations reported in the literature are different. However, the values of density and speed of sound of sucrose in water for some specific concentrations are in good agreement with the reported ones<sup>22-24</sup>. In a similar manner, the density values for the combination between [BMIM][PF<sub>6</sub>] and water, and the viscosity data of the binary constituents also resemble to some extent in those concentrations which resemble to ours<sup>16-18,25</sup>. The experimental density and speed of sound values are used to evaluate  $V_\phi$  and  $K_{\phi,s}$ . The values of apparent molar volumes of SUC increase with rising temperature as well as concentration are shown in Supplementary Data, Table S1. In the ternary system, SUC + water + [BMIM][PF<sub>6</sub>], the apparent molar volumes of SUC increase for all weight percentages of IL. These increasing trends are in good agreement with the increasing interactions between solute and solvent. The values of  $K_{\phi,s}$  for SUC in water and in aqueous ionic liquid solution at  $T = (293.15 \text{ to } 313.15) \text{ K}$  are also listed in Supplementary Data, Table S1. A representative plot for apparent molar volume and apparent molar isentropic compressibility versus molality of SUC in aqueous and  $0.0303 \text{ mol kg}^{-1}$  aqueous IL solutions at different temperatures is shown in Figs 1 and 2, respectively.

### Limiting apparent molar volume and limiting apparent molar isentropic compressibility

Limiting apparent molar volume ( $V_\phi^o$ ) and limiting apparent molar isentropic compressibility ( $K_{\phi,s}^o$ ) at infinite dilutions are evaluated by least-squares fitting of the following relations:

$$V_\phi = V_\phi^o + S_v m \quad \dots (4)$$

$$K_{\phi,s} = K_{\phi,s}^o + S_k m \quad \dots (5)$$

Where  $S_v$  and  $S_k$  represent respective experimental slopes. The infinite dilution values for  $V_\phi^o$  of SUC in aqueous medium and its comparison with literatures value<sup>26</sup> is given in Table 3. The usefulness of limiting apparent molar volume at infinite dilution lies in the fact that, at infinite dilution, the solute-solute interactions become negligible and the property provides information regarding solute-solvent interactions. The  $V_\phi^o$  values are positive and increase with an increase in concentration of SUC in aqueous and in aqueous solutions of [BMIM][PF<sub>6</sub>] as also with temperature, which indicate a strengthening of

Table 2 — Density ( $d$ ) and speed of sound ( $u$ ) for SUC in aqueous and aqueous solutions of [BMIM][PF<sub>6</sub>] at different temperatures and  $P = 0.1009$  MPa<sup>a</sup>

| $m/$<br>(mol kg <sup>-1</sup> )                            | $d \times 10^{-3}/$ (kg m <sup>-3</sup> ) |          |          |          |          | $u/$ (ms <sup>-1</sup> ) |          |          |          |          |
|--|---|----------|----------|----------|----------|--------------------------|----------|----------|----------|----------|
|  | 293.15 K                                  | 298.15 K | 303.15 K | 308.15 K | 313.15 K | 293.15 K                 | 298.15 K | 303.15 K | 308.15 K | 313.15 K |
| SUC + water  |   |          |          |          |          |                          |          |          |          |          |
| 0.00000  | 0.998205                                  | 0.997045 | 0.995652 | 0.994031 | 0.992213 | 1483.1                   | 1496.6   | 1510.8   | 1520.1   | 1528.2   |
| 0.00998  | 0.999540                                  | 0.998376 | 0.996975 | 0.995347 | 0.993522 | 1484.4                   | 1497.9   | 1512.1   | 1521.4   | 1529.5   |
| 0.02989  | 1.002165                                  | 1.000994 | 0.999571 | 0.997928 | 0.996091 | 1487.0                   | 1500.5   | 1514.7   | 1524.0   | 1532.1   |
| 0.04988  | 1.004755                                  | 1.003577 | 1.002128 | 1.000470 | 0.998623 | 1489.6                   | 1503.1   | 1517.4   | 1526.6   | 1534.7   |
| 0.06977  | 1.007299                                  | 1.006091 | 1.004632 | 1.002968 | 1.001077 | 1492.1                   | 1505.7   | 1520.0   | 1529.1   | 1537.3   |
| 0.08966  | 1.009783                                  | 1.008561 | 1.007079 | 1.005401 | 1.003469 | 1494.7                   | 1508.3   | 1522.6   | 1531.7   | 1539.9   |
| SUC + 0.0105 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ] |   |          |          |          |          |                          |          |          |          |          |
| 0.00000  | 0.999008                                  | 0.997647 | 0.996057 | 0.994761 | 0.993188 | 1484.5                   | 1497.1   | 1510.9   | 1520.4   | 1531.1   |
| 0.00997  | 1.000335                                  | 0.998967 | 0.997372 | 0.996070 | 0.994490 | 1485.8                   | 1498.4   | 1512.2   | 1521.7   | 1532.4   |
| 0.02991  | 1.002949                                  | 1.001565 | 0.999965 | 0.998645 | 0.997054 | 1488.4                   | 1501.0   | 1514.8   | 1524.3   | 1535.0   |
| 0.04993  | 1.005524                                  | 1.004123 | 1.002519 | 1.001179 | 0.999576 | 1491.0                   | 1503.6   | 1517.4   | 1526.9   | 1537.6   |
| 0.06989  | 1.008034                                  | 1.006614 | 1.005006 | 1.003645 | 1.002031 | 1493.6                   | 1506.2   | 1520.0   | 1529.5   | 1540.2   |
| 0.08966  | 1.010494                                  | 1.009048 | 1.007447 | 1.006039 | 1.004426 | 1496.2                   | 1508.7   | 1522.5   | 1532.1   | 1542.8   |
| SUC + 0.0303 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ] |   |          |          |          |          |                          |          |          |          |          |
| 0.00000  | 1.000054                                  | 0.998263 | 0.997123 | 0.995654 | 0.994091 | 1485.2                   | 1498.3   | 1511.2   | 1524.2   | 1534.3   |
| 0.00996  | 1.001371                                  | 0.999577 | 0.998431 | 0.996955 | 0.995386 | 1486.5                   | 1499.6   | 1512.5   | 1525.5   | 1535.6   |
| 0.02993  | 1.003972                                  | 1.002173 | 1.001014 | 0.999525 | 0.997945 | 1489.1                   | 1502.2   | 1515.1   | 1528.1   | 1538.2   |
| 0.04993  | 1.006528                                  | 1.004721 | 1.003548 | 1.002042 | 1.000451 | 1491.7                   | 1504.8   | 1517.7   | 1530.7   | 1540.8   |
| 0.06994  | 1.009032                                  | 1.007213 | 1.006031 | 1.004509 | 1.002903 | 1494.3                   | 1507.4   | 1520.3   | 1533.3   | 1543.4   |
| 0.08985  | 1.011456                                  | 1.009631 | 1.008470 | 1.006924 | 1.005289 | 1496.9                   | 1510.0   | 1522.8   | 1535.8   | 1546.0   |
| SUC + 0.0496 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ] |   |          |          |          |          |                          |          |          |          |          |
| 0.00000  | 1.001289                                  | 0.999254 | 0.998002 | 0.996763 | 0.995123 | 1486.3                   | 1499.5   | 1512.5   | 1525.6   | 1538.4   |
| 0.0998   | 1.002602                                  | 1.000561 | 0.999304 | 0.998058 | 0.996413 | 1487.6                   | 1500.8   | 1513.8   | 1526.9   | 1539.7   |
| 0.02995  | 1.005189                                  | 1.003138 | 1.001869 | 1.000617 | 0.998956 | 1490.2                   | 1503.4   | 1516.4   | 1529.5   | 1542.3   |
| 0.04996  | 1.007732                                  | 1.005661 | 1.004384 | 1.003123 | 1.001448 | 1492.8                   | 1506.0   | 1519.0   | 1532.1   | 1544.9   |
| 0.06993  | 1.010212                                  | 1.008127 | 1.006845 | 1.005563 | 1.003878 | 1495.4                   | 1508.6   | 1521.6   | 1534.7   | 1547.5   |
| 0.08982  | 1.012664                                  | 1.010547 | 1.009235 | 1.007937 | 1.006240 | 1498.0                   | 1511.2   | 1524.2   | 1537.3   | 1550.1   |
| SUC + 0.0698 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ] |   |          |          |          |          |                          |          |          |          |          |
| 0.00000  | 1.002378                                  | 1.001189 | 0.999238 | 0.997895 | 0.996269 | 1487.4                   | 1500.2   | 1513.5   | 1526.7   | 1539.3   |
| 0.00998  | 1.003682                                  | 1.002487 | 1.000531 | 0.999183 | 0.997551 | 1488.7                   | 1501.5   | 1514.8   | 1528.0   | 1540.6   |
| 0.02994  | 1.006257                                  | 1.005049 | 1.003086 | 1.001726 | 1.000082 | 1491.3                   | 1504.1   | 1517.4   | 1530.6   | 1543.2   |
| 0.04991  | 1.008786                                  | 1.007559 | 1.005584 | 1.004208 | 1.002553 | 1493.9                   | 1506.7   | 1520.0   | 1533.2   | 1545.8   |
| 0.06987  | 1.011256                                  | 1.010022 | 1.008032 | 1.006648 | 1.004978 | 1496.5                   | 1509.3   | 1522.6   | 1535.8   | 1548.4   |
| 0.08979  | 1.013667                                  | 1.012426 | 1.010399 | 1.009026 | 1.007323 | 1499.0                   | 1511.8   | 1525.2   | 1538.4   | 1551.0   |

<sup>a</sup>Standard uncertainties are:  $u(m) = \pm 2.0 \times 10^{-5}$  mol kg<sup>-1</sup>,  $u(d) = \pm 5.0 \times 10^{-3}$  kg m<sup>-3</sup>,  $u(T) = \pm 0.01$  K,  $u(P) = 0.0001$  MPa, and  $u(u) = \pm 0.5$  ms<sup>-1</sup>.  $m$  is the molality of SUC in per kg of water or (water + IL) mixture. Molality of IL in per kg of (water + IL) has a standard uncertainty of  $\pm 1.0 \times 10^{-4}$  mol kg<sup>-1</sup>.

attractive interactions between aqueous solutions of IL and SUC. On the other hand, the magnitude of  $K_{\phi,s}^0$  values for SUC in water and in aqueous solutions of IL are negative. The values decrease with concentration of SUC in water and in aqueous solutions of [BMIM][PF<sub>6</sub>], and also with temperature. This can be understood by the model proposed by

Kirkwood<sup>27</sup> which indicates a reduction in the electrostriction and as a result more water is released as the bulk water.

Limiting apparent molar transfer volume,  $\Delta_{tr}V_{\phi}^0$ , and limiting apparent molar transfer compressibility,  $\Delta_{tr}K_{\phi,s}^0$ , of SUC from water to aqueous solution of IL are evaluated using Eqns 6 and 7, respectively.

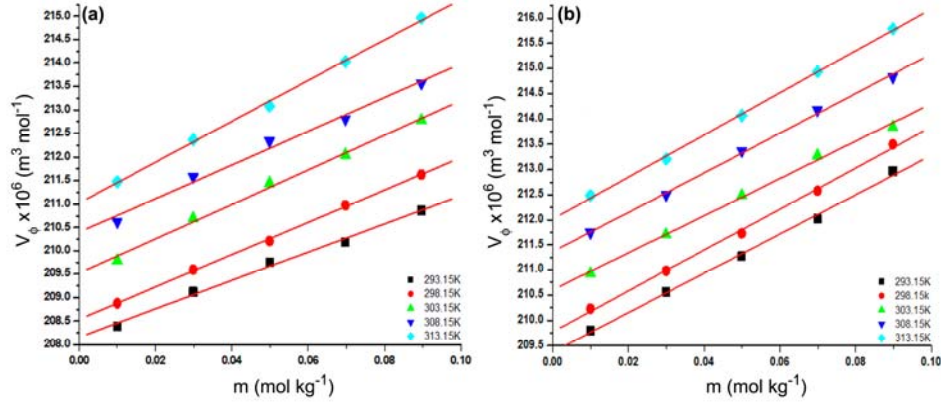


Fig. 1 — Plot of apparent molal volume versus molality as a function of temperature for SUC in (a) aqueous and (b) 0.0303 mol kg<sup>-1</sup> aqueous [BMIM][PF<sub>6</sub>] solutions.

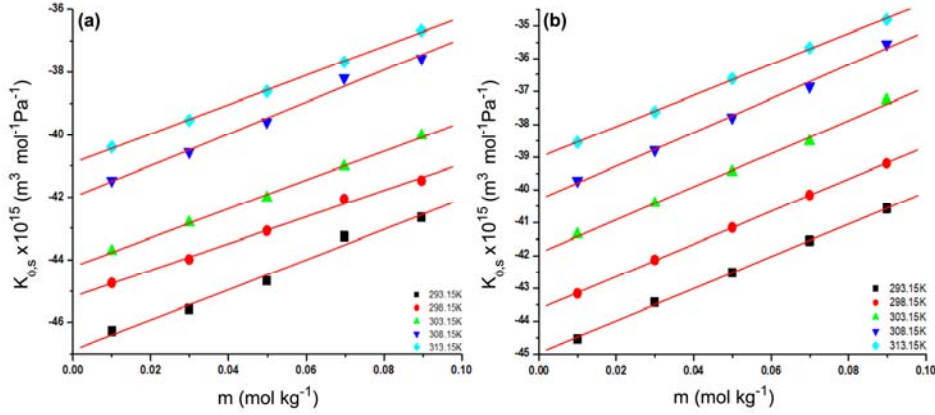


Fig. 2 — Plot of apparent molal compressibility versus molality for SUC in (a) aqueous and (b) 0.0303 mol kg<sup>-1</sup> aqueous [BMIM][PF<sub>6</sub>] solutions.

$$\Delta_{tr}V_{\phi}^0 = V_{\phi, aq [BMIM][PF_6]}^0 - V_{\phi, water}^0 \quad \dots (6)$$

$$\Delta_{tr}K_{\phi,s}^0 = K_{\phi,s, aq [BMIM][PF_6]}^0 - K_{\phi,s, water}^0 \quad \dots (7)$$

Where,  $V_{\phi, water}^0$  and  $K_{\phi,s, water}^0$  are limiting apparent molar volume and limiting apparent molar isentropic compressibility of SUC in water (Table 3).

The data indicates that  $V_{\phi}^0$  for SUC in aqueous solutions of [BMIM][PF<sub>6</sub>] is more than that in water, i.e.,  $\Delta_{tr}V_{\phi}^0$  values are positive and increase with increasing concentration of aqueous IL. Similarly, the magnitude of  $\Delta_{tr}K_{\phi,s}^0$  is found to be positive, which increase with cosolute concentration and temperature. When one molecule (solute) comes in the vicinity of another molecule (solvent), their outer spheres collide and hence considerable changes in the properties of solution thermodynamics take place. Such changes have been explained from time to time by many researchers<sup>28,29</sup>. The co-sphere model proposed by Gurney<sup>30</sup> and Desnoyers *et al.*,<sup>28</sup> is found to be more justified. According to this model, the interactions

between SUC and IL in ternary solutions can be classified into the following types: (a) hydrophilic - ionic interactions: between -OH, -O- and -C=O groups of SUC and ions of IL (b) hydrophobic - ionic interactions: between hydrophobic (alkyl) groups of SUC and ions of IL, (c) hydrophobic-hydrophobic interactions: between hydrophobic parts of SUC and IL, and (d) hydrophobic- hydrophilic interactions: between hydrophobic parts of IL and hydrophilic groups of SUC. There are competing interactions that result in both negative and positive contributions in transfer values. The interactions in types (b) to (d) are repulsive because the groups which interact are incompatible in their structural influence or their tendencies to orient water molecules, and hence favours for its negative transfer volume. On the other hand, the positive values of transfer ( $\Delta_{tr}V_{\phi}^0$  and  $\Delta_{tr}K_{\phi,s}^0$ ) arise as a result of the overlap of hydration co-spheres of hydrophilic sites and ionic species. In this work,

Table 3 — Limiting apparent molar volume ( $V_\phi^0$ ), slope ( $S_v$ ), transfer volume ( $\Delta_{tr}V_\phi^0$ ), limiting apparent molar isentropic compressibility ( $K_{\phi,s}^0$ ), slope ( $S_k$ ) and transfer compressibility ( $\Delta_{tr}K_{\phi,s}^0$ ) for SUC in aqueous and aqueous solutions of [BMIM][PF<sub>6</sub>] at different temperatures

| Property   | T/K                   |                       |                       |                       |                       |
|--|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|  | 293.15 K              | 298.15 K              | 303.15 K              | 308.15 K              | 313.15 K              |
| SUC + Water  |                       |                       |                       |                       |                       |
| $V_\phi^0 \times 10^6 / (\text{m}^3 \text{mol}^{-1})$                                  | 208.16 ( $\pm 0.08$ ) | 208.53 ( $\pm 0.03$ ) | 209.52 ( $\pm 0.09$ ) | 210.40 ( $\pm 0.13$ ) | 211.02 ( $\pm 0.07$ ) |
| $S_v \times 10^6 / (\text{m}^3 \text{mol}^{-2} \text{kg})$                             | 30.27 ( $\pm 1.34$ )  | 34.58 ( $\pm 0.58$ )  | 36.79 ( $\pm 1.53$ )  | 35.79 ( $\pm 2.32$ )  | 43.36 ( $\pm 1.24$ )  |
| $K_{\phi,s}^0 \times 10^{15} / (\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1})$            | -46.88 ( $\pm 0.07$ ) | -45.18 ( $\pm 0.10$ ) | -44.23 ( $\pm 0.07$ ) | -42.01 ( $\pm 0.17$ ) | -40.90 ( $\pm 0.05$ ) |
| $S_k \times 10^{15} / (\text{m}^3 \text{mol}^{-2} \text{Pa}^{-1} \text{kg})$           | 48.13 ( $\pm 2.94$ )  | 42.46 ( $\pm 1.82$ )  | 46.22 ( $\pm 1.17$ )  | 50.84 ( $\pm 2.89$ )  | 46.63 ( $\pm 0.83$ )  |
| SUC + 0.0105 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ]                             |                       |                       |                       |                       |                       |
| $V_\phi^0 \times 10^6 / (\text{m}^3 \text{mol}^{-1})$                                  | 208.68 ( $\pm 0.08$ ) | 209.46 ( $\pm 0.06$ ) | 210.10 ( $\pm 0.08$ ) | 210.74 ( $\pm 0.14$ ) | 211.59 ( $\pm 0.05$ ) |
| $S_v \times 10^6 / (\text{m}^3 \text{mol}^{-2} \text{kg})$                             | 36.27 ( $\pm 1.41$ )  | 39.33 ( $\pm 1.08$ )  | 35.17 ( $\pm 1.39$ )  | 42.78 ( $\pm 0.42$ )  | 40.23 ( $\pm 0.81$ )  |
| $\Delta_{tr}V_\phi^0 \times 10^6 / (\text{m}^3 \text{mol}^{-1})$                       | 0.52                  | 0.93                  | 0.58                  | 0.34                  | 0.57                  |
| $K_{\phi,s}^0 \times 10^{15} / (\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1})$            | -46.07 ( $\pm 0.07$ ) | -44.26 ( $\pm 0.09$ ) | -42.74 ( $\pm 0.08$ ) | -41.45 ( $\pm 0.13$ ) | -39.98 ( $\pm 0.11$ ) |
| $S_k \times 10^{15} / (\text{m}^3 \text{mol}^{-2} \text{Pa}^{-1} \text{kg})$           | 50.91 ( $\pm 1.82$ )  | 51.86 ( $\pm 1.53$ )  | 49.05 ( $\pm 1.50$ )  | 53.26 ( $\pm 2.21$ )  | 49.65 ( $\pm 1.88$ )  |
| $\Delta_{tr}K_{\phi,s}^0 \times 10^{15} / (\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1})$ | 0.81                  | 0.92                  | 1.49                  | 0.56                  | 0.92                  |
| SUC + 0.0303 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ]                             |                       |                       |                       |                       |                       |
| $V_\phi^0 \times 10^6 / (\text{m}^3 \text{mol}^{-1})$                                  | 209.37 ( $\pm 0.07$ ) | 209.77 ( $\pm 0.06$ ) | 210.60 ( $\pm 0.07$ ) | 211.37 ( $\pm 0.06$ ) | 212.02 ( $\pm 0.05$ ) |
| $S_v \times 10^6 / (\text{m}^3 \text{mol}^{-2} \text{kg})$                             | 39.09 ( $\pm 1.27$ )  | 40.74 ( $\pm 1.12$ )  | 36.99 ( $\pm 1.26$ )  | 39.19 ( $\pm 0.96$ )  | 41.64 ( $\pm 0.81$ )  |
| $\Delta_{tr}V_\phi^0 \times 10^6 / (\text{m}^3 \text{mol}^{-1})$                       | 1.21                  | 1.24                  | 1.08                  | 0.97                  | 1.00                  |
| $K_{\phi,s}^0 \times 10^{15} / (\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1})$            | -44.97 (0.05)         | -43.63 ( $\pm 0.02$ ) | -41.93 ( $\pm 0.09$ ) | -40.31 ( $\pm 0.12$ ) | -39.01 ( $\pm 0.04$ ) |
| $S_k \times 10^{15} / (\text{m}^3 \text{mol}^{-2} \text{Pa}^{-1} \text{kg})$           | 49.00 (0.88)          | 49.50 ( $\pm 0.31$ )  | 50.55 ( $\pm 1.73$ )  | 51.40 ( $\pm 2.02$ )  | 47.20 ( $\pm 0.64$ )  |
| $\Delta_{tr}K_{\phi,s}^0 \times 10^{15} / (\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1})$ | 1.91                  | 1.55                  | 2.30                  | 1.70                  | 1.89                  |
| SUC + 0.0496 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ]                             |                       |                       |                       |                       |                       |
| $V_\phi^0 \times 10^6 / (\text{m}^3 \text{mol}^{-1})$                                  | 210.02 ( $\pm 0.11$ ) | 210.73 ( $\pm 0.07$ ) | 211.32 ( $\pm 0.02$ ) | 211.96 ( $\pm 0.13$ ) | 212.68 ( $\pm 0.05$ ) |
| $S_v \times 10^6 / (\text{m}^3 \text{mol}^{-2} \text{kg})$                             | 35.86 ( $\pm 1.95$ )  | 39.72 ( $\pm 1.24$ )  | 40.77 ( $\pm 0.43$ )  | 41.47 ( $\pm 2.30$ )  | 42.72 ( $\pm 0.94$ )  |
| $\Delta_{tr}V_\phi^0 \times 10^6 / (\text{m}^3 \text{mol}^{-1})$                       | 1.86                  | 2.20                  | 1.80                  | 1.56                  | 1.66                  |
| $K_{\phi,s}^0 \times 10^{15} / (\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1})$            | -43.91 ( $\pm 0.08$ ) | -42.41 ( $\pm 0.13$ ) | -40.70 ( $\pm 0.03$ ) | -39.36 ( $\pm 0.05$ ) | -37.69 ( $\pm 0.02$ ) |
| $S_k \times 10^{15} / (\text{m}^3 \text{mol}^{-2} \text{Pa}^{-1} \text{kg})$           | 49.73 ( $\pm 1.41$ )  | 52.24 ( $\pm 2.21$ )  | 45.98 ( $\pm 0.49$ )  | 49.34 ( $\pm 0.95$ )  | 46.23 ( $\pm 0.39$ )  |
| $\Delta_{tr}K_{\phi,s}^0 \times 10^{15} / (\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1})$ | 2.97                  | 2.77                  | 3.53                  | 2.65                  | 3.21                  |
| SUC + 0.0698 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ]                             |                       |                       |                       |                       |                       |
| $V_\phi^0 \times 10^6 / (\text{m}^3 \text{mol}^{-1})$                                  | 210.62 ( $\pm 0.07$ ) | 211.38 ( $\pm 0.04$ ) | 211.88 ( $\pm 0.09$ ) | 212.59 ( $\pm 0.07$ ) | 213.25 ( $\pm 0.07$ ) |
| $S_v \times 10^6 / (\text{m}^3 \text{mol}^{-2} \text{kg})$                             | 36.87 ( $\pm 1.26$ )  | 36.72 ( $\pm 0.73$ )  | 41.27 ( $\pm 1.67$ )  | 39.87 ( $\pm 1.19$ )  | 42.83 ( $\pm 1.15$ )  |
| $\Delta_{tr}V_\phi^0 \times 10^6 / (\text{m}^3 \text{mol}^{-1})$                       | 2.46                  | 2.85                  | 2.36                  | 2.19                  | 2.23                  |
| $K_{\phi,s}^0 \times 10^{15} / (\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1})$            | -43.19 ( $\pm 0.15$ ) | -41.33 ( $\pm 0.12$ ) | -39.79 ( $\pm 0.05$ ) | -38.43 ( $\pm 0.10$ ) | -36.84 ( $\pm 0.04$ ) |
| $S_k \times 10^{15} / (\text{m}^3 \text{mol}^{-2} \text{Pa}^{-1} \text{kg})$           | 53.24 ( $\pm 2.60$ )  | 50.29 ( $\pm 2.05$ )  | 46.43 ( $\pm 0.95$ )  | 51.19 ( $\pm 1.74$ )  | 46.08 ( $\pm 0.73$ )  |
| $\Delta_{tr}K_{\phi,s}^0 \times 10^{15} / (\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1})$ | 3.69                  | 3.85                  | 4.44                  | 3.58                  | 4.06                  |

<sup>a</sup>Ref. No. [23]

the observed positive transfer values, for all concentration ranges and at all temperatures, suggest the dominance of type (a) interactions between SUC and the ions of studied IL. The magnitude of transfer values increases with increase in cosolute concentration. The dominance of type (a) interactions between SUC and [BMIM][PF<sub>6</sub>] causes the reduction of electrostriction of water molecules in the vicinity of SUC molecules and consequently

contributes positively to  $\Delta_{tr}V_\phi^0$  and  $\Delta_{tr}K_{\phi,s}^0$ . The positive transfer volumes have also been reported for some saccharides in aqueous solution of imidazolium based ILs<sup>31,32</sup>, thus, strengthening the view point of hydrophilic - ionic type of interactions.

In order to explain the magnitude of  $V_\phi^0$ , the following relation can be used.

$$V_\phi^0 = V_{vdw} + V_{void} + V_{shrinkage} \quad \dots (8)$$

Where  $V_{vdw}$  and  $V_{void}$  represents Van der Waal's volume and volume due to the associated voids, while  $V_{shrinkage}$  is the volume of shrinkage due to interactions of hydrogen bonding between groups of SUC and water molecules. If the first two volumes are assumed to be same in water and in aqueous IL solutions, the relation between  $\Delta_{tr}V_{\phi}^{\circ}$  and change in the volume of shrinkage can be expressed as:  $\Delta_{tr}V_{\phi}^{\circ} = -\Delta V_{shrinkage}$ , that is, the positive transfer  $\Delta_{tr}V_{\phi}^{\circ}$  values for SUC in presence of IL may be due to decrease in  $V_{shrinkage}$ . The same assumption has also been shown by other authors as well<sup>31,32</sup>.

The change in volume due to electrostriction effect can be related to the hydration number ( $n_H$ ) that is, the average number of water molecules which surrounds solute molecule. It can be calculated by many methods which give out different values depending on the method used. Here, this parameter is calculated by using the following relation<sup>33</sup>:

$$n_H = -K_{\phi,s}^{\circ}(\text{elect})/(V_{\phi,b}^{\circ} \cdot K_{s,\phi,b}^{\circ}) \quad \dots (9)$$

Where  $K_{\phi,s}^{\circ}(\text{elect})$  is the electrostriction limiting apparent molar isentropic compressibility,  $K_{s,\phi,b}^{\circ}$  is the isothermal compressibility of bulk water or bulk solvent and  $V_{\phi,b}^{\circ}$  is the molar volume of bulk water or bulk solvent. The hydration number of sucrose in water agrees to some extent with the literature values reported at 298.15 K by Shioo<sup>34</sup> and Gaida *et al.*<sup>35</sup>. Further, the magnitude of hydration number values (Supplementary data, Table S2) of SUC in aqueous [BMIM][PF<sub>6</sub>] solutions is lower in comparison to their values in aqueous medium, which indicates an increase in solute–cosolute interactions and, thus, a reduction in the electrostriction.

#### Interaction coefficients

In order to evaluate the interaction coefficients, a theory of solutions based on McMillan and Mayer<sup>36</sup> was proposed by Kozak *et al.*<sup>37</sup>. According to this theory, volume and compressibility of transfers may be expressed as:

$$\Delta_{tr}V_{\phi}^{\circ} = 2V_{AB}m_B + 3V_{ABB}m_B^2 + \dots \quad \dots (10)$$

$$\Delta_{tr}K_{s,\phi}^{\circ} = 2K_{AB}m_B + 3K_{ABB}m_B^2 + \dots \quad \dots (11)$$

Here, A denotes solute (SUC) and B stands for cosolute [BMIM][PF<sub>6</sub>],  $m_B$  is the molality of co-solute.  $V_{AB}$ ,  $V_{ABB}$  and  $K_{AB}$ ,  $K_{ABB}$  are pair and triplet interaction coefficients for volume and compressibility, respectively, obtained by least squares regression.  $\Delta_{tr}V_{\phi}^{\circ}$  and  $\Delta_{tr}K_{s,\phi}^{\circ}$  values, from Table 3, have been

fitted into the above equations to get the interaction coefficients (Table 4). The positive volumetric and compression pair interaction coefficients at all temperatures show that interactions between SUC and [BMIM][PF<sub>6</sub>] are mainly pair wise. This can be interpreted on the basis of structural interactions model proposed by Desnoyers *et al.*<sup>28</sup>. The positive values are mainly due to the hydrophilic – ionic interactions, as the dehydration of ions and -OH, -C=O, -O- groups contribute a positive value to the volume. The triplet volumetric and compression interaction coefficients, on the other hand, can contribute positively or negatively. In this study, both volumetric and compressibility triplet interactions coefficients have positive values at all temperatures. Overall, both pair and triplet coefficients represent strong interactions for SUC-water-[BMIM][PF<sub>6</sub>] system.

#### Viscosity

The experimental obtained values of viscosity for series of solutions of SUC in (0.0105, 0.0303, 0.0496 and 0.0698) mol kg<sup>-1</sup> aqueous solutions of [BMIM][PF<sub>6</sub>] at varying temperatures is presented in Table 5. Following this, the relative viscosity has been analyzed in terms of least squares fitting of the Jones – Dole empirical equation<sup>38</sup>.

$$\eta_r = \eta / \eta_o = 1 + AC^{1/2} + BC \quad \dots (12)$$

Where  $\eta$  is the viscosity of solution (SUC + Water + IL), and  $\eta_o$  is the viscosity of solvent (water + IL).  $A$  is the Falkenhagen coefficient that depends on the long range coulomb forces related to solute – solute interactions.  $B$ , also called as viscosity  $B$ -coefficients, is an adjustable parameter which reflects the effects of solute–solvent interactions on the solution viscosity. It also provides information about the solvation of solute.  $C$  is the concentration in moles per unit volume (molarity). The conversion from molality to molarity is obtained using the density values. For non-electrolytes,  $A$  is negligible and Jones-Dole equation reduces to:

Table 4 — Pair and triplet interaction coefficients for SUC and [BMIM][PF<sub>6</sub>] at different temperatures

| T/K    | $V_{AB} \times 10^6$<br>(m <sup>3</sup> mol <sup>-2</sup><br>kg) | $V_{ABB} \times 10^6$<br>(m <sup>3</sup> mol <sup>-3</sup><br>kg <sup>2</sup> ) | $K_{AB} \times 10^{15}$<br>(Pa <sup>-1</sup> m <sup>3</sup> mol <sup>-2</sup><br>kg) | $K_{ABB} \times 10^{15}$<br>(Pa <sup>-1</sup> m <sup>3</sup> mol <sup>-3</sup><br>kg <sup>2</sup> ) |
|--------|--|---|--|---|
| 293.15 | 37.60  | 1.15  | 22.62  | 0.97  |
| 298.15 | 29.30  | 4.02  | 26.91  | 4.91  |
| 303.15 | 49.29  | 6.45  | 21.27  | 2.00  |
| 308.15 | 29.64  | 0.43  | 16.34  | 0.30  |
| 313.15 | 37.60  | 2.67  | 19.52  | 2.22  |

Table 5 — Viscosity ( $\eta$ ) and relative viscosity ( $\eta_r$ ) for SUC in aqueous and aqueous solutions of [BMIM][PF<sub>6</sub>] at different temperatures

| $m/(\text{mol kg}^{-1})$                                   | $\eta \times 10^3 / (\text{Pa s})$ |          |          |          |          | $\eta_r$ |          |          |          |          |
|--|------------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|  | 293.15 K                           | 298.15 K | 303.15 K | 308.15 K | 313.15 K | 293.15 K | 298.15 K | 303.15 K | 308.15 K | 313.15 K |
| SUC + water  |                                    |          |          |          |          |          |          |          |          |          |
| 0.00000  | 1.0019                             | 0.8920   | 0.7980   | 0.7170   | 0.6531   |          |          |          |          |          |
| 0.00998  | 1.0150                             | 0.9017   | 0.8050   | 0.7217   | 0.6570   | 1.0131   | 1.0093   | 1.0088   | 1.0066   | 1.0031   |
| 0.02989  | 1.0351                             | 0.9157   | 0.5125   | 0.7320   | 0.6633   | 1.0332   | 1.0266   | 1.0182   | 1.0162   | 1.0156   |
| 0.04988  | 1.0551                             | 0.9326   | 0.8269   | 0.7426   | 0.6728   | 1.0531   | 1.0455   | 1.0362   | 1.0357   | 1.0302   |
| 0.06977  | 1.0767                             | 0.9513   | 0.8426   | 0.7530   | 0.6818   | 1.0746   | 1.0666   | 1.0559   | 1.0502   | 1.0439   |
| 0.08966  | 1.0928                             | 0.9669   | 0.8576   | 0.7669   | 0.6931   | 1.0907   | 1.0840   | 1.0747   | 1.0696   | 1.0602   |
| SUC + 0.0105 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ] |                                    |          |          |          |          |          |          |          |          |          |
| 0.00000  | 1.0086                             | 0.9025   | 0.8038   | 0.7270   | 0.6609   |          |          |          |          |          |
| 0.00997  | 1.0231                             | 0.9146   | 0.8131   | 0.7344   | 0.6664   | 1.0168   | 1.0134   | 1.0116   | 1.0102   | 1.0083   |
| 0.02991  | 1.0452                             | 0.9318   | 0.8273   | 0.7458   | 0.6758   | 1.0363   | 1.0324   | 1.0292   | 1.0259   | 1.0225   |
| 0.04993  | 1.0652                             | 0.9482   | 0.8414   | 0.7575   | 0.6870   | 1.0561   | 1.0506   | 1.0468   | 1.0420   | 1.0342   |
| 0.06989  | 1.0878                             | 0.9668   | 0.8548   | 0.7685   | 0.6932   | 1.0785   | 1.0712   | 1.0635   | 1.0571   | 1.0489   |
| 0.08966  | 1.1124                             | 0.9823   | 0.8709   | 0.7814   | 0.7039   | 1.1029   | 1.0884   | 1.0835   | 1.0748   | 1.0651   |
| SUC + 0.0303 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ] |                                    |          |          |          |          |          |          |          |          |          |
| 0.00000  | 1.0186                             | 0.9114   | 0.8161   | 0.7313   | 0.6703   |          |          |          |          |          |
| 0.00996  | 1.0344                             | 0.9285   | 0.8260   | 0.7396   | 0.6772   | 1.0172   | 1.0145   | 1.0138   | 1.0131   | 1.0113   |
| 0.02993  | 1.0576                             | 0.9439   | 0.8413   | 0.7520   | 0.6875   | 1.0383   | 1.0359   | 1.0318   | 1.0283   | 1.0257   |
| 0.04993  | 1.0788                             | 0.9617   | 0.8565   | 0.7647   | 0.6982   | 1.0621   | 1.0561   | 1.0495   | 1.0457   | 1.0416   |
| 0.06993  | 1.1034                             | 0.9809   | 0.8721   | 0.7787   | 0.7075   | 1.0834   | 1.0783   | 1.0686   | 1.0648   | 1.0555   |
| 0.08985  | 1.1272                             | 0.9974   | 0.8908   | 0.7958   | 0.7182   | 1.1066   | 1.0949   | 1.0895   | 1.0842   | 1.0763   |
| SUC + 0.0496 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ] |                                    |          |          |          |          |          |          |          |          |          |
| 0.00000  | 1.0256                             | 0.9282   | 0.8296   | 0.7419   | 0.6850   |          |          |          |          |          |
| 0.00998  | 1.0425                             | 0.9412   | 0.8400   | 0.7511   | 0.6931   | 1.0169   | 1.0151   | 1.0141   | 1.0138   | 1.0118   |
| 0.02995  | 1.0670                             | 0.9620   | 0.8586   | 0.7651   | 0.7051   | 1.0404   | 1.0364   | 1.0350   | 1.0313   | 1.0293   |
| 0.04996  | 1.0894                             | 0.9802   | 0.8747   | 0.7791   | 0.7166   | 1.0622   | 1.0571   | 1.0544   | 1.0501   | 1.0461   |
| 0.06993  | 1.1121                             | 1.0006   | 0.8911   | 0.7938   | 0.7292   | 1.0843   | 1.0789   | 1.0741   | 1.0700   | 1.0645   |
| 0.08982  | 1.1362                             | 1.0182   | 0.9073   | 0.8090   | 0.7419   | 1.1071   | 1.0970   | 1.0937   | 1.0904   | 1.0831   |
| SUC + 0.0698 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ] |                                    |          |          |          |          |          |          |          |          |          |
| 0.00000  | 1.0355                             | 0.9305   | 0.8377   | 0.7537   | 0.6929   |          |          |          |          |          |
| 0.00997  | 1.0543                             | 0.9457   | 0.8506   | 0.7648   | 0.7023   | 1.0182   | 1.0156   | 1.0153   | 1.0150   | 1.0134   |
| 0.02994  | 1.0791                             | 0.9661   | 0.8691   | 0.7788   | 0.7145   | 1.0421   | 1.0400   | 1.0392   | 1.0333   | 1.0302   |
| 0.04991  | 1.1014                             | 0.9855   | 0.8856   | 0.7937   | 0.7285   | 1.0634   | 1.0600   | 1.0572   | 1.0531   | 1.0514   |
| 0.06994  | 1.1256                             | 1.0062   | 0.9025   | 0.8107   | 0.7420   | 1.0870   | 1.0798   | 1.0774   | 1.0765   | 1.0709   |
| 0.08979  | 1.1491                             | 1.0306   | 0.9237   | 0.8267   | 0.7544   | 1.1097   | 1.1045   | 1.1027   | 1.0969   | 1.0889   |

<sup>a</sup>Standard uncertainties are:  $u(m) = \pm 2.0 \times 10^{-5} \text{ mol kg}^{-1}$ ,  $u(d) = \pm 5.0 \times 10^{-3} \text{ kg m}^{-3}$ ,  $u(T) = \pm 0.01 \text{ K}$ ,  $u(P) = 0.0001 \text{ MPa}$ , and  $u(\eta) = \pm 1.0 \times 10^{-6} \text{ Pa s}$ ,  $m$  is the molality of SUC in per kg of water or (water + IL) mixture. Molality of IL in per kg of (water + IL) has a standard uncertainty of  $\pm 1.0 \times 10^{-4} \text{ mol kg}^{-1}$ .

$$\eta_r = \eta / \eta_o = I + BC \quad \dots (13)$$

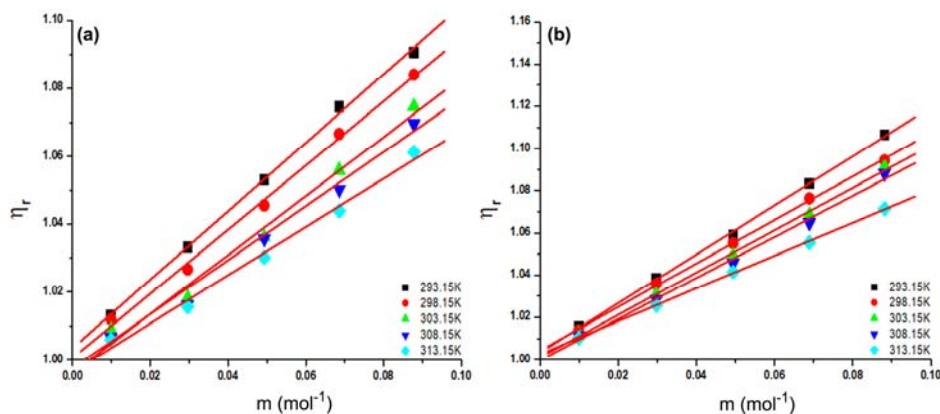
The viscosity table shows an increase in  $\eta_r$  values with the concentration of solute, but registers a decrease with the rise of temperature of the solution. The sign of viscosity  $B$ -coefficients usually represents the structure making/breaking ability of a solute, which can help in understanding the solvation effects

of ions. The viscosity  $B$ -coefficients (Table 6), obtained by plotting relative viscosity of SUC verses molarity of solution (Fig. 3), is found to be positive which indicates that the structure of solution is strengthened. This indicates that SUC + [BMIM][PF<sub>6</sub>]-water interactions are dominating over SUC-SUC and [BMIM][PF<sub>6</sub>]-[BMIM][PF<sub>6</sub>] interactions. It also signifies the structure making tendency of



Table 6 — Viscosity  $B$ -coefficients, solvation number ( $S_n$ ), Viscosity  $B$ -coefficients of transfer and  $dB/dT$  for SUC in aqueous and aqueous solutions of [BMIM][PF<sub>6</sub>] at different temperatures

| Molality of SUC in aqueous and aqueous IL | <sup>a</sup> Viscosity $B$ -coefficients |                             |         |         |         | $dB/dT$ |
|---|--|-----------------------------|---------|---------|---------|---------|
|   | <sup>b</sup> $S_n \times 10^{-3}$        | <sup>c</sup> $\Delta_{tr}B$ |         |         |         |         |
|   | 293.15K                                  | 298.15K                     | 303.15K | 308.15K | 313.15K |         |
| 0.0000m IL                                | <sup>a</sup> 1.0038                      | 1.0008                      | 0.9964  | 0.9956  | 0.9947  | -0.0005 |
|   | <sup>b</sup> 4.82                        | 4.80                        | 4.76    | 4.73    | 4.71    |         |
| 0.0105m IL                                | <sup>a</sup> 1.0042                      | 1.0036                      | 1.0021  | 1.0016  | 1.0006  | -0.0002 |
|   | <sup>b</sup> 4.81                        | 4.79                        | 4.77    | 4.75    | 4.73    |         |
| 0.0303m IL                                | <sup>c</sup> 0.0004                      | 0.0027                      | 0.0057  | 0.0060  | 0.0060  | -0.0002 |
|   | <sup>a</sup> 1.0052                      | 1.0048                      | 1.0033  | 1.0028  | 1.0019  |         |
| 0.0496m IL                                | <sup>b</sup> 4.80                        | 4.79                        | 4.76    | 4.74    | 4.73    | -0.0002 |
|   | <sup>c</sup> 0.0014                      | 0.0039                      | 0.0069  | 0.0067  | 0.0072  |         |
| 0.0698m IL                                | <sup>a</sup> 1.0057                      | 1.0050                      | 1.0044  | 1.0028  | 1.0022  | -0.0002 |
|   | <sup>b</sup> 4.78                        | 4.77                        | 4.75    | 4.73    | 4.71    |         |
| 0.0698m IL                                | <sup>c</sup> 0.0019                      | 0.0041                      | 0.0080  | 0.0072  | 0.0075  | -0.0002 |
|   | <sup>a</sup> 1.0068                      | 1.0052                      | 1.0048  | 1.0029  | 1.0027  |         |
|   | <sup>b</sup> 4.78                        | 4.76                        | 4.74    | 4.72    | 4.70    |         |
|   | <sup>c</sup> 0.0030                      | 0.0043                      | 0.0084  | 0.0073  | 0.0080  |         |

Fig. 3 — Plot of relative viscosity versus molarity for SUC in (a) aqueous and (b) 0.0303 mol kg<sup>-1</sup> aqueous [BMIM][PF<sub>6</sub>] solutions.

SUC with [BMIM][PF<sub>6</sub>] + water which results in the dominance of strong intermolecular interactions occurring in the solution. To confirm it further, the dependence of  $B$ -coefficients values over temperature has been observed in terms of  $dB/dT$  values. These values are negative thus reinforces the conclusion that the solute is showing structure making ability with the solvent<sup>39-41</sup>. The viscosity  $B$ -coefficients of transfer can also be calculated by using the equation:

$$\Delta_{tr}B = B_{aq [BMIM]PF_6} - B_{water} \quad \dots (14)$$

The evaluated values are reported in Table 6 and they show a regular increase with increase in concentration of solute. The positive values suggest that an overall structural increase occurs, while negative values mean that a structural decrease occurs in solution. Another property based on  $B$ -coefficients

is the solvation number,  $S_n$ <sup>42</sup>. This property is used to find out the solvation of solute due to presence of solvent molecules in its vicinity. It is calculated as:

$$S_n = B / V_\phi^\circ \quad \dots (15)$$

Where  $B$  is viscosity  $B$ -coefficients and  $V_\phi^\circ$  is the limiting apparent molar volume at infinite dilution. From the calculated values of  $S_n$ , it is found that these values are high (>2.5) and hence shows increasing interaction of solute with solvent molecule. The  $\Delta_{tr}B$  values and  $S_n$  further confirms the strong interactions occurring in solution.

#### Thermodynamics of the viscous flow

Some important parameters which are useful in explaining the solution thermodynamics are changes in enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ), chemical potential ( $\Delta \mu$ ), etc. For calculating standard partial molar

enthalpy ( $\Delta H_2^{\ddagger}$ ) and entropy ( $\Delta S_2^{\ddagger}$ ) of activation for the viscous flow of the solution, we have the following relations:

$$\Delta H_2^{\ddagger} = \Delta\mu_2^{\ddagger} + T\Delta S_2^{\ddagger} \quad \dots (16)$$

$$\Delta S_2^{\ddagger} = -d(\Delta\mu_2^{\ddagger})/dT \quad \dots (17)$$

Where all the symbols have their usual meanings. Further, Gibbs free energy of activation or chemical potential per mole of solvent (water and aqueous solutions of [BMIM][PF<sub>6</sub>]), i.e.,  $\Delta\mu_1^{\ddagger}$ , and solute, i.e.,  $\Delta\mu_2^{\ddagger}$ , are calculated by the relations obtained from the transition state theory<sup>43,44</sup>.

$$\Delta\mu_1^{\ddagger} = RT \ln (\eta_0 \bar{V}_1^{\ddagger} / hN_A) \quad \dots (18)$$

$$\Delta\mu_2^{\ddagger} = \Delta\mu_1^{\ddagger} + (RT / \bar{V}_1^{\ddagger}) [1000B - (\bar{V}_1^{\ddagger} - \bar{V}_2^{\ddagger})] \quad \dots (19)$$

where,  $R$ ,  $h$ ,  $N_A$  are gas constant, Planck's constant and Avogadro number, respectively,  $\eta_0$  and  $B$  are the

solvent viscosity and viscosity  $B$ -coefficients.  $\bar{V}_1^{\ddagger}$  represents the mean apparent molar volume of solvent and  $\bar{V}_2^{\ddagger}$  represents the limiting apparent molar volume of solute (reported earlier).  $\bar{V}_1^{\ddagger}$  is calculated by taking the average of mole fraction and molecular weight of solvent (water and [BMIM][PF<sub>6</sub>]) normalized by density at a particular temperature<sup>45</sup>, i.e., it can be expressed as:

$$\bar{V}_1^{\ddagger} = \sum xi Mi / \rho_0 \quad \dots (20)$$

All the evaluated values are presented in Table 7. The value of  $\Delta\mu_2^{\ddagger}$  determines the potential to form the transition state via the solute-solvent interactions from the ground state of the solvent. Here,  $\Delta\mu_1^{\ddagger}$  and  $\Delta\mu_2^{\ddagger}$  are found to be positive for all the concentration terms and at all temperatures. Also,  $\Delta\mu_2^{\ddagger}$  values are found to be much higher than  $\Delta\mu_1^{\ddagger}$  values indicating the strong intermolecular interactions among SUC and [BMIM][PF<sub>6</sub>] molecules. These interactions are less in transition state and more in ground state. Since the

Table 7 — Values of  $\Delta\mu_1^{\ddagger}$ ,  $\Delta\mu_2^{\ddagger}$ ,  $\Delta H_2^{\ddagger}$  and  $T\Delta S_2^{\ddagger}$  for SUC in aqueous solutions of [BMIM][PF<sub>6</sub>] at  $T = (298.15 \text{ to } 313.15) \text{ K}$  and pressure  $P = 0.1009 \text{ MPa}$

| Property   | $T/K$    |          |          |          |          |
|--|----------|----------|----------|----------|----------|
|  | 293.15 K | 298.15 K | 303.15 K | 308.15 K | 313.15 K |
| SUC + Water  |          |          |          |          |          |
| $\Delta\mu_1^{\ddagger}/(kJ \text{ mol}^{-1})$             | 9.29     | 9.16     | 9.04     | 8.92     | 8.83     |
| $\Delta\mu_2^{\ddagger}/(kJ \text{ mol}^{-1})$             | 119.17   | 120.31   | 121.18   | 122.54   | 123.87   |
| $T\Delta S_2^{\ddagger}/(kJ \text{ mol}^{-1})$             | 68.19    | 69.35    | 70.51    | 71.68    | 72.84    |
| $\Delta H_2^{\ddagger}/(kJ \text{ mol}^{-1})$              | 187.36   | 188.50   | 191.69   | 194.22   | 196.71   |
| SUC + 0.0105 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ] |          |          |          |          |          |
| $\Delta\mu_1^{\ddagger}/(kJ \text{ mol}^{-1})$             | 9.31     | 9.19     | 9.06     | 8.81     | 8.86     |
| $\Delta\mu_2^{\ddagger}/(kJ \text{ mol}^{-1})$             | 119.23   | 120.62   | 121.82   | 123.20   | 124.67   |
| $T\Delta S_2^{\ddagger}/(kJ \text{ mol}^{-1})$             | 78.92    | 80.26    | 81.61    | 82.95    | 84.30    |
| $\Delta H_2^{\ddagger}/(kJ \text{ mol}^{-1})$              | 198.15   | 200.88   | 203.43   | 206.15   | 208.97   |
| SUC + 0.0303 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ] |          |          |          |          |          |
| $\Delta\mu_1^{\ddagger}/(kJ \text{ mol}^{-1})$             | 9.29     | 9.23     | 9.11     | 8.99     | 8.95     |
| $\Delta\mu_2^{\ddagger}/(kJ \text{ mol}^{-1})$             | 118.64   | 120.13   | 121.42   | 122.72   | 124.21   |
| $T\Delta S_2^{\ddagger}/(kJ \text{ mol}^{-1})$             | 80.50    | 81.87    | 83.24    | 84.62    | 85.99    |
| $\Delta H_2^{\ddagger}/(kJ \text{ mol}^{-1})$              | 199.14   | 202.00   | 204.66   | 207.34   | 210.20   |
| SUC + 0.0496 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ] |          |          |          |          |          |
| $\Delta\mu_1^{\ddagger}/(kJ \text{ mol}^{-1})$             | 9.37     | 9.29     | 9.16     | 9.03     | 8.97     |
| $\Delta\mu_2^{\ddagger}/(kJ \text{ mol}^{-1})$             | 118.26   | 119.61   | 121.04   | 122.31   | 123.72   |
| $T\Delta S_2^{\ddagger}/(kJ \text{ mol}^{-1})$             | 79.85    | 81.22    | 82.58    | 83.94    | 85.30    |
| $\Delta H_2^{\ddagger}/(kJ \text{ mol}^{-1})$              | 198.11   | 200.83   | 203.62   | 206.25   | 209.02   |
| SUC + 0.0698 mol kg <sup>-1</sup> [BMIM][PF <sub>6</sub> ] |          |          |          |          |          |
| $\Delta\mu_1^{\ddagger}/(kJ \text{ mol}^{-1})$             | 9.41     | 9.30     | 9.20     | 9.08     | 9.02     |
| $\Delta\mu_2^{\ddagger}/(kJ \text{ mol}^{-1})$             | 117.86   | 119.17   | 120.55   | 121.82   | 123.23   |
| $T\Delta S_2^{\ddagger}/(kJ \text{ mol}^{-1})$             | 78.51    | 79.84    | 81.18    | 82.52    | 83.86    |
| $\Delta H_2^{\ddagger}/(kJ \text{ mol}^{-1})$              | 196.37   | 199.01   | 201.73   | 204.73   | 207.09   |

transition state is formed by breaking or loosening of some older bonds and formation of some new bonds or interactions, this fact is supported by the explanation given earlier that  $\Delta\mu_1^{\circ\ddagger} \ll \Delta\mu_2^{\circ\ddagger}$ . The larger the  $\Delta\mu_2^{\circ\ddagger}$  value, larger is the structure making ability of solute in the solution. However, the increase in  $\Delta\mu_2^{\circ\ddagger}$  values as the temperature is increased shows that higher temperature is more preferred for the formation of transition state. Hence, the decrease in solute-solvent interactions becomes apparent when the system is subjected to increase in temperature. The values for  $\Delta H_2^{\circ\ddagger}$  and  $T\Delta S_2^{\circ\ddagger}$  are positive and further  $\Delta H_2^{\circ\ddagger} > T\Delta S_2^{\circ\ddagger}$  (Table 7). This suggests that the formation of transition state is associated with bond breaking and a decrease in order.

### Conclusions

In the present study, various volumetric, acoustic and viscometric parameters have been evaluated from experimentally determined values of density, speed of sound and viscosity data. The results obtained for limiting parameters indicates the dominance of solute-solvent interactions over solute-solute interactions. The transfer parameters like limiting apparent molar transfer volume, limiting apparent molar transfer compressibility and viscosity  $B$ -coefficients of transfer indicates the presence of hydrophilic-ionic interactions between SUC and [BMIM][PF<sub>6</sub>] and being influenced by the concentration of [BMIM][PF<sub>6</sub>] as well as temperature. The negative values of  $dB/dT$  have been explained for the structure-making behaviour of SUC in aqueous [BMIM][PF<sub>6</sub>] solutions. The values of  $\Delta\mu_1^{\circ\ddagger}$  and  $\Delta\mu_2^{\circ\ddagger}$  shows that the formation of transition state is less favoured in terms of free energy and hence justifying the structure maker behaviour of SUC in solutions of aqueous [BMIM][PF<sub>6</sub>]. Moreover, the creation of the transition state is involved by bond breaking and decrease in order as represented by positive  $\Delta H_2^{\circ\ddagger}$  and  $T\Delta S_2^{\circ\ddagger}$  values.

### Supplementary Data

Supplementary data associated with this article are available in the electronic form at [http://nopr.niscair.res.in/jinfo/ijca/IJCA\\_59A\(01\)31-42\\_SupplData.pdf](http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(01)31-42_SupplData.pdf).

### References

- Demir S, Damarhan Y & Ozdemir I, *J Mol Liq*, 204 (2015) 210.
- Strehmel V, Berdzinski S & Rexhausen H, *J Mol Liq*, 192 (2014) 153.
- Pinkert A, Marsh K N, Pang S & Straiger M P, *Chem Rev*, 109 (2009) 6712.
- Swatloski R P, Spear S K, Holbrey J D & Rogers R D, *J Am Chem Soc*, 124 (2002) 4974.
- Atihan M, Jacquemin J, Rooney D, Khraisheh M & Aparicio S, *Ind Chem Eng Res*, 52 (2013) 16774.
- Tao R, Tamas G, Xue L, Simon S L & Quitevis E L, *J Chem Eng Data*, 59 (2014) 2717.
- Coleman D & Gathergood N, *Chem Soc Rev*, 39 (2010) 600.
- Chaudhary G R, Bansal S, Mehta S K & Ahluwalia A S, *J Sol Chem*, 43 (2014) 340.
- Wu B, Zhang Y & Wang H, *J Phys Chem B*, 112 (2008) 6426.
- Wu B, Zhang Y, Wang H & Yang L, *J Phys Chem B*, 112 (2008) 13163.
- Jin X & Chen H Y, *J Chem Eng Data*, 56 (2011) 4392.
- Wu B, Zhang Y M & Wang H P, *J Chem Eng Data*, 54 (2009) 1430.
- Zafarani-Moattar M T, Shekaari H & Mazaher E, *J Chem Thermodyn*, 93 (2016) 60.
- Chaudhary G R, Bansal S, Mehta S K & Ahluwalia A S, *J Chem Thermodyn*, 50 (2012) 63.
- Ali M, Sarkar A, Tariq M, Ali A & Pandey S, *Green Chem*, 9 (2007) 1252.
- Jacquemin J, Husson P, Padua A A H & Majer V, *Green Chem*, 8 (2006) 172.
- Wang S, Jacquemin J, Husson P, Hardacre C & Gomes M F C, *J Chem Thermodyn*, 41 (2009) 1206.
- Zhang J, Wu W, Gao H, Liu Z & Han B, *J Chem Eng Data*, 48 (2003) 1315.
- Liavitskaya T, Paulechka E, Blokhin A V & Shevelyova M, *J Chem Thermodyn*, 131 (2019) 262.
- Bennett V, Dikio C W, Angaye S S, Wankasi D, Dikio E D, Bahadur I & Ebenso E E, *J Mol Liq*, 219 (2016) 661.
- Yan Q, Fangyou Y, Shuqian X & Peisheng M A, *Chin J Chem Eng*, 21 (2013) 1284.
- Nain A K, Pal R & Neetu, *J Chem Thermodyn*, 64 (2013) 172.
- Banipal P K, Chahal A K & Banipal T S, *J Chem Thermodyn*, 41 (2009) 452.
- Barbosa R D, *High pressure and temperature dependence of thermodynamic properties of model food solutions obtained from in situ ultrasonic measurements*, Ph D dissertation, University of Florida, Florida, USA, 2003.
- Chen Y, Fang M, Bai G, Zhuo K & Yan C, *J Chem Eng Data*, 61 (2016) 3779.
- Singh V, Chhotaray P K & Gardas R L, *Food Chem*, 169 (2015) 478.
- Kirkwood J G, *Chem Rev*, 24 (1939) 233.
- Desnoyers J E, Arel M, Perron G & Jolicoeur C, *J Phys Chem*, 73 (1969) 3346.
- Savage J J & Wood R H, *J Sol Chem*, 5 (1976) 733.
- Gurney R W, *Ionic processes in solution*, (McGraw Hill, New York, 1-20) 1953.
- Shekaari H & Kazempour A, *Fluid Phase Equilib*, 309 (2011) 1.
- Jin H X & Chen H Y, *J Chem Eng Data*, 57 (2011) 4392.
- Millero F J, Surdo A L & Shin C, *J Phys Chem*, 82 (1978) 784.
- Shioo H, *J Am Chem Soc*, 80 (1958) 70.
- Gaida L B, Dussap C G & Gros J B, *Food Chem*, 96 (2006) 387.
- McMillan Jr W G & Mayer J E, *J Chem Phys*, 13 (1945) 276.
- Kozak J J, Knight W S & Kauzman W, *J Chem Phys*, 48 (1968) 675.

- 38 Jones G & Dole M, *J Am Chem Soc*, 51 (1929) 2950.
- 39 Feakins D, Freemantle D J & Lawrence K G, *J Chem Soc Faraday Trans*, 70 (1974) 795.
- 40 Kaminsky M, *Discuss Faraday Soc*, 24 (1957) 171.
- 41 Zhao H, *Biophys Chem*, 122 (2006) 157.
- 42 Sarkar A & Sinha B, *Food Chem*, 211 (2016) 590.
- 43 Feakins D, Freemantle D J & Lawrence K G, *J Chem Soc Faraday Trans*, 70 (1974) 795.
- 44 Glasstone S, Laidler K & Eyring H, *Theory of Rate Processes*, (McGraw-Hill New York) 1941.
- 45 Poling B E, Prausnitz J M & O'Connell J P, *The Properties of Gases and Liquids*, (McGraw-Hill, New York, 5th Edition) 2001.