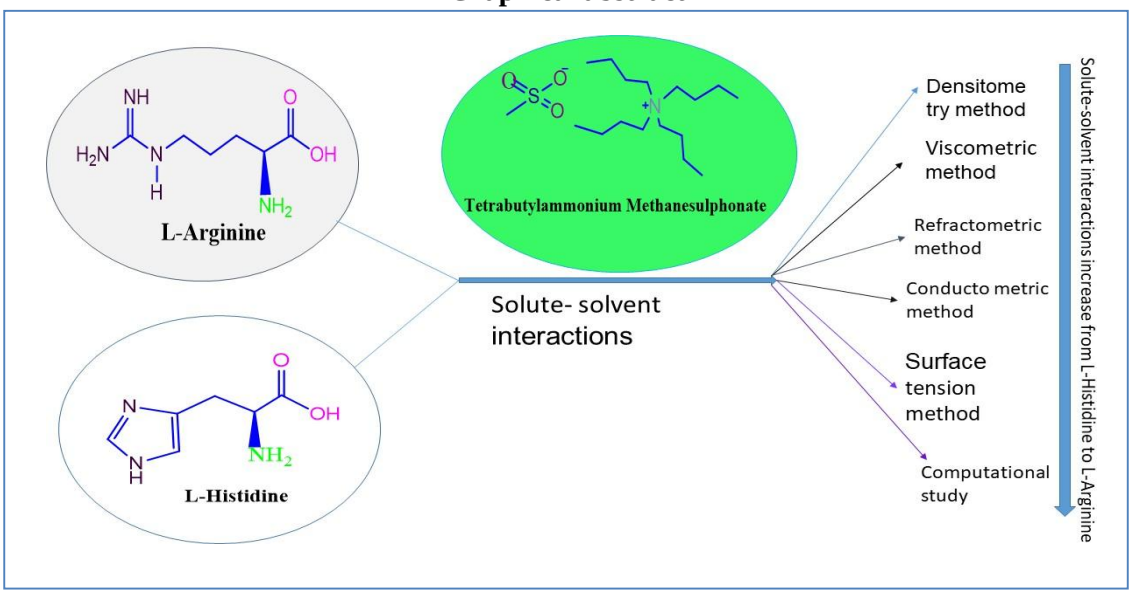
CHAPTER-VII

SUBSISTENCE OF ASSORTED MOLECULAR INTERACTIONS OF SUBSTANTIAL AMINO ACIDS PREVALENT IN AQUEOUS SOLUTIONS OF IONIC LIQUID (TBMS) PROBED BY EXPERIMENTAL AND COMPUTATIONAL INVESTIGATIONS

ABSTRACT:

Solution behaviour prevailing in L-Arginine and L-Histidine in aqueous Tetrabutylammonium methanesulphonate (TBMS) has been studied to investigate the mode of interactions by means of density (ρ), viscosity (η), surface tension (σ), refractive index (n_D) and electrolytic conductivity at three different temperatures. The nature of interactions occurring in the solutions have been elucidated on the basis of apparent molar volume (Φ_V^0), limiting molar expansivities (Φ_E^0), viscosity *A*- and *B*- coefficients, molar refraction (^R_M) and concentration measurements. Molar conductance (Λ), as well as specific conductance (κ), obtained, so, describe the nature of solute-solute and solute-solvent interactions in the solution mixtures. Using Gaussian 09W quantum chemical package, optimum energies with the optimised geometries of molecular assembly for (TBMS+L-Arginine) and (TBMS+L-Histidine) systems and also critical micelle concentration (CMC) values were calculated and found supportive to the practical outcomes that show the solute-solvent interactions prevailing between the TBMS (IL) and amino acids; L-Arginine and L-Histidine are dominant over the solute–solute interactions. Furthermore, L-Arginine shows a higher extent of interaction that is also influenced by the concentrations and temperatures in comparison to L-Histidine in aqueous IL solutions. The theoretical observations of the study determining $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $\Delta H^{0\neq}$, and $T\Delta S^{0\neq}$ also imply the presence of strong interactions in the systems. The various types of interactions between amino acids which are the protein backbone, in presence of ionic liquids would develop a many-dimensional challenge in the field of solution chemistry. Studies of such systems could be advanced further using the correlated outcomes of the investigation.

Graphical abstract



1. Introduction

It is well recognized that the reaction medium plays a significant role in the determination of the reactivity reflected in thermodynamic, transport and spectral properties [1]. Gaining perception in the mechanism of such types of interactions, studies on thermodynamic and transport properties concerning one or more solutes in different mixed solvent systems are greatly useful. Experimental studies on apparent molar volume, the viscosity of electrolytes and the temperature of solutions have been employed as a function of reviewing ion-ion and ion-solvent interactions [2]. The outcome of a number of workers [3] is that the accumulation of an electrolyte could disrupt or construct the structure of a liquid system. The accretion of solutes to a solution of electrolyte makes happen a variation in ion's solvation and often cause an enormous change in the reactivity of dissolved electrolytes present in the studied systems. The Physico-chemical property; viscosity of a liquid depending upon the intermolecular forces as well as structural features of the liquid can be inferred at different concentrations and temperatures of the solutions.

Since, ionic liquids comprise respective ions that could be available for the different types of interactions with susceptible solutes present in the systems under investigation, the Physico-chemical study of such systems provides a scope to investigate possible solute-solute and solute-solvent interactions for a wide range of solutes in a series of ionic liquids to determine the possibility of these solutes along with the definite solvents for general applications in chemistry and technology. The distinctive properties and uses of ionic liquids have made it possible for a new revolution in the field of materials sciences [4]. Presently, the importance of various studies on ionic liquids has developed in the way of pharmaceuticals and life sciences. In a review, Egorova et al. proposed that biochemical applications of ionic liquids will be the

most important research area in the near future [5]. Thus, ionic liquids are considerable of much attention in the field of sustainable chemical engineering, green chemistry, advanced material sciences etc.

The Physico-chemical properties of amino acids in various aqueous solutions are noteworthy to recognize the nature of interactions for understanding the characteristics of the chemical and biological systems. The stabilization of instinctive conformation of proteins is accompanied by various molecular interactions [6] like solute–solute, solute-solvent and solvent-solvent interactions.

L-Arginine is utilized by the cells of the immune system where the enzyme inducible NOS generates nitric oxide for cell signalling; oxidative bactericidal activities [7]. It is helpful to diminish infection rates, specifically in conditions that compromise immune function for example surgical procedures or precarious ailments [8]. On the other hand, L-Histidine is a nutritionally crucial amino acid with distinctive biochemical and physiological properties that have generated a good theoretical rationale to suggest the use of Histidine as a nutritional supplement in a wide range of circumstances. Primarily it was exposed to treat the patients with anaemia and rheumatoid arthritis having chronic renal failure [9].

Environmental characteristics in addition to "green chemistry" have attracted the attention of researchers on the usage of renewable raw resources for the designing and producing of ionic liquids. Therefore, in contemporary years, ionic liquids have been produced from amino acids, sugars, and terpenes [10]. Amino acid ionic liquids have a great hydrogen bonding capability convenient for dissolution of biomaterials for example DNA, cellulose, and different other carbohydrates [11]. This hydrogen bonding formation ability enhances its use as chiral solvents and substances for dissolution and stabilization of biomolecules like nucleic acids, cellulose, carbohydrates etc. in medicinal chemistry, synthetic chemistry along with pharmaceutical chemistry [12]. Specifically, in industrial and pharmaceutical chemistry, ionic liquids along with amino acids have many diverse applications, for example, an intermediate in the production of peptides, chiral solvents as well as absorbents for acid gases [13].

Quaternary ammonium-based ionic liquids may perhaps attract indeed the negatively charged constituents like bacterial proteins and successively gets denatured as a consequence of disorganization in the protein chain caused by the positive charge on the nitrogen atom. There are extensive volumetric and viscometric research works on amino acids in aqueous electrolyte solutions [14]. Accordingly, the study of the Physico-chemical properties of amino acids in aqueous solutions of ionic liquids will be very convenient for the procurement of information about several types of interactions taking place in these solutions, which are mostly hydrophobic

and electrostatic in nature. That eventually provide significant information about the insight into the conformational stability and unfolding activities of globular proteins.

Moreover, research works on solubility and stability of amino acids in the occurrence of ammonium-based ionic liquids are existing [15] but the study on Physico-chemical properties of amino acids in aqueous solutions of ammonium-based ionic liquids with respect to concentration and temperature are inadequate. Thus, with the aim to realize the actions of amino acids in ionic liquids and with the purpose of understanding the solvation behaviour of amino acids [16], we have tried to report herein Physico-chemical characteristics of L-Arginine and L-Histidine in aqueous Tetrabutylammonium methanesulphonate solution at temperatures 298.15 K, 303.15 K and 308.15 K. Several derived thermodynamic parameters such as density, viscosity, refractive index, surface tension, conductance study and also quantum chemical calculations have been considered to study the solvation behaviour in terms of Physico-chemical characteristics along with the effect of molality and temperatures on the interactions present in the solutions of amino acids; L-Arginine and L-Histidine of different concentration in aqueous Tetrabutylammonium methanesulphonate (TBMS) solution of 0.001 mole/kg, 0.003 mole/kg and 0.005 mole/kg. In this regard, different thermodynamic parameters i.e. apparent molar volume (Φ_v), limiting apparent molar volume (Φ_v^0), limiting molar expansivities (Φ_E^0), Surface tension (σ), refractive index (n_D), molar refraction (^R_M), Molar conductance (Λ), specific conductance (κ), viscosity A-, B-coefficients also temperature derivative of B; dB/dT; $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $\Delta H^{0\neq}$, and $T\Delta S^{0\neq}$, critical micelle concentration (CMC) values have been determined and analysed accordingly to understand more noticeably the interactions taking place in the studied solution mixtures.

2. Experimental Section

2.1 Source and Purity of Samples

Materials used in this work; Tetrabutylammonium methanesulphonate, $C_{17}H_{39}NO_3S$ (M.W. 337.6 g/mole) and amino acids, L-Arginine, $C_6H_{14}N_4O_2$ (M.W. 174.204 g/mole) and L-Histidine, $C_6H_9N_3O_2$ (M.W. 155.1546 g/mole) of purest grade were obtained from Sigma Aldrich Germany, SRL India and TLC Japan, respectively and was used as bought. The mass purity of studied IL was ≥ 0.98 and for studied amino acids were ≥ 0.99. Amino acids and IL were dried in a vacuum desiccator over anhydrous $CaCl_2$ for a minimum of 72 hours at room temperature and these were taken under consideration for the experiment without further purification. The amount of water content in IL (TBMS) was evaluated by Karl Fischer Titrator at approximately 0.05% (w%). A small amount of water has been considered for the preparations of stock solutions. To prepare the solutions, doubly distilled deionized water with a conductivity of approximately 0.7 $\mu S \cdot cm^{-1}$ was used. The specifications of chemicals used in this work are described in **Table 1.**

2.2 Apparatus and Procedure

To measure the densities (ρ) of experimental aqueous systems and the solutions of different concentrations at the different experimental temperatures, vibrating-tube Anton Paar Density-Meter (DMA 4500M) was used. The overall uncertainty in density was found to be in the range of ±0.00093 $g.cm^{-3}$. The instrument was calibrated by doubly distilled deionized degassed water and bypassing hot dry air [17]. The temperature was maintained within the range ±0.01 K with the help of an automatic built-in Peltier device.

Measurement of viscosities of the prepared solutions (η) under experiment was carried out by Brookfield DV-III Ultra Programmable Rheometer having a spindle size-42 with an accuracy of ±1%. The specifics about the viscometer have already been illustrated previously [18]. The instrument was calibrated using known viscosities of water and aqueous solutions of $CaCl_2$ by means of reference [19]. Prior to each investigation, calibration was done to avoid any unwanted errors. Brookfield Digital TC-500 temperature thermostat bath was used to maintain the experimental temperatures of the solutions.

Refractive indices of the experimental solutions were measured with the help of a Digital Refractometer Mettler Toledo with a light-emitting diode (LED). The accuracy for the refractive index measurement was almost ±0.0002 units. The refractometer was calibrated twice with distilled water before the measurement of the refractive indices of prepared solutions. The calibration of the instrument was repeated after a few seconds of each experiment [20]. The light source used was a light-emitting diode, λ=589.3 nm. The temperature of the experimental solutions was retained throughout the experiment in a Brookfield Digital TC-500 Thermostatic water bath.

Specific conductivity of the solutions was measured through Systronics- 308 conductivity meter of working frequency 1 kHz with an accuracy of ±1%. The cell constant was carried out using freshly prepared 0.01 M aqueous KCl solution [21] and it was maintained within the range 0.09–1.00 cm^{-1} during the experiment. All the solutions were placed in a dip-type immersion conductivity (CD-10) cell with a cell constant of about (0.1 ± 0.001) cm^{-1}. The cell was attached to a temperature-controlled water bath to sustain the investigational temperature. The cell constant was decided by means of the technique as suggested by Lind et al. [22].

To minimize any loss due to evaporation, sufficient precautions were taken in the course of the actual measurements. Mettler AG-285 electronic balance with a precision of ±0.01 mg was used for mass measurements to prepare stock solutions. After preparation of stock solutions of ionic liquid and amino acids were further used to prepare different concentration sets by proper dilution. Experimental density values were used to convert molarity into molality and the combined standard uncertainty according to mass purity was assessed as ±0.0071 mol. kg^{-1}.

K9 digital Tensiometer (KrussGmbH, Hamburg, Germany) instrument was used to determine the surface tension of different concentrations of mixed and pure experimental solutions. The accuracy of the instrument was±0.3mN/m For the determination of surface tension the platinum ring detachment technique was used. The calibration of the K9 digital Tensiometer was carried out with doubly distilled water and the calibration value of surface tension was found to be 71.6 mN/m which is in good agreement with the literature values of surface tension (71.99±0.05). This tensiometer is a very good precision instrument that contains a solid and vibration-free base. This instrument puts on such a place that same demand on its neighbour as a laboratory balance with a resolution of 0.1 mg. In addition, a clean and dust-free atmosphere is needed for the measurements of surface tension.

Theoretical i.e. Ab-initio calculations were executed through Gaussian09Wquantum chemical package [23].

3. Results and Discussion

Experimental values of density (ρ), viscosity (η), molar refraction ($^{R}_{M}$) of different molality (m) of aqueous TBMS solution at 298.15 K, 303.15 K and 308.15 K are presented in **Table S1. Table S2** provides the experimental values of refractive index (n_D), specific conductance (κ) and surface tension (σ) of different aqueous ionic liquid solutions of TBMS at temperatures 298.15 K, 303.15 K and 308.15 K.

3.1. Apparent Molar Volume

Here, we present information occurring the chemistry of ionic liquid interactions with amino acids in an aqueous solution that has been obtained from the apparent molar volume (Φ_v), limiting apparent molar volume (Φ_v^0) and experimental slope (S_v^*) of amino acid in an aqueous solution of ionic liquid. All the three parameters governed by the solvent environment surrounding solute molecules, give the information that relates to the structural penalties of solute-solvent interactions. The experimental values of density (ρ) at 0.001, 0.003 and 0.005 mole/kg concentrations of an aqueous ionic liquid solution of TBMS at 298.15 K, 303.15 K and 308.15 K for different concentrations of L-Arginine and L-Histidine solutions have been represented in Table S3. Table S4 provides the apparent molar volume (Φ_v) of L-Arginine and L-Histidine solution, respectively in (0.001, 0.003, 0.005) mole/kg aqueous ionic liquid (TBMS) solution at temperatures 298.15 K, 303.15 K and 308.15 K. This apparent molar volume is the summation of the geometric volume of the central solute molecule and deviations in the solvent volume owing to interaction with the solute nearby the periphery or co-sphere. The apparent molar volumes were calculated from the solution densities **(Table S3) of** the solutions using the following equation [24].

$$\Phi_V = M/\rho_0 - (\rho - \rho_0)/m\,\rho\rho_0 \quad (1)$$

where M stands for the molar mass of the solute, m signifies the molality of the solution, ρ and ρ_0 imply the densities of the solution and solvent respectively. The Φ_V values are positive and get decrease with the intensification of the concentration (molality, m) of (L-Arginine + TBMS + H_2O) and (L-Histidine + TBMS + H_2O) solutions. Conversely, Φ_V values increase with the increase in temperature at all the concentrations of L-Arginine and L-Histidine as well. The experimental values of Φ_V also increase with an increase in mass fraction of the aqueous TBMS solution accordingly. It was further observed that L-Arginine have Φ_V values higher than that of L-Histidine.

The limiting apparent molar volumes (Φ_V^0), i.e. apparent molar volume at infinite dilution were determined using a least-squares fitting linear method as the plots of Φ_V versus square root of the molar concentration, √m using the Masson equation as follows [23] to analyse the different interactions taking place in the solutions:

$$\Phi_V = \Phi_V^0 + S_V^*\sqrt{m} \quad (2)$$

where Φ_V^0, the limiting apparent molar volume at infinite dilution which shows the existence of interactions between solute-solvent and S_V^*stands for the experimental slope which gives the information about the nature of interactions between the solute molecules. **Table 2** represents the values of limiting apparent molar volumes (Φ_V^0) and experimental slopes (S_V^*) of L-Arginine and L-Histidine solutions, respectively in ionic liquid TBMS at experimental temperatures.

Figure 1 & 2 implies the variation of Φ_V^0 values of L-Arginine and L-Histidine solutions, respectively at 0.001, 0.003 and 0.005 (mole/kg), mass fraction of the ionic liquid TBMS and as a function of temperature. The positive Φ_V^0 values seem to increase with an increase in temperature as with the increase in the concentration of TBMS for both the amino acids. However, S_V^* values are negative for all the solutions and decrease with the rise in temperature and also with the increase in the concentration of the ionic liquid. Experimental data also reveal that L-Histidine has lower Φ_V^0 but higher S_V^* values in comparison to L-Arginine.

Positive Φ_V^0 values for all of the studied solvent mixtures show the presence of solute-solvent interactions. The order of solute-solvent interaction is (TBMS+L-Arg > TBMS+L-His) as represented in **Figures 1 & 2.** At infinite dilution, each solute molecule seems to be surrounded only by solvent molecules and keeps indefinitely distant from each other resulting in a greater extent of solute-solvent interaction rather than solute-solute interaction. Again the dipole-dipole interactions taking place in the solution phase that explains the above-mentioned order of interactions (solute-solvent), since higher the dipole-dipole interactions which suggested the

lower values of Φ_V as well as Φ_V^0. Theoretically, the dipole moment of TBMS, L-Arg, L-His were calculated with the help of the Gaussian 09 quantum chemical package are listed in **Table 12.**

A review of **Table 2** indicates that the positive Φ_V^0 values are maximum for L-Arginine in case of 0.005 m aqueous ionic liquid solution of TBMS at 308.15 K signifying utmost solute-solvent interaction and minimum for L-Histidine in case of 0.001 mole/kg aqueous ionic liquid solution at 298.15 K, suggesting the least solute-solvent interaction which was quite similar with some previous literature values [25]. This is perhaps owing to the release of a number of solvent molecules from unfastened solvation layers in the course of the solute-solvent interactions [26]. The higher Φ_V^0 values of L-Arginine specifies its more interaction with TBMS than that of L-Histidine under experimental conditions. Further, the S_V^* values point toward the extent of solute-solute interaction taking place in the mixture of solutions. The values of S_V^* are negative for all the experimental solutions which were in good agreement with the previous literature values [14, 25]. The higher values of S_V^* in L-Histidine seem to be the presence of interaction among itself to a greater extent in comparison to L-Arginine in respect of all the experimental conditions. This may be due to the presence of the imidazole side chain in the skeletal structure of L-Histidine as depicted by their molecular structures in **Scheme 1.**

Comparing the magnitude of Φ_V^0 and S_V^* values quantitatively, it was observed that Φ_V^0 values are much greater in magnitude than S_V^* values for all the experimental solutions and under all conditions. This recommends, the occurrence of stronger solute-solvent interactions and weaker solute-solute interactions in all the solutions [27-28]. There may be the effect of hydrophobic hydration or the caging effect of water molecules present in the solution mixtures [29] resulting in hydrophobic interactions occurring in amino acids that cause volume contractions. Thus the values of S_V* given in **Table 2,** provides useful information about solute−solute interactions [30]. The positive sign of the slope specifies interactions between the hydrophilic groups in solution, while the negative sign leads to the hydrophobic cospheres as described by Hedwig [31]. Here the values of S_V* are negative indicating weak solute−solute interactions. The same trend was observed by Harsh Kumar et al. [32].

Through **Scheme 3** the plausible molecular interactions occurring in the ionic liquid with two amino acids may be interpreted.

The temperature dependence of Φ_V^0, studied here in the solution mixture from 298.15 K to 308.15 K at the interval of 5 K of temperature can be expressed by the following polynomial equation [33] as follows:

$$\Phi_V^0 = a_0 + a_1 T + a_2 T^2 \qquad (3)$$

Where T is the temperature in Kelvin scale. The values of coefficients a_0, a_1 and a_2 are three empirical coefficients depending on the nature of the solute and mass fraction (W) of solvent at (298.15, 303.15 and 308.15) K. The empirical coefficient values (a_0, a_1 and a_2) of L-Arginine and L-Histidine solution in different concentration (0.001, 0.003, 0.005) mole/kg of the TBMS at 298.15 K, 303.15 K and 308.15 K are recorded in **Table 3.**

Partial molar volume of transfer at infinite dilution is calculated using eq. 4 as given bellow and represented in **Table S5.**

$$\Delta\Phi_v^0 = \Phi_v^0 \text{(in aqueous IL)} - \Phi_v^0 \text{(in water)} \quad (4)$$

The obtained values of partial molar volume of transfer at infinite dilution are all positive and increase with an increase in the concentration of ionic liquid. The co-sphere overlap model plays a dynamic role in defining the nature of interactions occurring in the system. In fact, there are three discrete forms of interactions between TBMS+L-Arg and TBMS+L-His in view of the Cosphere overlap model [34-35]. (i) ion-ion interactions between COO^- group of amino acids with [N+] part of TBMS and $-NH_3^+$ groups of the amino acids with the negative part ($CH_3SO_3^-$) of TBMS; (ii) ion-hydrophobic interactions between the $-NH_3^+$ or COO^- of amino acids and hydrophobic portion (alkyl part) of IL TBMS; (iii) H-bonding interaction between the negative part ($CH_3SO_3^-$) of the IL, one (N-H) part of the imidazole ring and hydrogens attached with N in the amino acids and (iv) hydrophobic-hydrophobic interactions between the hydrophobic parts of the amino acids and alkyl part of TBMS that may be more operative in the present analysis. A negative value of transfer volume is approved by ion−hydrophobic interactions and hydrophobic−hydrophobic interactions while ion−hydrophilic and hydrophilic−hydrophilic interactions demonstrate reverse contributions toward $\Delta\Phi_v^0$ values. The accumulation of co-solutes to the aqueous solution of ionic liquids rescinds the cage structure of solvent and solute. In the present system, the ion−ion interactions prevail to a greater extent than the hydrophobic−hydrophilic and hydrophobic−hydrophobic interactions resulting in a positive change in volumes. Thus the positive transfer values reproduce the strong ion−ion interactions of amino acids with ionic liquids.

$$\Phi_E^0 = (\delta\Phi_v^0 / \delta T)_P = a_1 + 2a_2T \quad (5)$$

The values of Φ_E^0, assess the extent of long-range structure-making or structure breaking potential of a solute in a solution mixture. The values of Φ_E^0 for the studied solution mixtures at (298.15, 308.15, and 318.15) K are recorded in **Table 4.**

The positive Φ_E^0 values except for a little negative value for 0.005 mole/kg IL solution of L-Histidine, for all of the examined solutions at all the temperatures, suggest that expansivities of all the experimental solutions are greater than that of the pure solvent. Also, it has been

observed that the Φ_E^0 values of the solutions are getting decreased with increase in temperature which indicates that some water molecules may be removed free from the hydration layers by increasing the temperature resulting in the increase of the solution volume faster to some extent than that of the pure solvent [36]. Also, positive Φ_E^0 values suggest the absence of caging or packing effect in the investigated solutions at all the temperatures.

The solute-solvent interaction may cause structure break or synergistic structure make. In this regard, Hepler developed a way to inspect the nature of the solute-solvent interaction going on in the solution phase [37]. According to Hepler opinion, $(\delta\Phi_E^0/\delta T)_P$ values determine whether the interaction is structure breaker or structure maker [38].

$$(\delta\Phi_E^0/\delta T)_P = (\delta^2\Phi_v^0 / \delta T^2)_P = 2a_2 \qquad (6)$$

In general, negative and small positive $(\delta\Phi_E^0/\delta T)_P$ values intensely show structure-breaking more willingly than structure-making interaction. In our case, the negative values recorded in **Table 4** respectively for L-Arginine and L-Histidine solutions in IL (TBMS) at 298.15 K, 303.15 K and 308.15 K temperatures endorse that the solute-solvent interaction acts as a structure-breaker. Thus all in the solutions, both the amino acids (solutes) are undoubtedly structure–breakers and result in disruption of the solvent structure with increasing solute-solvent interactions.

3.2. Viscosity

In the case of aqueous electrolytic solutions, the extent of ionic hydration [39] as well as structural interactions [40-41] within the ionic hydration cospheres [42] can be exposed by reviewing the viscosity coefficient with changing concentration and also the temperature of the aqueous solution. **Table S6** and **Table S7** provide viscosity (η) values of L-Arginine and L-Histidine in aqueous ionic liquid solution which were in good agreement with the earlier literature values [14, 25] at temperatures 298.15 K, 303.15 K and 303.15 K respectively. The experimental results indicate that the viscosity of all the studied solutions increases with increasing the molality of IL solutions. Sarkar et al. also studied on Physico-chemical properties of TBMS [43]. This may be due to the increasing number of collisions taking place among the molecules with the increase in molality of the ionic liquid causing a loss of kinetic energy, the molecules are likely to be disposed to stick together with increasing viscosity.

Viscosity data obtained were studied with the help of the Jones-Dole equation [44].

$$\eta_r = \eta / \eta^0 = 1 + A\sqrt{c} + Bc \qquad (7)$$

Where η and η^0 signify viscosities of solution and solvent respectively, c stands for the concentration of the solution in molality. Experimental Values of $(\eta/\eta^0 - 1)/\sqrt{m}$ for all the studied solution mixtures in 0.001, 0.003 and 0.005 mole/kg aqueous IL solution at temperatures 298.15 K, 303.15 K and 303.15 K have been represented in **Table S6** and **Table S7.**

The experimental values of $(\eta/\eta^0 - 1)/\sqrt{m}$ are positive and increase with increasing concentration of both the amino acids in solutions and also with increasing temperature from 298.15 K to 308.15 K. Further, the $(\eta/\eta^0 - 1)/\sqrt{m}$ values seem to be increased with the concentration of aqueous IL (TBMS) solution from 0.001 mole/kg to 0.005 mole/kg accordingly.

Rearranging the above Equation (7) following equation is obtained:

$$(\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \qquad (8)$$

In the above equation, viscosity *A*-coefficient is a constant, also recognized as Falkenhagen coefficient [45] signifying long-range coulombic forces representing the solute-solute interaction and a weak solute–solute interaction (amino acid-amino acid) in solution mixtures as also observed from previous investigations. The *B*-coefficient is an adjustable parameter in this equation, which determines the extent of the effective hydrodynamic volume and reveals the solute-solvent interactions [46]. It is governed by the size and shapes effect of solute as well as structural effect persuaded by solute-solvent interaction as also happened in the present study that the viscosity *B*-coefficient values are positive in all conditions and quite greater than the A-coefficient indicating dominancy of the solute-solvent interaction over the solute–solute interaction. The viscosity *B*-coefficient seems to be increased with increasing temperature and also mass fraction of aqueous TBMS mixture implying that the solute-solvent interaction is developing with increasing mass fraction of TBMS mixture along with the temperature. In relation to the Jones-Dole equation the values of viscosity *A*- and *B*-coefficients obtained by linear least-square analysis from the plots of $(\eta_r - 1)/\sqrt{c}$ vs $\sqrt{c}$, are reported in Table 5 for L-Arginine and L-Histidine solutions at temperatures 298.15 K, 303.15 K and 303.15 K. **Figure 3** and **Figure 4** show the variation of *B* values of L-Arginine and L-Histidine respectively against 0.001, 0.003 and 0.005 mole/kg IL solutions as a function of temperature whereas, Figure S1 and Figure S2 represent the variation of viscosity *B*-coefficient of L-Arginine and L-Histidine against temperature in different concentration of IL respectively.

Table 5 show that the viscosity *B*-coefficient are positive for all the studied solutions signifying the existence of strong solute-solvent interactions that strengthen with an increase in the solvent viscosity value, which also supports the results obtained from Φ_v^0 values described before. Conversely, the negative values of the viscosity *A*-coefficient for most of the cases are smaller in comparison to viscosity *B*-coefficients thereby, indicating solute-solvent interactions are prominent over the solute-solute interactions. These outcomes specify the presence of very

weak solute–solute interactions in the solutions which also qualify with the results obtained from S_v^* values. The solute-solvent interaction obtained from the viscosity *B*-coefficient which were in good agreement with the former literature values [14, 21-25] takes place into the local vicinity of the solute molecules in the solution mixtures. The higher *B*-coefficient values for higher viscosity values is due to the solvated solute molecules associated by the solvent molecules all around because of the formation of an associated molecule by solute-solvent interactions [47]. Again, here the solute-solvent interactions are getting more strengthened with the increasing temperatures and also with the concentration of the IL solutions with more interaction between L-Arginine and aqueous IL solutions. The B-values of L-Arginine in aqueous TBMS solution in all respects are much larger than that for L-Histidine that signifying a greater solute-solvent interaction prevails in L-Arginine and aqueous TBMS solution. These consequences are comparable to those achieved from Φ_v^0 values.

Further, extensive study of the viscosity *B*-coefficient shows that the first derivative of *B*-coefficient over temperature is a measure of viscosity *B*-coefficient in visualizing the nature of solute-solvent interaction as structure-breaker or structure-maker. The *dB/dT* values determine the measure of activation energy necessary for the viscous flow in the solution. The measure of *dB/dT* is more indicative of the structure making or structure breaking ability than the sign or magnitude of the *B*-coefficient [48-49]. **Table 5** represent the values viscosity *B*-coefficients of L-Arginine and L-Histidine solutions along with the values of *dB/dT* at 0.001, 0.003 and 0.005 mole/kg solution of IL at (298.15, 303.15 and 308.15) K. The small positive values of dB/dT for all the experimental solutions designate about the structure-breaker effect of the L-Arginine and also L-Histidine in the aqueous ionic liquid solution of TBMS. The *dB/dT* theory as in Eyring's viscosity theory [50], indicates the negative value of *dB/dT* resembles the presence of higher energy of activation for viscous flow in solution rather than in pure solvent.

Overall, positive *B*-coefficient values suggest kosmotropes because strongly and firmly hydrated solutes exhibit a greater improvement in viscosity with concentration, while negative *B*-coefficients suggest chaotropes for weakly and feebly hydrated solutes [51]. In contrast, viscosity B-coefficients may not be evocative all the cases, predominantly for large hydrophobic components but the sign and magnitude of the *B*-coefficient, the values of is a superior indicator of the degree of structure-making or breaking potential [52-53]. The ratio of (B/Φ_v^0) which has a high value [54] indicates that the primary solvation shell is formed.

According to **Table 5** and **Table 6,** *B*-coefficients for both the amino acids increase with temperature (positive *dB/dT*) and also the high value of the ratio (B/Φ_v^0) signifying the construction of a primary solvation shell as structure-disruptor.

Eyring and co-workers [50], show that the free energy of activation, $\Delta\mu_1^{0\neq}$ per mole of the solvent of viscous flow can be determined using the equation as follows:

$$\eta_o = \frac{hN}{V_1^0} exp\ (\frac{\Delta\mu 1^{0\#}}{RT}) \qquad (9)$$

where h means Planck's constant, N_A represents Avogadro's number and V_1^0 indicates the solvent's partial molar volume. This can be reorganized as the equation (10)

$$\Delta\mu_1^{0\neq} = RT \ln (\eta_0\ V_1^0 / hN_A) \qquad (10)$$

If Equations. (8) as well as (10) [55-56] are followed, then the following equation can be obtained

$$B = (V_1^0 - V_2^0) / 1000 + V_1^0\ (\Delta\mu_1^{0\#} - \Delta\mu_2^{0\neq}) / 1000\ RT \qquad (11)$$

where V_2^0 is limiting partial molar volume (Φ_v^0) of the solute present, $\Delta\mu_2^{0\neq}$ denotes ionic activation energy per mole of solute at infinite dilution. From the equation. (11), the following equation can be get

$$\Delta\mu_2^{0\#} = \Delta\mu_1^{0\#} + \frac{RT}{V_1^0}[B - (V_1^0 - V_2^0] \qquad (12)$$

Table 7 shows that the $\Delta\mu_2^{0\neq}$ values are all positive and much higher than $\Delta\mu_1^{0\neq}$ representing that in the ground state, the interaction between the amino acids and the aqueous TBMS mixture is stronger than that in the transition state. The entropy for activation, $\Delta S_2^{0\neq}$ [57] of the experimental solution mixtures has been calculated using the following equation

$$d(\Delta\mu_2^{0\#}) / dt = - \Delta S_2^{0\neq} \qquad (13)$$

Using the least-squares method, the value of $\Delta S_2^{0\#}$ has been obtained from the negative slope of the plots of $\Delta\mu_2^{0\neq}$ versus T.

Enthalpy of activation, $\Delta H_2^{0\neq}$ [57] has been calculated from the following relation

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\ \Delta S_2^{0\neq} \qquad (14)$$

Values of $\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ are also represented in **Table 7** which displays that the value of $\Delta\mu_2^{0\neq}$ depends on the viscosity coefficients and the terms (V_1^0 -V_2^0). $\Delta\mu_2^{0\neq}$ is the variation in free energy of activation of viscous flow per mole of aqueous amino acid solutions in presence of ionic liquid TBMS. The transition state theory states that the solvent molecules should pass through the viscous transition state. In view of Feakins et al. [55], if $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$ for positive viscosity B-coefficient that indicates greater solute-solvent interactions resulting in the formation of the transition state followed by breaking and altering the intermolecular forces prevailing in the solvent structure of the medium [57-58]. Further positive values of $\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ suggest that the formation of the transition state is associated with bond-breaking and rising accordingly.

However, any specific mechanism in this context is quite difficult to develop though the disordered state of the slip-plane may be proposed [57]. Finally, according to Feakins et al. model, as $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$ both the amino acids performs as structure breakers that again supports the *dB/dT* characteristics in an aqueous TBMS mixture.

3.3. Refractive Index

Optical Data of the refractive index of the experimental solutions provide important information regarding molecular interactions in terms of molecular structures in the solutions. Refractive index signifies the speed of light which with increasing concentration due to interactions among the components of a system value also increase. The refractive index of a solution mixture can be interrelated by the application of a composition-dependent polynomial equation and molar refraction; $^{R}_{M}$ in solution.

The molar refraction $^{R}_{M}$ can be estimated from the Lorentz–Lorenz relation as follows [59]:

$$^{R}_{M} = \{(n_D^2 - 1) / (n_D^2 + 2)\}(M/\rho) \qquad (15)$$

where $^{R}_{M}$, n_D, M and ρ stand for the molar refraction, the refractive index, the molar mass and the density of the solution, respectively. The refractive index of a substance refers to its ability to refract light as it travels from one medium to another and consequently, the higher the refractive index of a system, the more the light gets refracted [60]. It can simultaneously measure the compactness of that system involved in my research work. Further, as opined by Deetlefs et al. the refractive index of a substance is higher when its molecules are more strongly packed or generally while the substance is denser [61].

Table S8 and **Table S9** represent the experimental values of refractive index (n_D) and molar refraction ($^{R}_{M}$) of L-Arginine and L-Histidine in different concentrations (0.001, 0.003 and 0.005 mole/kg) of aqueous IL; Tetrabutylammonium methanesulphonate at temperatures 298.15 K, 303.15 K and 308.15 K, respectively.

From the experimental values of refractive index (n_D) and molar refraction ($^{R}_{M}$), it has been observed that refractive index (n_D) values for all the solutions decrease with increasing temperature whereas molar refraction ($^{R}_{M}$) values show the opposite trend with increasing temperature. But, both the parameters (n_D) and ($^{R}_{M}$) display an increasing trend with an increase in the concentration of L-Arginine and L-Histidine and also the concentration of ionic liquid solutions. Again, L-Arginine shows higher values of refractive index (n_D) than L-Histidine. This result is in good agreement with the volumetric and viscometric results obtained earlier. Analysis of the data from **Table S2** and **Table 8** enables us to draw the sequence of compactness of the systems indicating that the molecules are more tightly packed in the solution mixture of L-

Arginine. Therefore, the higher refractive index values for the L-Arginine indicate the presence of more tightly packed molecules in the solution. The following is the sequence of compactness of the two systems in the solution phase; (TBMS+L-Arg) > (TBMS+L-His) [25].

The limiting molar refraction, ($^{R}_{M}{}^{0}$) listed in Table 8 can be determined from the following equation-

$$^{R}_{M} = {}^{R}_{M}{}^{0} + R_S\sqrt{m} \qquad (16)$$

where 'm' is the molality of solution and $^{R}_{M}{}^{0}$ is the limiting molar refraction that suggests solute-solvent interaction. This study of limiting molar refraction operates as an informative parameter for studying the molecular interaction that takes place in the solution. **Figure 5** show a gradual increase in the values of $^{R}_{M}{}^{0}$ with the rise in the concentration of co-solvent and temperature that also supports the fact that here the solute-solvent interaction dominates over solute-solute interactions and is reinforced with an increase in temperature and also the mass fraction of aqueous TBMS mixture. The $^{R}_{M}{}^{0}$ values of L-Arginine in aqueous TBMS solution are much higher than that for L-Histidine, representing a greater extent of solute-solvent interaction prevailing in L-Arginine that were found to be similar remarks as assessed from apparent molar volume and viscosity B-coefficients mentioned earlier.

3.4 Electrical Conductance

The nature of solute-solvent interactions and the structure making or structure breaking tendency of components in a given solvent can be assumed with the help of an electrical conductance study. The conductance study of the interaction (solute-solvent) between L-Arginine and L- Histidine with the aqueous solution of ILs, BTAMS has been performed at three different temperatures. The advantage of this study is that this measurement provides information about the interaction and transport phenomena of the (L-Arg + ILs + H_2O) and (L-His + ILs + H_2O) ternary systems [62]. Experimental values of specific conductance (κ) of different molality of aqueous IL(TBMS) solution at 298.15 K, 303.15 K and 308.15 K are represented in **Table S10.** Such a type of investigation was also done by Sarkar et al. [44]. The specific conductance (κ) values increase with increasing temperature and also with the increase in the concentration of aqueous IL solution and the solutions of L-Arginine and L-Histidine. However, the molar conductance (Λ) values as reported in **Table 9,** decrease with the increasing concentration of L-Arginine and L-Histidine solutions. On the other hand, solutions of L-Histidine have higher molar conductance (Λ) values in comparison to that of L-Arginine under all experimental conditions.

Figure 6 and **Figure 7** provide the variation of molar conductance (Λ) with different concentrations of amino acids, L-Arginine and L-Histidine in aqueous (0.001, 0.003, 0.005)m of IL (TBMS) solution at different temperature 298.15 K, 303.15 K and 308.15 K respectively.

The molar conductance (Λ) is obtained from the values of specific conductance (κ) with the help of the following equation [41]:

$$\Lambda = (1000\kappa) / C \quad (17)$$

Linear conductivity curves (Λ vs. C) were estimated for the amino acids; L-Arginine and L-Histidine in IL solutions and extrapolation of $\sqrt{C} = 0$ were used to calculate the limiting molar conductance. It has been observed that Λ value increases with increasing temperature for every experimental system and with increasing concentration of amino acids as well as IL (TBMS) solutions. While gradual addition of either L-Arginine or L-Histidine to ILs solution causes a constant decrease in molar conductance values. Here, the mobility of the ions present in solution plays the principal role, despite developing ionic substances on the addition of aqueous L-Arginine or L-Histidine solution [63] showing the decreasing trend of molar conductance values. It may be caused by the solute-solvent interaction governed by the ion-hydrophilic, ion hydrophobic as well as hydrophobic-hydrophobic interaction occurring in the solution mixtures. The development of the molecular association, therefore, forces the ionic substances to be less mobile indicating such conductivity results of the present study. Thus, the conductometric study also supports the observation obtained from the investigation of density, viscosity, refractive index and surface tension as well.

Furthermore, in order to investigate the critical micelle concentration (CMC) value of studied ionic liquid TBMS and the amino acids under experiment, we have made systematic measurements of electrical conductance. The different concentrations, 0.001, 0.003, 0.005 molality/mol.kg^{-1} of TBMS solutions are stepwise added for the measurement of the conductance in a fixed amount of amino acids (0.01 mol/kg, 20 mL) at different temperatures. The conductivity data in this regard are listed in **Table S11-S13** and **S14-S16** and the plots related to it are shown in Figure S3, S4, S5. From the figures, it is clear that there is present a sharp breakpoint in each case in different temperatures and concentrations that are summarized in Table 10. Thus the CMC value so obtained are of good agreement with the former study and reveals that the solute-solvent interactions are predominating over solute-solute interaction in the case of TBMS+L-Arginine than TBMS+L-Histidine in each concentration and temperature.

3.5 Surface Tension

The investigation of surface tension is of great importance in many scientific and technological fields. As an important parameter, surface tension is the unique most available experimental parameter that designates the thermodynamic features and provides information about the internal structure of the studied liquid systems. From **Table 11** and also **Figure 8** and **9,** it is observed that with increasing the concentration of ionic liquid in water the surface tension decreases because the molecules of the ionic liquid can get aggregates in water [64].

However, when the addition of amino acid takes place into the ionic liquid solution, the solute molecule can interact with ionic liquid and aggregation of ionic liquid decreases, as a result the surface tension gradually increases. The Tetra butylammonium methanesulphonate (IL) has a long butyl chain, so it can easily aggregate in water with increasing the concentration of ionic liquid, therefore, the surface tension generally decreases but with the addition of L-Arginine and L-Histidine in the ionic liquid mixture, the surface tension increases due to the inward pull of the solute molecules (L-Arginine, L-Histidine) from the surface by the bulk molecules (Ionic liquid). The inward pull of solute molecules depends upon the interaction between the L-Arginine and L-Histidine with the ionic liquid mixture [65]. The values obtained from the surface tension measurement, it was observed that the surface tension of the solution mixtures of L-Arginine is greater than the L-Histidine solution, which indicates the higher inward pull taking place in the case of L-Arginine solution mixture and can be illustrated by the interaction between zwitterionic groups of amino acids and a polar solvent, therefore, the solute-solvent interaction is more prominent in L-Arginine solution than that of L-Histidine solution.

3.6 Gaussian 09W Quantum Chemical Calculation: Theoretical basis of the Interaction

Theoretically, this field is very much important. For applying in quantum, mechanical calculation there is no use or maintenance sequence of configurations and no straight use of known structure. The main idea is to establish a realistic function that replicates the physical forces and chemical contacts. UB3YLP function is used for the calculation. Diffused basic functions are found to be effective in describing the weak interaction associated with the atoms in molecules. For this purpose, we have used a basis set 6-311G (d) for an exact description of performing weak interaction prevail in the transition structures.

This calculation has been carried out through Gaussian 09W quantum chemical package. The quantum mechanical calculations of optimum energy estimate the extent of $O\cdots N\cdots O$, $C{=}O\cdots O-H$ interactions. Such interaction involving in L-Arginine and L-Histidine cluster in the sphere of ionic liquid [66] the aforesaid statements were well thought out in our present work. We depicted the molecular assembly between the L-Arg$\cdots$IL(1) and L-His $\cdots$IL(1) through quantum chemical calculations which support the existence of such type of cluster. The calculated theoretical value through Gaussian 09w quantum mechanical tools that support the above results obtained from different types of experimental parameters in the manuscript.The several properties of different systems in computational technique are summarized in **Table 12.**

The extent of stabilization energy of pure and as well as their molecular assembly can be evaluated by optimization energy value. While the formation of molecular gather is assorted by the solute-solvent interaction in the solution phase. The value of optimization energy can explain the possibility of higher solute-solvent interaction. More minimization of optimization energy, higher is the solute-solvent interaction associated with the atmos. Prominent solute-solvent

interaction is observed in (TBMS+L-Arg+H_2O) system over (TBMS+L-His+H_2O) system and discussed here with especially in consort with the optimum geometry of the system depicted in **Scheme 2.**

The solute molecule surrounded by solvent molecule by non-covalent interaction can also be explained on the basis of thermodynamics [67].

4. Conclusion

The aim of the present paper was to establish the nature of solute-solute and solute-solvent interactions in the solutions of TBMS + amino acid systems of several concentrations and temperatures for chemical and technological applications. The investigation of Physico-chemical parameters through density, viscosity, refractive index, surface tension and conductance study refers to the mode of interactions taking place in the amino acids; L-Arginine and L-Histidine in ionic liquid solutions of TBMS at different concentrations as well as different temperatures. In the present study, all the parameters were interpreted in terms of solute–solute and solute-solvent interactions occurring among the various components of the experimental solution mixtures. Analysis of apparent molar volume, limiting apparent molar volume, molar refraction, limiting molar refraction, viscosity B coefficient and surface tension signify the solute-solvent interaction is predominant over solute–solute interaction. The $(\delta\Phi_E^0/\delta T)_P$ and (dB/dT) values have been considered to illustrate the facts that, the solute-solvent interaction is significantly structure breaking which is further established by Hepler's constant values. From the study of the investigated solutions presence of strong solute-solvent interaction was observed and also supposed to be more effective and predominant than the solute–solute interaction occurring in experimental systems. Amino acid L-Histidine fused with the imidazole ring undergoes a lower degree of interactions in the presence of ionic liquid (TBMS) as compared to L-Arginine. Surface tension indicated the starring role of the hydrophilic and hydrophobic character of solutes in molecular interactions with TBMS in aqueous solutions. Again, conductance data also recommends the mode of interactions going on between the solute and solvent thereby the presence of mobility in the solution phase. Ultimately, strong hydrophobic-hydrophobic interactions are playing an important role too. Furthermore, electrostatic and hydrophobic interactions are more predominant for the L-Arginine-TBMS system, associating the experimental outcomes. The experiment definitely would provide for a more inclusive understanding of such systems to a large extent.

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Tables

Table 1. Specification of chemical samples.

SL. No.	Name of Chemicals and their IUPAC name	CAS NO.	Supplier	[b]Purity of Mass Fraction	[a]Water Contain (w%)	Molar mass(g/mole)
1	Tetrabutylammonium Methanesulphonate ($C_{17}H_{39}NO_3S$) methanesulfonate;tetrabutylazanium	65411-49- 6	Sigma Aldrich	≥ 0.98	~0.05%	337.6
2	L-Arginine ($C_6H_{14}N_4O_2$) (S)-2-Amino-5-guanidinopentanoic acid	74-79-3	SRL	≥0.99	−	174.204
3	L-Histidine ($C_6H_9N_3O_2$) (2S)-2-amino-3-(1H-imidazol-5-yl)propanoic acid	71-00-1	TLC	≥0.99	−	155.1546

[a]The (w%) of water in TBMS(IL) are measured by using the Karl–Fischer Titrator.

[b]amino acids and IL are dried in a vacuum desiccator minimum of 72 hours over anhydrous $CaCl_2$.

All chemicals are taken without further purification**.**

Table 2. Limiting apparent molar volumes (Φ_v^0) and Experimental slopes (S_v^*) of (L-ARGININE+TBMS+H_2O) and (L-HISTIDINE+TBMS+H_2O) systems in aqueous solutions of (0.001, 0.003, 0.005) m IL (TBMS) at 298.15 K, 303.15 K, 308.15 K at atmospheric pressure 0.1MPa.

Temperature/ (K)	Φ_v^0 x 10^6 /(m^3. mol^{-1})	S_v^* x 10^6 /(m^3. $mol^{-3/2}$.$kg^{1/2}$)	Φ_v^0 x 10^6 /(m^3. mol^{-1})	S_v^* x 10^6 /(m^3.$mol^{-3/2}$.$kg^{1/2}$)
(L-ARGININE+TBMS+H_2O)system			(L-Histidine+TBMS +H_2O)system	
0.001mIL/mol.kg^{-1}				
298.15K	127.46±0.02	-9.85±0.01	103.20 ±0.01	-7.74 ±0.01
303.15K	129.28±0.01	-16.00±0.01	104.76 ±0.00	-11.99±0.03
308.15K	130.59±0.01	-17.12±0.01	106.09 ±0.00	-14.24±0.01
0.003mIL/ mol.kg^{-1}				
298.15K	130.63±0.02	-20.11±0.03	105.92±0.01	-15.50±0.01
303.15K	133.87±0.02	-28.65±0.01	107.71±0.00	-19.00±.00
308.15K	136.06±0.01	-33.40±0.01	108.92±0.01	-20.67±0.02
0.005mIL/ mol.kg-1				
298.15K	131.74±0.01	-23.16±0.02	107.17±0.00	-18.03±0.01
303.15K	135.53±0.00	-32.65±0.03	109.15±0.00	-26.92±0.01
308.15K	137.36±0.03	-38.42±0.04	109.75±0.00	-28.10±0.00

*Standard uncertainties values of u are: u (T) =±0.01K (0.68 level of confidence), #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}. *molality has been expressed per kg of (TBMS + water) solvent mixture. * Standard uncertainty in pressure u (P)= ±0.01 MPa.

Table 3. Empirical coefficient values (a_0, a_1 and a_2) of L-Arginine & L-Histidine in different concentrations (0.001, 0.003, 0.005)m in aqueous IL (TBMS) solutions at 298.15 K, 303.15 K, 308.15 K and at atmospheric pressure 0.1MPa.

Molality of IL /mol.kg-1	a_0 x 10^6 /m^3mol^{-1}	a_1 x 10^6 /$m^3mol^{-1}K^{-1}$	a_2 x 10^6 /$m^3mol^{-1}K^{-2}$	a_0 x 10^6 /m^3mol^{-1}	a_1 x 10^6 /$m^3mol^{-1}K^{-1}$	a_2 x 10^6 /$m^3mol^{-1}K^{-2}$
0.001	-902.99	6.4973	-0.0102	-405.59	3.078	-0.0046
0.003	-1960.6	13.275	-0.0210	-1049.3	7.3331	-0.0116
0.005	-3637.3	24.329	-0.0392	-2505.5	16.992	-0.0276

*Standard uncertainties values of u are: u (T) =±0.01K, Standard uncertainty in pressure u (P)= ±0.01 MPa *molality has been expressed per kg of (TBMS + water) solvent mixture. *#Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}.

Table 4. Values of limiting molar expansivities Φ_E^0 & $(\delta\Phi_E^0/\delta T)_P$ of L-Arginine and L-Histidine of different concentrations (0.001, 0.003, 0.005) m in aqueous IL (TBMS) solutions at different temperature and pressure 0.1MPa

Molality of IL/ mol.kg-1	$\Phi_E^0 \times 10^6$ /m^3 mol^{-1} K^{-1}	$(\delta\Phi_E^0/\delta T)_P \times 10^6$/$m^3$ mol^{-1} K^{-2}	$\Phi_E^0 \times 10^6$ /m^3 mol^{-1} K^{-1}	$(\delta\Phi_E^0/\delta T)_P \times 10^6$/$m^3$ mol^{-1} K^{-2}
	298.15K 303.15K 308.15K		298.15K 303.15K 308.15K	
0.001	0.41504 0.31304 0.21104	-0.0204	0.33502 0.28902 0.24302	-0.0092
0.003	0.7527 0.5427 0.3327	-0.0420	0.41602 0.30002 0.18402	-0.0232
0.005	0.95404 0.56204 0.17004	-0.0784	0.53412 0.25812 -0.01788	-0.0552

Standard uncertainties values of u are: u (T) =±0.01K, Standard uncertainty in pressure u (P)=± 0.01 MPa. *molality has been expressed per kg of (TBMS + water) solvent mixture. * #Combined standard uncertainties in molality according to stated purity u((m) =±0.0092 mol kg^{-1}.

Table 5. Viscosity *B*-coefficients, *A*-coefficients of (L-ARGININE+TBMS+H_2O) and L-HISTIDINE+TBMS+H_2O) systems along with *dB/dT* values in aqueous IL(TBMS) solutions of different concentrations (0.001,0.003,0.005)m at 298.15 K, 303.15 K, 308.15 K and at atmospheric pressure 0.1MPa.

	0.001mIL/ mol.kg-1		0.003mIL/ mol.kg-1		0.005mIL/ mol.kg-1		dB/dT
Temperature (K)	B (kg ½ $mol^{1/2}$)	A ($kg.mol^{-1)}$	B (kg ½ $mol^{1/2}$)	A ($kg.mol^{-1}$)	B (kg ½ $mol^{1/2}$)	A ($kg.mol^{-1}$)	
(L-ARGININE+TBMS+H_2O)							
298.15	0.632±0.013	0.026	0.707±0.012	0.025	0.819±0.014	0.024	0.027
303.15	0.816±0.013	0.024	0.888±0.012	0.024	0.971±0.014	0.023	0.029
308.15	0.904±0.013	0.023	0.999±0.012	0.022	1.116±0.014	0.017	0.029
(L-HISTIDINE+TBMS+H_2O)							
298.15	0.467±0.011	0.033	0.572±0.012	0.032	0.662±0.013	0.031	0.019
303.15	0.580±0.011	0.032	0.671±0.012	0.028	0.757±0.013	0.025	0.020
308.15	0.658±0.011	0.026	0.769±0.012	0.026	0.874±0.013	0.019	0.021

*Standard uncertainties values of u are: u (T) =±0.01K (0.68 level of confidence), Falkenhagen coefficient (A), Viscosity *B*-Coefficients (B) are given in the parentheses. *Standard uncertainty in pressure u (P)= 0.01 MPa *molality has been expressed per kg of (TBMS + water) solvent mixture. *#Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}.

Table 6. Values of (B/Φ_v^0) for L-Arginine and L-Histidine in different concentrations of aqueous TBMS (IL) solutions at different temperature and atmospheric pressure 0.1MPa.

Temperature (K)	B / Φ_v^0			B / Φ_v^0		
	0.001m	0.003m	0.005m	0.001m	0.003m	0.005m
	L-ARGININE+ aq.TBMS			L-HISTIDINE +aq.TBMS		
298.15	4.960	5.415	6.218	4.527	5.401	6.178
303.15	6.312	6.640	7.169	5.659	6.237	6.940
308.15	6.927	7.348	8.129	6.139	7.062	7.963

[a]Mass fractions of TBMS in aqueous solution; #Standard uncertainty in molality u (m) = ±0.0001mol kg^{-1}. *Standard uncertainty in temperature u (T) = ± 0.01 K. *Standard uncertainty in pressure u (P)= ± 0.01MPa *molality has been expressed per kg of (TBMS + water) solvent mixture. *#Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}.

Table 7. Values of (V_1^0 -V_2^0), $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $T\Delta S_2^{0\neq}$, $\Delta H_2^{0\neq}$ for L-Arginine and L-Histidine in different concentrations of an aqueous solution of IL(TBMS) mixture at different temperatures and atmospheric pressure 0.1MPa.

Parameters	0.001mIL/ mol.kg^{-1}			0.003mIL/ mol.kg^{-1}			0.005mIL mol.kg^{-1}		
	T=298.15K	303.15K	308.15K	T=298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
L-Arginine									
(V_1^0 -V_2^0)/m^3.mol^{-1}	-109.457	-111.277	-112.587	-112.62	-115.86	-118.05	-113.72	-117.51	-119.34
$\Delta\mu_1^{0\neq}$/KJ.mol^{-1}	9.39	9.39	9.35	9.47	9.41	9.37	9.51	9.43	9.44
$\Delta\mu_2^{0\neq}$/KJ.mol^{-1}	111.53	140.08	154.10	122.35	150.04	168.41	137.89	161.83	185.22
$T\Delta S_2^{0\neq}$/KJ.mol^{-1}	1260.13	1282.74	1302.39	1373.30	1396.34	1419.37	1411.35	1435.02	1458.69
$\Delta H_2^{0\neq}$/KJ.mol^{-1}	1371.66	1422.82	1456.50	1495.66	1546.38	1587.78	1549.23	1596.88	1643.91
L-Histidine									
(V_1^0 -V_2^0)/m^3.mol^{-1}	-85.19	-86.75	-88.08	-87.91	-89.70	-90.91	-89.15	-91.13	-91.73
$\Delta\mu_1^{0\neq}$/KJ.mol^{-1}	9.39	9.33	9.35	9.47	9.41	9.37	9.51	9.43	9.35
$\Delta\mu_2^{0\neq}$/KJ.mol^{-1}	86.83	102.73	115.53	100.32	116.01	131.74	112.91	128.20	146.71
$T\Delta S_2^{0\neq}$/KJ.mol^{-1}	855.63	869.98	884.32	936.79	952.50	968.20	1007.96	1024.86	1041.76
$\Delta H_2^{0\neq}$/KJ.mol^{-1}	942.46	972.71	999.86	1037.11	1068.50	1099.96	112.87	1153.05	1188.48

[m]different concentrations of TBMS in aqueous solution; *Standard uncertainty in temperature u (T) = ± 0.01 K. *Standard uncertainty in pressure u (P)=± 0.01 MPa *molality has been expressed per kg of (TBMS + water) solvent mixture. *#Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}.

Table 8. Limiting molar refraction ($^{R}_{M}{}^{0}$) of L-Arginine and L-Histidine in aqueous ionic liquid IL (TBMS) solutions of different concentrations, (0.001, 0.003, 0.005) m at different temperature and atmospheric pressure 0.1MPa.

Temperature/K	298.15 K	303.15 K	308.15 K
Molalityof IL/mol.kg^{-1}			
	L-ARGININE+aq.TBMS		
0.001	35.856±0.028	35.877±0.027	35.920±0.027
0.003	35.884±0.027	35.904±0.027	35.946±0.028
0.005	35.902±0.027	35.929±0.028	35.972±0.028
	L-HISTIDINE+aq.TBMS		
0.001	31.870±0.042	31.897±0.039	31.944±0.042
0.003	31.886±0.039	31.911±0.039	31.957±0.039
0.005	31.919±0.042	31.944±0.042	31.992±0.042

*Standard errors for limiting molar refraction ($^{R}_{M\,0}$) are given in their parenthesis. *Standard uncertainties values of u are: u (T)=±0.01K (0.68 level of confidence),*Standard uncertainty in pressure u (P)= ±0.01 MPa *molality has been expressed per kg of (TBMS + water) solvent mixture. *#Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}.

Table 9. Molar conductance (Λ) of L-Arginine and L-Histidine in aqueous IL (TBMS) solution of different concentrations, (0.001, 0.003, 0.005) m at 298.15 K, 303.15 K, 308.15 K and at atmospheric pressure 0.1MPa.

Molality(m) /mol.kg^{-1}	Λ /S.cm^2.mol^{-1}	Molality(m) /mol.kg^{-1}	Λ /S.cm^2.mol^{-1}	Molality(m) /mol.kg^{-1}	Λ /S.cm^2.mol^{-1}
	298.15K		303.15K		308.15K
L-ARGININE+aq.TBMS					
0.001mIL/ mol.kg^{-1}					
0.01004	8.300±0.001	0.01005	9.100±0.003	0.01007	10.100±0.002
0.02515	4.520±0.002	0.02518	4.800±0.001	0.02523	5.160±0.004
0.04032	3.525±0.001	0.04037	3.750±0.004	0.04044	4.025±0.001
0.05554	2.890±0.004	0.05562	3.090±0.003	0.05572	3.327±0.001
0.07082	2.571±0.005	0.07092	2.771±0.001	0.07105	2.985±0.003
0.08616	2.470±0.001	0.08628	2.635±0.001	0.08644	2.835±0.006

0.003mIL/ mol.kg^{-1}					
0.01004	11.000±0.001	0.01005	11.700±0.001	0.01007	12.400±0.001
0.02515	5.200±0.004	0.02518	5.920±0.007	0.02523	6.240±0.004
0.04031	4.250±0.002	0.04037	4.450±0.001	0.04044	4.700±0.003
0.05554	3.363±0.003	0.05562	93.454±0.005	0.05572	3.727±0.001
0.07082	3.057±0.008	0.07092	3.214±0.005	0.07104	3.357±0.001
0.08615	2.929±0.001	0.08628	3.152±0.002	0.08643	3.294±0.001
0.005mIL/ mol.kg^{-1}					
0.01004	13.600±0.003	0.01005	14.800±0.005	0.01007	17.500±0.001
0.02515	6.480±0.001	0.02518	8.120±0.001	0.02522	8.560±0.007
0.04031	4.725±0.002	0.04037	5.350±0.001	0.04044	5.650±0.001
0.05554	3.909±0.001	0.05561	4.400±0.003	0.05571	4.654±0.002
0.07082	3.357±0.002	0.07091	3.928±0.001	0.07104	4.028±0.001
0.08615	3.117±0.002	0.08627	3.705±0.002	0.08642	3.800±0.004
L-HISTIDINE+aq.TBMS					
0.001mIL/ mol.kg^{-1}					
0.01003	12.600±0.001	0.01005	13.600±0.008	0.01007	14.800±0.004
0.02513	5.480±0.001	0.02517	6.120±0.001	0.02518	6.720±0.0001
0.04028	4.275±0.001	0.04033	4.550±0.002	0.04041	4.800±0.001
0.05547	7.45±0.001	0.05549	3.600±0.005	0.05564	3.854±0.003
0.07070	3.290±0.001	0.07080	3.242±0.001	0.07093	3.414±0.001
0.08598	3.171±0.001	0.08610	3.223±0.003	0.08626	3.352±0.002
0.003mIL/ mol.kg^{-1}					
0.01003	15.500±0.007	0.01005	16.600±0.003	0.01007	17.600±0.004
0.02513	6.920±0.010	0.02517	7.440±0.001	0.02521	8.040±0.001
0.04028	4.950±0.002	0.04033	5.175±0.005	0.04040	5.675±0.007
0.05554	4.036±0.002	0.05540	4.272±0.002	0.05564	4.472±0.001
0.07070	3.657±0.003	0.07080	3.957±0.001	0.07093	4.071±0.002
0.08598	3.470±0.004	0.08610	3.705±0.007	0.08626	3.952±0.001
0.005mIL/ mol.kg^{-1}					
0.01003	18.600±0.001	0.01005	19.400±0.003	0.01006	20.800±0.001
0.02513	8.760±0.002	0.02516	8.960±0.001	0.02521	9.320±0.003
0.04027	6.200±0.001	0.04033	6.475±0.002	0.04040	6.575±0.001
0.05546	4.890±0.006	0.05553	5.363±0.001	0.05563	5.636±0.004
0.07070	4.542±0.001	0.07079	4.671±0.004	0.07091	4.785±0.001
0.08598	4.070±0.001	0.08609	4.188±0.003	0.08623	4.305±0.005

*Standard errors in molar conductivity Λ /S.cm^2.mol^{-1} is given in their parenthesis. (T) = ±0.01K (0.68 level of confidence)and pressure u (P) = 0.01 MPa *molality has been expressed per kg of (TBMS + water) solvent mixture. *#Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}.

Table 10. CMC values of L-Arginine and L-Histidine in different concentrations(0.001, 0.003, 0.005)m aqueous solutions of TBMS at different temperatures at atmospheric pressure 0.1MPa.

Molality/m of IL	Temperatures	Con. of L-Arginine(mole/kg) from conductance	CMC break point from conductance(mL)	Con. of L-Histidine(mole/kg) from conductance	CMC break point from conductance(mL)
0.001	298.15K	0.00514	38.90	0.00510	39.15
0.001	303.15K	0.00580	34.42	0.00567	35.25
0.001	308.15K	0.00614	32.56	0.00585	34.48
0.003	298.15K	0.00619	32.27	0.00567	35.12
0.003	303.15K	0.00640	31.22	0.00593	33.72
0.003	308.15K	0.00664	30.11	0.00580	34.48
0.005	298.15K	000684	29.23	0.00669	29.87
0.005	303.15K	0.00664	30.11	0.00607	32.92
0.005	308.15K	0.00718	27.87	0.00681	29.36

*Standard uncertainty of CMC (u):±0.01,*Standard uncertainty in pressure u (*P*)= ±0.01MPa *molality has been expressed per kg of (TBMS + water) solvent mixture. *#Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}.

Table 11. Surface tension (σ) of L-Arginine and L-Histidine of different molality at 298.15 K in different concentrations(0.001, 0.003, 0.005) m of IL (TBMS) solutions and at atmospheric pressure 0.1MPa.

Molality(m) /mol.kg^{-1}	σ(mN/m)	Molality(*m*) /mol.kg^{-1}	σ(mN/m)	Molality(*m*) /mol.kg^{-1}	σ(mN/m)
L-ARGININE+aq.TBMS					
0.001mIL/ mol.kg^{-1}		0.003mIL/ mol.kg^{-1}		0.005mIL/ mol.kg^{-1}	
0.01004	62.7±0.01	0.01004	61.2±0.02	0.01004	59.8±0.03
0.02515	63.6±0.01	0.02515	62.0±0.02	0.02515	60.5±0.03
0.04032	64.6±0.01	0.04031	62.9±0.02	0.04032	61.4±0.03
0.05540	65.3±0.01	0.05554	63.6±0.02	0.05554	62.3±0.03
0.07082	66.3±0.01	0.07082	64.3±0.02	0.07082	63.1±0.03
0.08616	66.9±0.01	0.08615	65.1±0.02	0.08616	63.9±0.03
L-HISTIDINE+aq.TBMS					
0.001mIL/ mol.kg^{-1}		0.003mIL/ mol.kg^{-1}		0.005mIL/ mol.kg^{-1}	
0.01003	60.9±0.02	0.01003	57.8±0.01	0.01003	55.7±0.01
0.02513	61.6±0.02	0.02513	58.3±0.01	0.02513	56.6.3±0.01
0.04028	62.2±0.02	0.04028	59.3±0.01	0.04027	57.8.1±0.01
0.05547	63.3±0.02	0.05547	60.2±0.01	0.05546	58.6±0.01
0.07070	64.1±0.02	0.07070	61.3±0.01	0.07070	59.9±0.01
0.08598	64.6±0.02	0.08598	62.7±0.01	0.08598	61.2±0.01

*Standard uncertainties u (σ)= (±0.03mN/m) *Standard uncertainty in pressure u (*P*) =± 0.01 MPa and u (*T*) = ±0.01K (0.68 level of confidence). *molality has been expressed per kg of (TBMS + water) solvent mixture. *#Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}.

Table 12. Optimizations Energy of pure TBMS, L-ARG, L-HIS and (TBMS+L-ARG), (TBMS+L-HIS) systems using appropriate methodology and 6-311G (d) basis set.

System	Calculation method	Basis set	Optimization energy(a.u)	Dipole moment(D)
TBMS	UB3LYP	6-311G (d)	-1350.3115	13.9546
L-ARG	UB3LYP	6-311G (d)	-606.49617	3.5197
L-HIS	UB3LYP	6-311G (d)	-549.92985	5.9015
(TBMS+L-ARG)	UB3LYP	6-311G (d)	-1236.6553	14.4551
(TBMS+L-HIS)	UB3LYP	6-311G (d)	-1143.2869	15.5051

Supporting Information

Tables

Table S1. Experimental values of density (ρ), viscosity (η), molar refraction ($^{R}_{M}$) of different concentrations (0.001, 0.003, 0.005) m of aqueous solvent (TBMS) solutions at 298.15 K, 303.15 K, 308.15 K at atmospheric pressure 0.1MPa.

Aqueous solvent Molality/mol.kg^{-1}	298.15 K	303.15 K	308.15 K
ρ(g/cm^3)			
0.001	0.99706	0.99570	0.99395
0.003	0.99713	0.99580	0.99408
0.005	0.99719	0.99589	0.99420
η/mPa.s			
0.001	0.981±0.011	0.899±0.011	0.854±0.011
0.003	1.013±0.011	0.93±0.011	0.860±0.011
0.005	1.028±0.011	0.936±0.011	0.884±0.011
$^{R}_{M}$			
0.001	35.839±0.018	35.858±0.018	35.901±0.018
0.003	35.844±0.018	35.87±0.018	35.897±0.018
0.005	35.869±0.018	35.91±0.018	35.917±0.018

Overallstandard uncertainties u are: u (ρ) =±0.00093g.cm^{-3}, u (n_D) =±0.0002 and u (T) = ±0.01K, (0.68 level of confidence),*Standard error in molar refraction ($^{R}_{M}$) and refractive index (η/mPa.s) is in their parenthesis, #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}. Standard uncertainty in pressure u(P)= ±0.01 MPa

Table S2. Experimental values of refractive index (n_D), sp. conductance (κ), surface tension (σ) of different concentrations (0.001, 0.003, 0.005) m of aqueous solvent (TBMS) solution at 298.15 K, 303.15 K, 308.15 K and at atmospheric pressure 0.1MPa.

Aqueous solvent Molality/mol.kg-1	n_D			σ (mN/m)
	298.15K	303.15K	308.15K	298.15K
0.001	1.3322	1.3319	1.3315	64.7
0.003	1.3323	1.3318	1.3317	63.6
0.005	1.3325	1.3322	1.3319	60.6
κ (ms/cm)				
0.001	0.102±0.013	0.115±0.010	0.120±0.014	
0.003	0.170±0.009	0.192±0.017	0.213±0.009	
0.005	0.250±0.012	0.270±0.011	0.303±0.014	

*Standard Uncertainties (u) are :u ($n_{D)=}$ ±0.0002, u (κ)=±0.01(mScm^{-1} u (σ)=0.3mN/m

*Standard uncertainty in pressure u (P)= ±0.01 MPa *molality has been expressed per kg of (TBMS + water) solvent mixture. * #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}.

Table S3. Density (ρ) of (L-ARGININE+TBMS+H_2O) and (L-HISTIDINE+TBMS+H_2O) systems in aqueous TBMS solutions of different concentrations (0.001, 0.003, 0.005) m at 298.15 K, 303.15 K and 308.15 K and at atmospheric pressure 0.1MPa.

Molality(m) /mol.kg^{-1}	Density(ρ) *g/cm3*	Molality(*m*) /mol.kg^{-1}	Density(ρ) *g/cm3*	Molality(*m*) /mol.kg^{-1}	Density(ρ) *g/cm3*
	298.15K		303.15K		308.15K
(L-ARGININE+ aq.TBMS)					
0.001m/mol.kg^{-1}					
0.01004	0.99754	0.01005	0.99617	0.01007	0.99441
0.02515	0.99828	0.02518	0.99690	0.02523	0.99513
0.04032	0.99902	0.04037	0.99765	0.04044	0.99587
0.05554	0.99979	0.05562	0.99842	0.05572	0.99661
0.07082	1.00054	0.07092	0.99918	0.07105	0.99737
0.08616	1.00130	0.08628	0.99995	0.08644	0.99815
0.003mIL/mol.kg^{-1}					
0.01004	0.99759	0.01005	0.99624	0.01007	0.99450
0.02515	0.99830	0.02518	0.99692	0.02523	0.99519
0.04031	0.99906	0.04037	0.99767	0.04044	0.99592
0.05554	0.99982	0.05562	0.99844	0.05572	0.99665
0.07082	1.00058	0.07092	0.99920	0.07104	0.99743
0.08615	1.00135	0.08628	0.99997	0.08643	0.99820
0.005mIL/mol.kg^{-1}					
0.01004	0.99764	0.01005	0.99631	0.01007	0.99461
0.02515	0.99835	0.02518	0.99701	0.02522	0.99530
0.04031	0.99910	0.04037	0.99774	0.04044	0.99603
0.05554	0.99986	0.05561	0.99849	0.05571	0.99678
0.07082	1.00062	0.07091	0.99925	0.07104	0.99754
0.08615	1.00138	0.08627	1.00000	0.08642	0.99832
L-HISTIDINE+aq.TBMS					
0.001mIL/mol.kg^{-1}					
0.01003	0.99759	0.01005	0.99622	0.01007	0.99446
0.02513	0.9984	0.02517	0.99702	0.02518	0.99525
0.04028	0.99921	0.04033	0.99783	0.04041	0.99606
0.05547	1.00003	0.05549	0.99865	0.05564	0.99687
0.07070	1.00086	0.07080	0.99948	0.07093	0.99769
0.08598	1.0017	0.08610	1.00032	0.08626	0.99852
0.003mIL/mol.kg^{-1}					
0.01003	0.99764	0.01005	0.99630	0.01007	0.99457
0.02513	0.99843	0.02517	0.99707	0.02521	0.99533
0.04028	0.99924	0.04033	0.99786	0.04040	0.99612
0.05554	1.00006	0.05540	0.99867	0.05564	0.99693
0.07070	1.00088	0.07080	0.99951	0.07093	0.99775
0.08598	1.00172	0.08610	1.00036	0.08626	0.99857
0.005mIL/mol.kg^{-1}					
0.01003	0.99769	0.01005	0.99641	0.01006	0.99469
0.02513	0.99847	0.02516	0.99719	0.02521	0.99546
0.04027	0.99927	0.04033	0.99800	0.04040	0.99626
0.05546	1.00008	0.05553	0.99882	0.05563	0.99709
0.07070	1.00090	0.07079	0.99967	0.07091	0.99795
0.08598	1.00174	0.08609	1.00053	0.08623	0.99882

#Overall Standard uncertainties u are: u (ρ) =0.00093g/cm^3, u (T) =$\pm$0.01K, (0.68 level of confidence). #Combined standard uncertainties in molality according to stated purity u(m) =$\pm$0.0092 mol kg^{-1}. *Standard uncertainty in pressure u (P)= $\pm$0.01 MPa

Table S4. Apparent Molar volume (Φ_v) of (L-ARGININE+TBMS+H_2O) and (L-HIS TIDINE+TBMS+H_2O) systems in aqueous IL (TBMS) of different concentrations (0.00, 0.003, 0.005) m mass fractions, W_1=0.001, 0003, 0.005 at 298.15 K, 303.15 K, 308.15 K and at atmospheric pressure0.1MPa.

Molality(m) /mol.kg^{-1}	Φ_v x 10^6 (m^3. mol^{-1})	Molality(m) /mol.kg^{-1}	Φ_v x 10^6 (m^3. mol^{-1})	Molality(m) /mol.kg^{-1}	Φ_v x 10^6 (m^3. mol^{-1})
	298.15K		303.15K		308.15K
(L-ARGININE+ aq.TBMS)					
0.001mIL/mol.kg-1					
0.01004	126.57±0.02	0.01005	127.75±0.02	0.01007	128.98±0.02
0.02515	125.77±0.02	0.02518	126.74±0.02	0.02523	127.77±0.02
0.04032	125.57±0.02	0.04037	125.99±0.02	0.04044	126.97±0.02
0.05554	124.93±0.02	0.05562	125.28±0.02	0.05572	126.60±0.02
0.07082	124.85±0.02	0.07092	125.02±0.02	0.07105	126.10±0.02
0.08616	124.68±0.02	0.08628	124.74±0.02	0.08644	125.55±0.02
0.003mIL/mol.kg-1					
0.01004	128.57±0.02	0.01005	130.75±0.02	0.01007	132.99±0.02
0.02515	127.77±0.02	0.02518	129.94±0.02	0.02523	130.57±0.02
0.04031	126.31±0.02	0.04037	127.99±0.02	0.04044	128.96±0.02
0.05554	125.65±0.02	0.05562	126.73±0.02	0.05572	128.23±0.02
0.07082	125.27±0.02	0.07092	126.16±0.02	0.07104	127.09±0.02
0.08615	124.91±0.02	0.08628	125.67±0.02	0.08643	126.48±0.02
0.005mIL/mol.kg-1					
0.01004	129.56±0.02	0.01005	132.74±0.02	0.01007	133.98±0.02
0.02515	128.16±0.02	0.02518	129.93±0.02	0.02522	130.96±0.02
0.04031	126.81±0.02	0.04037	128.48±0.02	0.04044	129.20±0.02
0.05554	126.01±0.02	0.05561	127.45±0.02	0.05571	128.03±0.02
0.07082	125.55±0.02	0.07091	126.72±0.02	0.07104	127.22±0.02
0.08615	125.26±0.02	0.08627	126.37±0.02	0.08642	126.46±0.02
L-HISTIDINE+aq.TBMS					
0.001mIL/mol.kg-1					
0.01003	102.45±0.01	0.01005	103.59±0.01	0.01007	104.78±0.01
0.02513	101.85±0.01	0.02517	102.79±0.01	0.02518	103.78±0.01
0.04028	101.70±0.01	0.04033	102.34±0.01	0.04041	103.02±0.01
0.05547	101.45±0.01	0.05549	101.95±0.01	0.05564	102.68±0.01
0.07070	101.16±0.01	0.07080	101.59±0.01	0.07093	102.34±0.01
0.08598	100.86±0.01	0.08610	101.23±0.01	0.08626	102.00±0.01
0.003mIL/mol.kg-1					
0.01003	104.45±0.01	0.01005	105.59±0.01	0.01007	106.78±0.01
0.02513	103.45±0.01	0.02517	104.79±0.01	0.02521	105.78±0.01
0.04028	102.69±0.01	0.04033	104.09±0.01	0.04040	104.77±0.01
0.05554	102.17±0.01	0.05540	103.40±0.01	0.05564	103.95±0.01
0.07070	101.87±0.01	0.07080	102.58±0.01	0.07093	103.33±0.01
0.08598	101.44±0.01	0.08610	101.93±0.01	0.08626	102.93±0.01
0.005mIL/mol.kg-1					
0.01003	105.45±0.01	0.01005	106.58±0.01	0.01006	106.77±0.01
0.02513	104.24±0.01	0.02516	104.78±0.01	0.02521	105.36±0.01
0.04027	103.44±0.01	0.04033	103.57±0.01	0.04040	104.25±0.01
0.05546	102.89±0.01	0.05553	102.84±0.01	0.05563	103.20±0.01
0.07070	102.44±0.01	0.07079	101.99±0.01	0.07091	102.17±0.01
0.08598	101.91±0.01	0.08609	101.33±0.01	0.08623	101.38±0.01

*Standard uncertainties u are: u (T) =±0.01K, (0.68 level of confidence), *molality has been expressed per kg of (TBMS + water) solvent mixture. #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1} (0.68 level of confidence). Standard uncertainty in pressure u (P)= ±0.01 MPa

Table S5. Volume transfer/$\Delta\Phi_v^0$ for L-Arginine and L-Histidine in aqueous solutions of (0.001, 0.003, 0.005) m IL (TBMS) at 298.15 K, 303.15 K, 308.15 K at atmospheric pressure 0.1MPa.

Temperature/ (K)	$\Delta\Phi_v^0$ x 10^6 /(m^3. mol^{-1})	$\Delta\Phi_v^0$ x 10^6 /(m^3. mol^{-1})
	L-Arginine	L-Histidine
0.001 mIL/mol.kg^{-1}		
298.15K	0.592	0.481
303.15K	0.572	0.477
308.15K	0.537	0.451
0.003 mIL/mol.kg^{-1}		
298.15K	1.085	0.856
303.15K	1.038	0.832
308.15K	0.989	0.802
0.005 mIL/mol.kg^{-1}		
298.15K	1.510	1.094
303.15K	1.401	0.998
308.15K	1.198	0.935

*Standard uncertainties values of u are: u (T) =±0.01K (0.68 level of confidence), #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}. *molality has been expressed per kg of (TBMS + water) solvent mixture. * Standard uncertainty in pressure u (P)= ±0.01MPa.

Table S6. Viscosity (η) and (η/η°-1)/$\sqrt{m}$ of (L-ARGININE+TBMS+H_2O) in aqueous IL (TBMS) of different concentrations (0.001, 0.003, 0.005) m at 298.15 K, 303.15 K, 308.15 K and at atmospheric pressure 0.1MPa.

Molality(m) / mol.kg-1	η (mPa.s)	Molality(m) / mol.kg-1	η (mPa.s)	Molality(m) / mol.kg-1	η (mPa.s)
	298.15K		303.15K		308.15K
(L-ARGININE+TBMS+H_2O)					
0.001mIL/mol.kg^{-1}					
0.01004	1.006±0.011	0.01005	0.912±0.011	0.01007	0.873±0.011
0.02515	1.017±0.011	0.02518	0.923±0.011	0.02523	0.886±0.011
0.04032	1.028±0.011	0.04037	0.936±0.011	0.04044	0.898±0.011
0.05554	1.038±0.011	0.05562	0.949±0.011	0.05572	0.911±0.011
0.07082	1.049±0.011	0.07092	0.960±0.011	0.07105	0.923±0.011
0.08616	1.059±0.011	0.08628	0.972±0.011	0.08644	0.937±0.011
0.003mIL/mol.kg^{-1}					
0.01004	1.022±0.011	0.01005	0.941±0.011	0.01007	0.877±0.011
0.02515	1.034±0.011	0.02518	0.954±0.011	0.02523	0.890±0.011
0.04031	1.046±0.011	0.04037	0.967±0.011	0.04044	0.905±0.011
0.05554	1.057±0.011	0.05562	0.980±0.011	0.05572	0.918±0.011
0.07082	1.070±0.011	0.07092	0.995±0.011	0.07104	0.933±0.011
0.08615	1.082±0.011	0.08628	1.009±0.011	0.08643	0.947±0.011
0.005mIL/mol.kg^{-1}					
0.01004	1.034±0.011	0.01005	0.958±0.011	0.01007	0.907±0.011
0.02515	1.048±0.011	0.02518	0.972±0.011	0.02522	0.922±0.011
0.04031	1.062±0.011	0.04037	0.987±0.011	0.04044	0.938±0.011
0.05554	1.075±0.011	0.05561	1.002±0.011	0.05571	0.954±0.011
0.07082	1.089±0.011	0.07091	1.017±0.011	0.07104	0.969±0.011
0.08615	1.103±0.011	0.08627	1.033±0.011	0.08642	0.987±0.011

	$(\eta/\eta^{\circ}-1)/\sqrt{m}$/ $kg^{1/2}mol^{-1/2}$		$(\eta/\eta^{\circ}-1)/\sqrt{m}$/ $kg^{1/2}mol^{-1/2}$		$(\eta/\eta^{\circ}-1)/\sqrt{m}$ / $kg^{1/2}mol^{-1/2}$
0.001mIL/mol.kg^{-1}					
0.01004	0.090±0.002	0.01005	0.111±0.003	0.01007	0.115±0.002
0.02515	0.126±0.002	0.02518	0.147±0.004	0.02523	0.168±0.002
0.04032	0.155±0.002	0.04037	0.188±0.004	0.04044	0.202±0.004
0.05554	0.174±0.003	0.05562	0.221±0.004	0.05572	0.236±0.005
0.07082	0.196±0.004	0.07092	0.241±0.005	0.07105	0.263±0.005
0.08616	0.212±0.004	0.08628	0.264±0.005	0.08644	0.292±0.006
0.003mIL/mol.kg^{-1}					
0.01004	0.099±0.003	0.01005	0.118±0.004	0.01007	0.127±0.003
0.02515	0.137±0.003	0.02518	0.163±0.004	0.02523	0.175±0.004
0.04031	0.167±0.004	0.04037	0.198±0.004	0.04044	0.224±0.005
0.05554	0.189±0.003	0.05562	0.229±0.005	0.05572	0.255±0.005
0.07082	0.215±0.003	0.07092	0.262±0.006	0.07104	0.290±0.006
0.08615	0.236±0.005	0.08628	0.289±0.004	0.08643	0.318±0.006
0.005mIL/mol.kg^{-1}					
0.01004	0.107±0.005	0.01005	0.127±0.005	0.01007	0.134±0.006
0.02515	0.154±0.005	0.02518	0.173±0.006	0.02522	0.190±0.006
0.04031	0.190±0.006	0.04037	0.216±0.006	0.04044	0.239±0.006
0.05554	0.216±0.006	0.05561	0.252±0.006	0.05571	0.280±0.007
0.07082	0.242±0.007	0.07091	0.282±0.007	0.07104	0.312±0.008
0.08615	0.266±0.005	0.08627	0.313±0.007	0.08642	0.350±0.009

*Standard uncertainties u are: u (T) =±0.01K, (0.68 level of confidence), *molality has been expressed per kg of (TBMS + water) solvent mixture. Standard errors in (η) and u (η_r-1)/$\sqrt{m}$ is given in the parenthesis #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}(0.68 level of confidence). Standard uncertainty in pressure u (P)= ±0.01 MPa

Table S7. Viscosity (η) and (η/η^0-1)/√m of (L-HISTIDINE+TBMS+H_2O) system in aqueous IL (TBMS) of different concentrations (0.001, 0.003, 0.005) m at 298.15 K, 303.15 K, 308.15 K and at atmospheric pressure 0.1MPa.

Molality(m) / mol.kg-1	η (mPa.s)	Molality(m) / mol.kg-1	η (mPa.s)	Molality(m) / mol.kg-1	η (mPa.s)
	298.15K		303.15K		308.15K
(L-HISTIDINE+TBMS+H_2O)					
0.001mIL/mol.kg^{-1}					
0.01003	1.005±0.011	0.01005	0.910±0.011	0.01007	0.871±0.011
0.02513	1.014±0.011	0.02517	0.920±0.011	0.02518	0.881±0.011
0.04028	1.024±0.011	0.04033	0.929±0.011	0.04041	0.891±0.011
0.05547	1.031±0.011	0.05549	0.938±0.011	0.05564	0.900±0.011
0.07070	1.038±0.011	0.07080	0.947±0.011	0.07093	0.909±0.011
0.08598	1.047±0.011	0.08610	0.955±0.011	0.08626	0.919±0.011
0.003mIL/mol.kg^{-1}					
0.01003	1.021±0.011	0.01005	0.939±0.011	0.01007	0.875±0.011
0.02513	1.032±0.011	0.02517	0.950±0.011	0.02521	0.886±0.011
0.04028	1.042±0.011	0.04033	0.960±0.011	0.04040	0.898±0.011
0.05554	1.052±0.011	0.05540	0.971±0.011	0.05564	0.908±0.011
0.07070	1.062±0.011	0.07080	0.981±0.011	0.07093	0.919±0.011
0.08598	1.071±0.011	0.08610	0.992±0.011	0.08626	0.930±0.011
0.005mIL/mol.kg^{-1}					
0.01003	1.033±0.011	0.01005	0.956±0.011	0.01006	0.905±0.011
0.02513	1.045±0.011	0.02516	0.968±0.011	0.02521	0.917±0.011

0.04027	1.057±0.011	0.04033	0.980±0.011	0.04040	0.930±0.011
0.05546	1.068±0.011	0.05553	0.992±0.011	0.05563	0.942±0.011
0.07070	1.079±0.011	0.07079	1.004±0.011	0.07091	0.956±0.011
0.08598	1.091±0.011	0.08609	1.017±0.011	0.08623	0.968±0.011
	$(\eta/\eta^{\circ}-1)/\sqrt{m}$/ $kg^{1/2}mol^{-1/2}$		$(\eta/\eta^{\circ}-1)/\sqrt{m}$/ $kg^{1/2}mol^{-1/2}$		$(\eta/\eta^{\circ}-1)/\sqrt{m}$ / $kg^{1/2}mol^{-1/2}$
0.001mIL/mol.kg^{-1}					
0.01003	0.080±0.002	0.01005	0.088±0.003	0.01007	0.092±0.006
0.02513	0.108±0.002	0.02517	0.126±0.002	0.02518	0.131±0.004
0.04028	0.131±0.002	0.04033	0.149±0.002	0.04041	0.160±0.006
0.05547	0.145±0.003	0.05549	0.169±0.002	0.05564	0.182±0.004
0.07070	0.155±0.003	0.07080	0.187±0.004	0.07093	0.200±0.006
0.08598	0.171±0.003	0.08610	0.200±0.006	0.08626	0.221±0.002
0.003mIL/mol.kg^{-1}					
0.01003	0.089±0.002	0.01005	0.097±0.005	0.01007	0.104±0.006
0.02513	0.125±0.003	0.02517	0.136±0.002	0.02521	0.146±0.003
0.04028	0.148±0.003	0.04033	0.161±0.002	0.04040	0.184±0.002
0.05554	0.168±0.002	0.05540	0.187±0.002	0.05564	0.206±0.004
0.07070	0.186±0.004	0.07080	0.206±0.003	0.07093	0.230±0.003
0.08598	0.199±0.004	0.08610	0.227±0.004	0.08626	0.252±0.003
0.005mIL/mol.kg^{-1}					
0.01003	0.098±0.004	0.01005	0.106±0.005	0.01006	0.111±0.005
0.02513	0.136±0.005	0.02516	0.147±0.005	0.02521	0.155±0.005
0.04027	0.166±0.006	0.04033	0.179±0.004	0.04040	0.193±0.005
0.05546	0.187±0.006	0.05553	0.206±0.006	0.05563	0.223±0.006
0.07070	0.207±0.007	0.07079	0.231±0.007	0.07091	0.256±0.007
0.08598	0.227±0.008	0.08609	0.256±0.008	0.08623	0.278±0.008

*Standard uncertainties values of u are: u (T) =±0.01K) , *molality has been expressed per kg of (IL + water) solvent mixture. Standard error in (η) and u (η_r-1)/$\sqrt{m}$ is given in the parenthesis. (0.68 level of confidence). #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1} *Standard uncertainty in pressure u (P)= ±0.01 MPa

Table S8. Refractive index (n_D) and molar refraction ($^{R}_{M}$) of (L-ARGININE+TBMS+H_2O) in aqueous IL (TBMS) solutions of different concentrations (0.001, 0.003, 0.005) m at 298.15 K, 303.15 K and 308.15 K and at pressure 0.1MPa.

Molality(m) / mol.kg-1	(n_D)	Molality(m) / mol.kg-1	(n_D)	Molality(m) / mol.kg-1	(n_D)
	298.15K		303.15K		308.15K
(L-ARGININE+TBMS+H_2O)					
0.001mIL/mol.kg^{-1}					
0.01004	1.3319	0.01005	1.3317	0.01007	1.3316
0.02515	1.3324	0.02518	1.3322	0.02523	1.332
0.04032	1.3328	0.04037	1.3326	0.04044	1.3324
0.05554	1.3332	0.05562	1.333	0.05572	1.3328
0.07082	1.3336	0.07092	1.3334	0.07105	1.3332
0.08616	1.3340	0.08628	1.3338	0.08644	1.3336
0.003mIL/mol.kg^{-1}					
0.01004	1.3321	0.01005	1.3319	0.01007	1.3318
0.02515	1.3326	0.02518	1.3324	0.02523	1.3323
0.04031	1.333	0.04037	1.3328	0.04044	1.3327
0.05554	1.3334	0.05562	1.3332	0.05572	1.3331
0.07082	1.3338	0.07092	1.3336	0.07104	1.3335
0.08615	1.3342	0.08628	1.334	0.08643	1.3339

0.005mIL/mol.kg^{-1}					
0.01004	1.3325	0.01005	1.3323	0.01007	1.3322
0.02515	1.333	0.02518	1.3328	0.02522	1.3326
0.04031	1.3334	0.04037	1.3332	0.04044	1.333
0.05554	1.3338	0.05561	1.3336	0.05571	1.3334
0.07082	1.3342	0.07091	1.334	0.07104	1.3338
0.08615	1.3346	0.08627	1.3344	0.08642	1.3342
	($^{R}_{M}$)		($^{R}_{M}$)		($^{R}_{M}$)
0.001mIL/mol.kg^{-1}					
0.01004	35.863±0.022	0.01005	35.882±0.022	0.01007	35.926±0.022
0.02515	35.865±0.022	0.02518	35.886±0.022	0.02523	35.930±0.022
0.04032	35.868±0.022	0.04037	35.888±0.022	0.04044	35.933±0.022
0.05554	35.870±0.022	0.05562	35.890±0.022	0.05572	35.935±0.022
0.07082	35.872±0.022	0.07092	35.892±0.022	0.07105	35.937±0.022
0.08616	35.874±0.022	0.08628	35.893±0.022	0.08644	35.939±0.022
0.003mIL/mol.kg^{-1}					
0.01004	35.890±0.022	0.01005	35.909±0.022	0.01007	35.953±0.022
0.02515	35.894±0.022	0.02518	35.914±0.022	0.02523	35.957±0.022
0.04031	35.896±0.022	0.04037	35.917±0.022	0.04044	35.960±0.022
0.05554	35.898±0.022	0.05562	35.918±0.022	0.05572	35.963±0.022
0.07082	35.900±0.022	0.07092	35.920±0.022	0.07104	35.964±0.022
0.08615	35.902±0.022	0.08628	35.922±0.022	0.08643	35.966±0.022
0.005mIL/mol.kg^{-1}					
0.01004	35.908±0.022	0.01005	35.936±0.022	0.01007	35.978±0.022
0.02515	35.912±0.022	0.02518	35.940±0.022	0.02522	35.983±0.022
0.04031	35.914±0.022	0.04037	35.944±0.022	0.04044	35.986±0.022
0.05554	35.916±0.022	0.05561	35.946±0.022	0.05571	35.988±0.022
0.07082	35.918±0.022	0.07091	35.948±0.022	0.07104	35.990±0.022
0.08615	35.920±0.022	0.08627	35.950±0.022	0.08642	35.991±0.022

*Standard uncertainties u are: u (n_D) =±0.0002, Standard error in u ($^{R}_{M}$) is given in parenthesis. and u (T) =±0.01K (0.68 is the level of confidence). #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1} *Standard uncertainty in pressure u (p)= ±0.01 MPa.

Table S9. Refractive index (n_D) and molar refraction ($^{R}_{M}$) of (L-HISTIDINE+TBMS+H_2O) in aqueous IL (TBMS) solutions of different concentrations (0.001, 0.003, 0.005) m at 298.15 K, 303.15 K and 308.15 K and at pressure 0.1MPa.

Molality(m) / mol.kg-1	(n_D)	Molality(m) / mol.kg-1	(n_D)	Molality(m) / mol.kg-1	(n_D)
	298.15K		303.15K		308.15K
(L-HISTIDINE+TBMS+H_2O)					
0.001mIL/mol.kg^{-1}					
0.01003	1.3324	0.01005	1.3321	0.01007	1.3319
0.02513	1.3327	0.02517	1.3324	0.02518	1.3322
0.04028	1.333	0.04033	1.3327	0.04041	1.3325
0.05547	1.3333	0.05549	1.333	0.05564	1.3328
0.07070	1.3336	0.07080	1.3333	0.07093	1.3331
0.08598	1.3339	0.08610	1.3336	0.08626	1.3334
0.003mIL/mol.kg^{-1}					
0.01003	1.3327	0.01005	1.3324	0.01007	1.3322
0.02513	1.333	0.02517	1.3327	0.02521	1.3325
0.04028	1.3333	0.04033	1.333	0.04040	1.3328
0.05554	1.3336	0.05540	1.3333	0.05564	1.3331

0.07070	1.3339	0.07080	1.3336	0.07093	1.3334
0.08598	1.3342	0.08610	1.3339	0.08626	1.3337
0.005mIL/mol.kg^{-1}					
0.01003	1.3329	0.01005	1.3327	0.01006	1.3325
0.02513	1.3332	0.02516	1.333	0.02521	1.3328
0.04027	1.3335	0.04033	1.3333	0.04040	1.3331
0.05546	1.3338	0.05553	1.3336	0.05563	1.3334
0.07070	1.3341	0.07079	1.3339	0.07091	1.3337
0.08598	1.3344	0.08609	1.3342	0.08623	1.3340
	($^{R}_{M}$)		($^{R}_{M}$)		($^{R}_{M}$)
0.001mIL/mol.kg^{-1}					
0.01003	31.895±0.019	0.01005	31.922±0.019	0.01007	31.969±0.019
0.02513	31.913±0.019	0.02517	31.940±0.019	0.02518	31.979±0.019
0.04028	31.922±0.019	0.04033	31.949±0.019	0.04041	31.988±0.019
0.05547	31.931±0.019	0.05549	31.957±0.019	0.05564	31.997±0.019
0.07070	31.939±0.019	0.07080	31.966±0.019	0.07093	32.005±0.019
0.08598	31.947±0.019	0.08610	31.973±0.019	0.08626	32.014±0.019
0.003mIL/mol.kg^{-1}					
0.01003	31.911±0.019	0.01005	31.937±0.019	0.01007	31.983±0.019
0.02513	31.929±0.019	0.02517	31.956±0.019	0.02521	32.003±0.019
0.04028	31.938±0.019	0.04033	31.965±0.019	0.04040	32.012±0.019
0.05554	31.947±0.019	0.05540	31.974±0.019	0.05564	32.021±0.019
0.07070	31.956±0.019	0.07080	31.982±0.019	0.07093	32.030±0.019
0.08598	31.964±0.019	0.08610	31.990±0.019	0.08626	32.038±0.019
0.005mIL/mol.kg^{-1}					
0.01003	31.944±0.019	0.01005	31.968±0.019	0.01006	32.015±0.019
0.02513	31.963±0.019	0.02516	31.987±0.019	0.02521	32.025±0.019
0.04027	31.972±0.019	0.04033	31.996±0.019	0.04040	32.034±0.019
0.05546	31.972±0.019	0.05553	32.004±0.019	0.05563	32.042±0.019
0.07070	31.990±0.019	0.07079	32.012±0.019	0.07091	32.049±0.019
0.08598	31.998±0.019	0.08609	32.019±0.019	0.08623	32.056±0.019

*Standard uncertainties u are: u (n_D) = ±0.0002, Standard uncertainty in u ($^{R}_{M}$) is given in parenthesis. u (T) = ±0.01K (0.68 level of confidence), #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}*Standard uncertainty in pressure u (p)= ±0.01 MPa.

Table S10. Specific conductance (κ) of (L-ARGININE+TBMS+H_2O) and (L-HISTIDINE+ TBMS+H_2O) Systems in aqueous TBMS solutions of different concentrations (0.001, 0.003, 0.005) m at 298.15 K, 303.15 K, 308.15 K at atmospheric pressure 0.1MPa.

Molality(m) / mol.kg-1	κ (mS/cm)	Molality(m) / mol.kg-1	κ (mS/cm)	Molality(m) / mol.kg-1	κ (mS/cm)
	298.15K		303.15K		308.15K
(L-ARGININE+TBMS+H_2O)					
0.001mIL/mol.kg^{-1}					
0.01004	0.185±0.008	0.01005	0.206±0.010	0.01007	0.221±0.010
0.02515	0.215±0.010	0.02518	0.235±0.010	0.02523	0.249±0.005
0.04032	0.243±0.003	0.04037	0.265±0.003	0.04044	0.281±0.010
0.05554	0.261±0.003	0.05562	0.285±0.010	0.05572	0.303±0.010
0.07082	0.282±0.005	0.07092	0.299±0.004	0.07105	0.329±0.010
0.08616	0.303±0.010	0.08628	0.339±0.010	0.08644	0.361±0.010
0.003mIL/mol.kg^{-1}					
0.01004	0.270±0.008	0.01005	0.309±0.010	0.01007	0.340±0.005
0.02515	0.290±0.010	0.02518	0.340±0.010	0.02523	0.369±0.010

0.04031	0.340±0.003	0.04037	0.370±0.010	0.04044	0.401±0.004
0.05554	0.355±0.010	0.05562	0.382±0.010	0.05572	0.418±0.010
0.07082	0.386±0.004	0.07092	0.417±0.005	0.07104	0.448±0.010
0.08615	0.423±0.005	0.08628	0.460±0.010	0.08643	0.493±0.010
0.005mIL/mol.kg^{-1}					
0.01004	0.386±0.005	0.01005	0.420±0.004	0.01007	0.478±0.004
0.02515	0.412±0.010	0.02518	0.473±0.010	0.02522	0.517±0.010
0.04031	0.439±0.004	0.04037	0.484±0.003	0.04044	0.529±0.003
0.05554	0.465±0.005	0.05561	0.512±0.010	0.05571	0.559±0.010
0.07082	0.485±0.006	0.07091	0.545±0.010	0.07104	0.585±0.008
0.08615	0.526±0.010	0.08627	0.585±0.010	0.08642	0.626±0.010
(L-HISTIDINE+TBMS+H_2O)					
0.001mIL/mol.kg^{-1}					
0.01003	0.228±0.006	0.01005	0.251±0.004	0.01007	0.268±0.005
0.02513	0.29±0.004	0.02517	0.268±0.010	0.02518	0.288±0.002
0.04028	0.273±0.010	0.04033	0.297±0.005	0.04041	0.312±0.010
0.05547	0.283±0.005	0.05549	0.313±0.010	0.05564	0.332±0.010
0.07070	0.324±0.010	0.07080	0.342±0.003	0.07093	0.359±0.010
0.08598	0.351±0.006	0.08610	0.389±0.010	0.08626	0.400±0.008
0.003mIL/mol.kg^{-1}					
0.01003	0.325±0.004	0.01005	0.358±0.005	0.01007	0.389±0.009
0.02513	0.343±0.010	0.02517	0.378±0.010	0.02521	0.414±0.010
0.04028	0.368±0.010	0.04033	0.399±0.010	0.04040	0.440±0.010
0.05554	0.392±0.008	0.05540	0.427±0.010	0.05564	0.459±0.007
0.07070	0.426±0.010	0.07080	0.469±0.009	0.07093	0.498±0.010
0.08598	0.465±0.007	0.08610	0.507±0.010	0.08626	0.549±0.009
0.005mIL/mol.kg^{-1}					
0.01003	0.436±0.002	0.01005	0.464±0.005	0.01006	0.511±0.010
0.02513	0.469±0.010	0.02516	0.494±0.010	0.02521	0.536±0.004
0.04027	0.498±0.010	0.04033	0.529±0.003	0.04040	0.566±0.010
0.05546	0.519±0.005	0.05553	0.565±0.010	0.05563	0.613±0.003
0.07070	0.568±0.010	0.07079	0.597±0.002	0.07091	0.638±0.002
0.08598	0.596±0.007	0.08609	0.626±0.010	0.08623	0.669±0.006

*Standard errors in specific conductance/ms.cm^{-1} is given in their parenthesis. #Combined standard uncertainties in molality according to stated purity u (m) =±0.0092 mol kg^{-1} u (*T*) =±0.01K (0.68 level of confidence), *Standard uncertainty in pressure u (*p*)= ±0.01 MPa.

Table S11. Specific conductance (κ) of (L-ARGININE+TBMS+H_2O) system in aqueous IL (TBMS) solutions of concentration 0.001m at298.15 K, 303.15 K and 308.15 K and at atmospheric pressure 0.1MPa.

Specific conductivity/ μS cm^{-1} 0.001mIL/mol.kg^{-1}						
Added IL/mL	Total volume (IL+AA)/mL	Conc. of AA at each titration point	Conc. of IL at each titration point	298.15K	303.15K	308.15K
0	20	0.01	0.00000	167	176	192
1	21	0.0095	0.00047	165	173	188
2	22	0.0090	0.00044	164	171	185
3	23	0.0086	0.00043	162	170	182
4	24	0.0083	0.00041	161	169	180
5	25	0.0080	0.00040	160	168	178
6	26	0.0076	0.00038	159	166	175
7	27	0.0074	0.00037	158	165	174
8	28	0.0071	0.00035	157	164	172
9	29	0.0068	0.00034	156	163	170

10	30	0.0066	0.00033	155	162	169
11	31	0.0064	0.00032	154	161	168
12	32	0.0062	0.00031	153	160	166
13	33	0.0060	0.00030	152	158	165
14	34	0.0058	0.00029	151	157	164
15	35	0.0057	0.00028	150	156	163
16	36	0.0055	0.00027	149	155	162
17	37	0.0054	0.00027	147	155	161
18	38	0.0052	0.00026	146	154	160
19	39	0.0051	0.00025	145	154	159
20	40	0.0050	0.00025	145	154	158

*Standard uncertainties u (κ)=±0.010(ms.cm^{-1}), u (T) =±0.01K(0.68 level of confidence), *Standard uncertainty in pressure u (p)= ±0.01 MPa. #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}. Initial concentration of Amino acid in the cell was 0.01mole/kg. Initial added concentration of IL in the cell in term of molality was 0.001mol/kg^{-1}.

Table S12. Specific conductance (κ) of (L-ARGININE+TBMS+H_2O) system in aqueous IL (TBMS) solutions of concentration 0.003m at 298.15K, 303.15K and 308.15 K and at atmospheric pressure 0.1MPa.

Specific conductivity/ μS cm^{-1} 0.003mIL/mol.kg^{-1}						
Added IL/mL	Total volume (IL+AA)/mL	Conc. of AA at each titration point	Conc. of IL at each titration point	298.15K	303.15K	308.15K
0	20	0.01	0.00000	310	330	355
1	21	0.0095	0.00014	308	327	351
2	22	0.0090	0.00013	306	325	348
3	23	0.0086	0.00013	303	323	345
4	24	0.0083	0.00012	300	320	342
5	25	0.0080	0.00011	298	317	339
6	26	0.0076	0.00011	296	316	337
7	27	0.0074	0.00010	294	314	335
8	28	0.0071	0.00010	292	311	332
9	29	0.0068	0.00010	291	309	330
10	30	0.0066	0.00009	289	307	328
11	31	0.0064	0.00009	287	304	326
12	32	0.0062	0.00009	284	303	323
13	33	0.0060	0.00008	283	302	322
14	34	0.0058	0.00008	282	301	321
15	35	0.0057	0.00008	281	300	320
16	36	0.0055	0.00007	280	299	319
17	37	0.0054	0.00007	279	298	317
18	38	0.0052	0.00007	278	298	316
19	39	0.0051	0.00007	277	298	315
20	40	0.0050	0.00006	277	298	315

*Standard uncertainties u (κ)=±0.010(ms.cm^{-1}), #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1} u (T) =±0.01K(0.68 level of confidence), *Standard uncertainty in pressure u (p)= ±0.01 MPa. Initial concentration of Amino acid in the cell was 0.01mole/kg. Initial added concentration of IL in the cell in term of molality was 0.003mol.kg$^{-1.}$

Table S13. Specific conductance (κ) of (L-ARGININE+TBMS+H_2O) system in aqueous IL (TBMS) solutions of concentration 0.005m at 298.1 K, 303.15 K and 308.15 K and at atmospheric pressure 0.1MPa.

Specific conductivity/ μS cm^{-1} 0.005mIL/mol.kg^{-1}						
Added IL/mL	Total volume (IL+AA)/mL	Conc. of AA at each titration point	Conc. of IL at each titration point	298.15K	303.15K	308.15K
0	20	0.01	0.00000	438	470	503
1	21	0.0095	0.00023	436	466	498
2	22	0.0090	0.00022	434	463	494
3	23	0.0086	0.00021	432	461	490
4	24	0.0083	0.00020	430	459	487
5	25	0.0080	0.00019	428	457	484
6	26	0.0076	0.00018	426	454	480
7	27	0.0074	0.00017	424	452	474
8	28	0.0071	0.00017	423	450	472
9	29	0.0068	0.00016	421	448	470
10	30	0.0066	0.00016	419	446	468
11	31	0.0064	0.00015	418	444	464
12	32	0.0062	0.00015	417	443	464
13	33	0.0060	0.00014	416	442	462
14	34	0.0058	0.00014	415	441	460
15	35	0.0057	0.00013	414	440	458
16	36	0.0055	0.00013	413	439	456
17	37	0.0054	0.00013	411	438	454
18	38	0.0052	0.00012	410	437	453
19	39	0.0051	0.00012	409	435	451
20	40	0.0050	0.00011	408	434	450

*Standard uncertainties u (κ)=±0.010(ms.cm^{-1}), #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1} u (T) =±0.01K(0.68 level of confidence), *Standard uncertainty in pressure u (p)= ±0.01 MPa. Initial concentration of Amino acid in the cell was 0.01mole/kg. Initial added concentration of IL in the cell in term of molality was 0.005mol.$kg^{-1.}$

Table S14. Specific conductance (κ) of (L-HISTIDINE +TBMS+H_2O) system in aqueous IL (TBMS) solutions of concentration 0.001m at 298.15 K, 303.15 K and 308.15 K and at atmospheric pressure 0.1MPa.

Specific conductivity/ μS cm^{-1} 0.001mIL/mol.kg^{-1}						
Added IL/mL	Total volume (IL+AA)/mL	Conc. of AA at each titration point	Conc. of IL at each titration point	298.15K	303.15K	308.15K
0	20	0.01	0.00000	210	239	261
1	21	0.0095	0.00047	208	236	258
2	22	0.0090	0.00044	206	234	256
3	23	0.0086	0.00043	205	231	254
4	24	0.0083	0.00041	204	229	251
5	25	0.0080	0.00040	203	226	249
6	26	0.0076	0.00038	202	223	247
7	27	0.0074	0.00037	201	221	245
8	28	0.0071	0.00035	200	219	244
9	29	0.0068	0.00034	198	217	242

10	30	0.0066	0.00033	197	215	239
11	31	0.0064	0.00032	196	213	236
12	32	0.0062	0.00031	194	210	235
13	33	0.0060	0.00030	193	209	233
14	34	0.0058	0.00029	192	207	232
15	35	0.0057	0.00028	191	205	230
16	36	0.0055	0.00027	190	204	229
17	37	0.0054	0.00027	188	203	228
18	38	0.0052	0.00026	187	202	227
19	39	0.0051	0.00025	186	201	228
20	40	0.0050	0.00025	186	201	225

*Standard uncertainties u (κ)=$\pm$0.010(ms.cm^{-1}), #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1} u (T) =$\pm$0.01K(0.68 level of confidence), *Standard uncertainty in pressure u (p)= ±0.01 MPa. Initial concentration of Amino acid in the cell was 0.01mole/kg. Initial added concentration of IL in the cell in term of molality was 0.001mol.kg^{-1}.

Table S15. Specific conductance (κ) of (L-HISTIDINE +TBMS+H_2O) system in aqueous IL (TBMS) solutions of concentration 0.003m at 298.15K, 303.15K and 308.15 K and at atmospheric pressure 0.1MPa.

Specific conductivity/ μS cm^{-1} 0.003mIL/mol.kg^{-1}						
Added IL/mL	Total volume (IL+AA)/mL	Conc. of AA at each titration point	Conc. of IL at each titration point	298.15K	303.15K	308.15K
0	20	0.01	0.00000	361	421	472
1	21	0.0095	0.00047	356	419	469
2	22	0.0090	0.00044	354	417	467
3	23	0.0086	0.00043	352	415	464
4	24	0.0083	0.00041	350	413	461
5	25	0.0080	0.00040	348	411	457
6	26	0.0076	0.00038	346	409	455
7	27	0.0074	0.00037	344	407	452
8	28	0.0071	0.00035	342	405	450
9	29	0.0068	0.00034	340	403	448
10	30	0.0066	0.00033	338	401	446
11	31	0.0064	0.00032	335	399	444
12	32	0.0062	0.00031	333	397	442
13	33	0.0060	0.00030	330	394	440
14	34	0.0058	0.00029	327	393	437
15	35	0.0057	0.00028	326	392	435
16	36	0.0055	0.00027	325	391	433
17	37	0.0054	0.00027	324	390	432
18	38	0.0052	0.00026	323	389	431
19	39	0.0051	0.00025	323	388	430
20	40	0.0050	0.00025	323	387	429

*Standard uncertainties u (κ)=$\pm$0.010(ms.cm^{-1}), #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1}u (T) =$\pm$0.01K(0.68 level of confidence), *Standard uncertainty in pressure u (p)= ±0.01 MPa. Initial concentration of Amino acid in the cell was 0.01mole/kg. Initial added concentration of IL in the cell in term of molality was 0.003mol.kg^{-1}.

Table S16. Specific conductance (κ) of (L-HISTIDINE +TBMS+H_2O) system in aqueous IL (TBMS) solutions of concentration 0.005m at 298.15K, 303.15 K and 308.15 K and at atmospheric pressure 0.1MPa

Specific conductivity/ μS cm^{-1} 0.005mIL/mol.kg^{-1}						
Added IL/mL	Total volume (IL+AA)/mL	Conc. of AA at each titration point	Conc. of IL at each titration point	298.15K	303.15K	308.15K
0	20	0.01	0.00000	520	578	702
1	21	0.0095	0.00047	518	575	698
2	22	0.0090	0.00044	516	572	695
3	23	0.0086	0.00043	514	570	692
4	24	0.0083	0.00041	512	568	689
5	25	0.0080	0.00040	510	566	686
6	26	0.0076	0.00038	507	564	683
7	27	0.0074	0.00037	505	562	680
8	28	0.0071	0.00035	503	560	677
9	29	0.0068	0.00034	501	558	675
10	30	0.0066	0.00033	499	556	673
11	31	0.0064	0.00032	498	554	672
12	32	0.0062	0.00031	497	553	671
13	33	0.0060	0.00030	496	550	670
14	34	0.0058	0.00029	495	549	669
15	35	0.0057	0.00028	494	548	668
16	36	0.0055	0.00027	493	547	667
17	37	0.0054	0.00027	492	546	666
18	38	0.0052	0.00026	491	545	665
19	39	0.0051	0.00025	490	544	664
20	40	0.0050	0.00025	489	543	663

*Standard uncertainties u (κ)=±0.010(ms.cm^{-1}), #Combined standard uncertainties in molality according to stated purity u(m) =±0.0092 mol kg^{-1} u (T) =±0.01K(0.68 level of confidence), *Standard uncertainty in pressure u (p)= ±0.01 MPa. Initial concentration of Amino acid in the cell was 0.01mole/kg. Initial added concentration of IL in the cell in term of molality was 0.005mol.kg^{-1}.

Figures

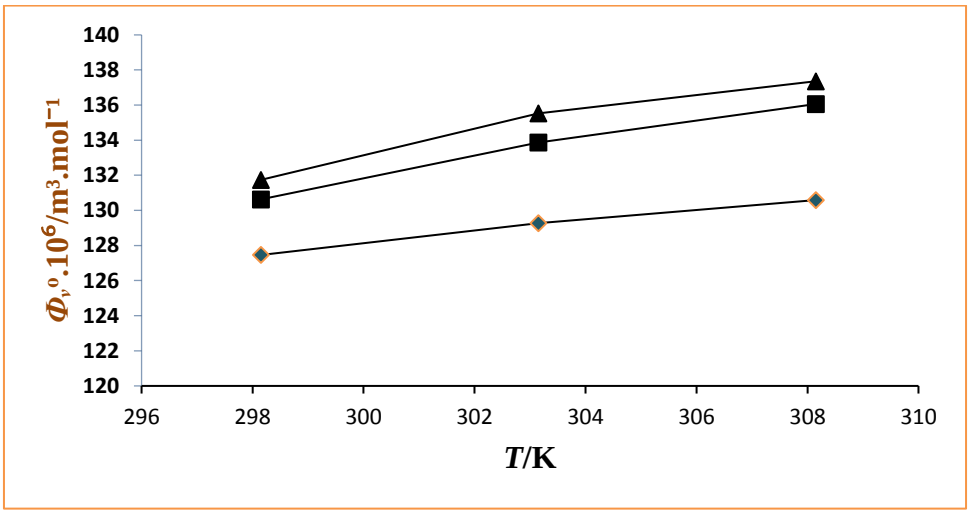


Figure 1. Variation of limiting apparent molar volumes (Φ_v^0) of L-Arginine as a function of temperature /K in aqueous TBMS solutions of different concentrations (-▲- 0.001m/mol.kg^{-1}; -■- 0.003m/mol.kg^{-1}; -♦- 0.005m/mol.kg-1).

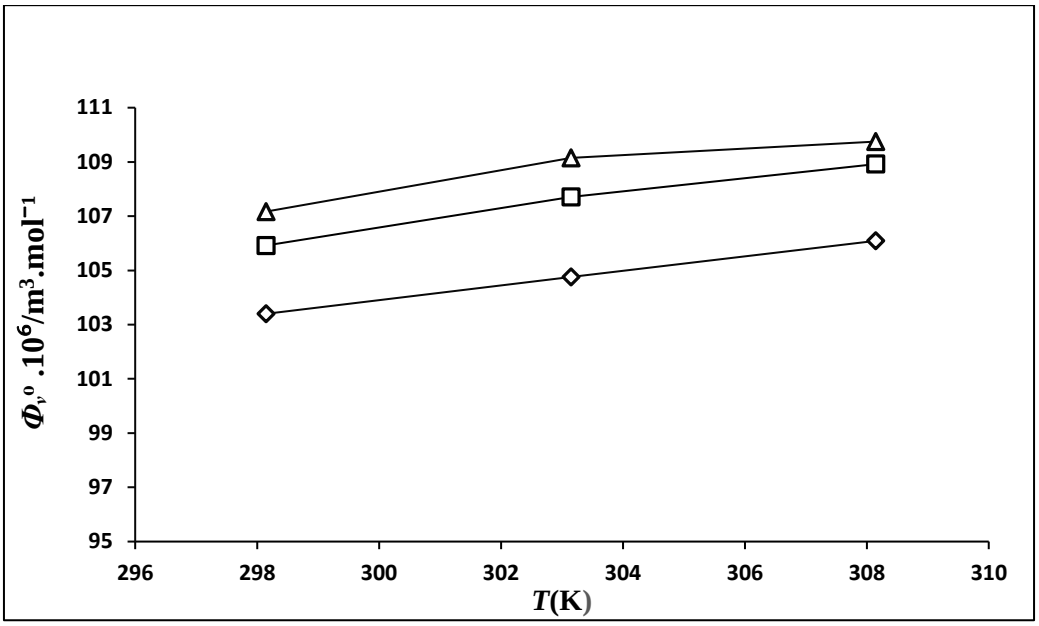


Figure 2. Variation of limiting apparent molar volumes (Φ_v^0) of L-Histidine as a function of temperature /K in aqueous TBMS solutions of different concentrations (-Δ- 0.001m/mol.kg^{-1}; -□- 0.003m/mol.kg^{-1}; -◊- 0.005m/mol.kg^{-1}).

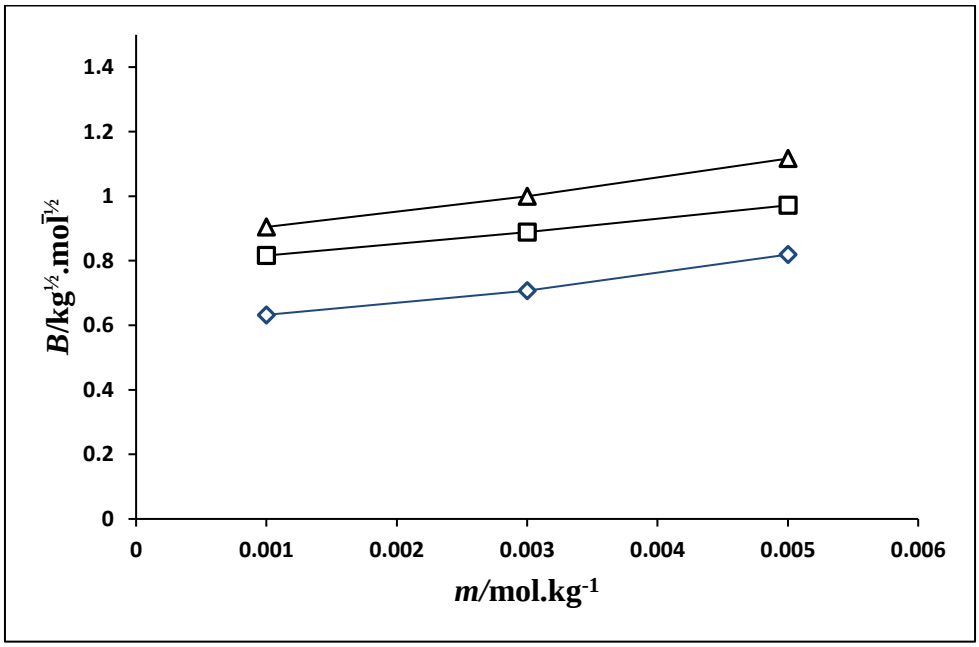


Figure 3. Variation of viscosity *B*-coefficient of L-Arginine as a function of different concentrations of aqueous TBMS (IL) solutions at (-◊- 298.15K; -□- 303.15K; -Δ- 308.15K).

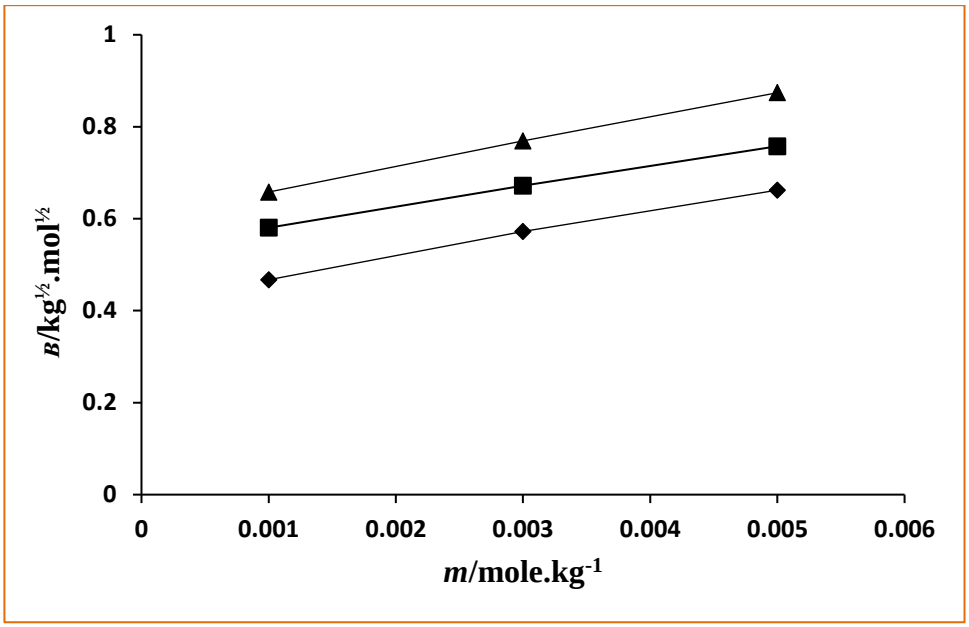


Figure 4. Variation of viscosity *B*-coefficient of L-Histidine as a function of different concentrations of aqueous TBMS (IL) solutions at (-♦- 298.15K; -■- 303.15K; -▲- 308.15K).

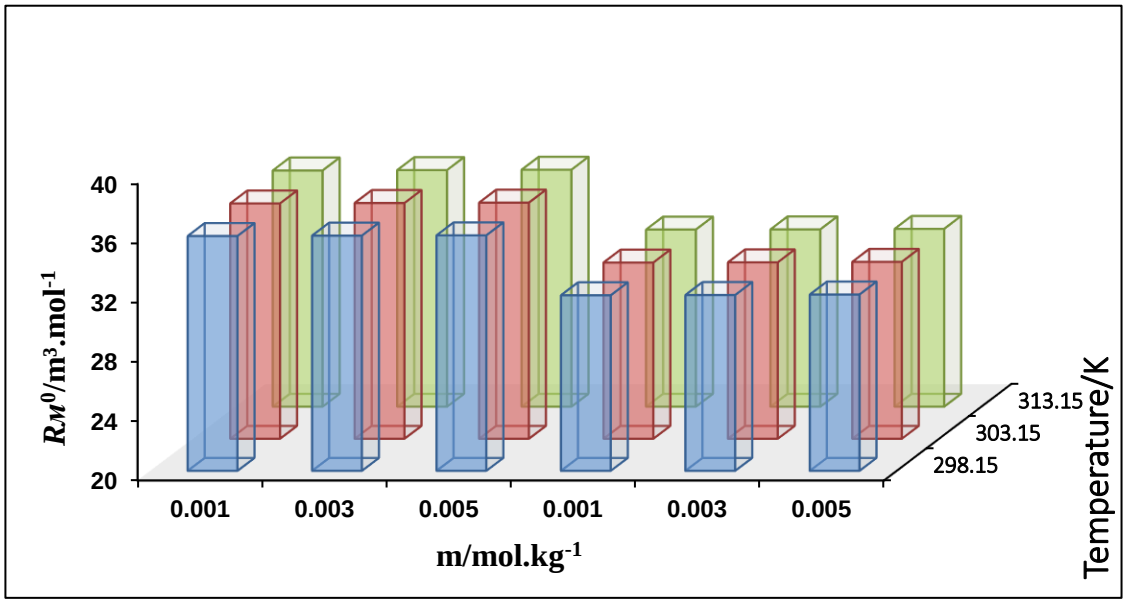


Figure 5. Variation of limiting molar refraction (R_m^0) plot of L-Arginine (big size figure) and L-Histidine (small size figure) as a function of different concentrations of aqueous TBMS solutions and as a function of temperature (*T*/K).

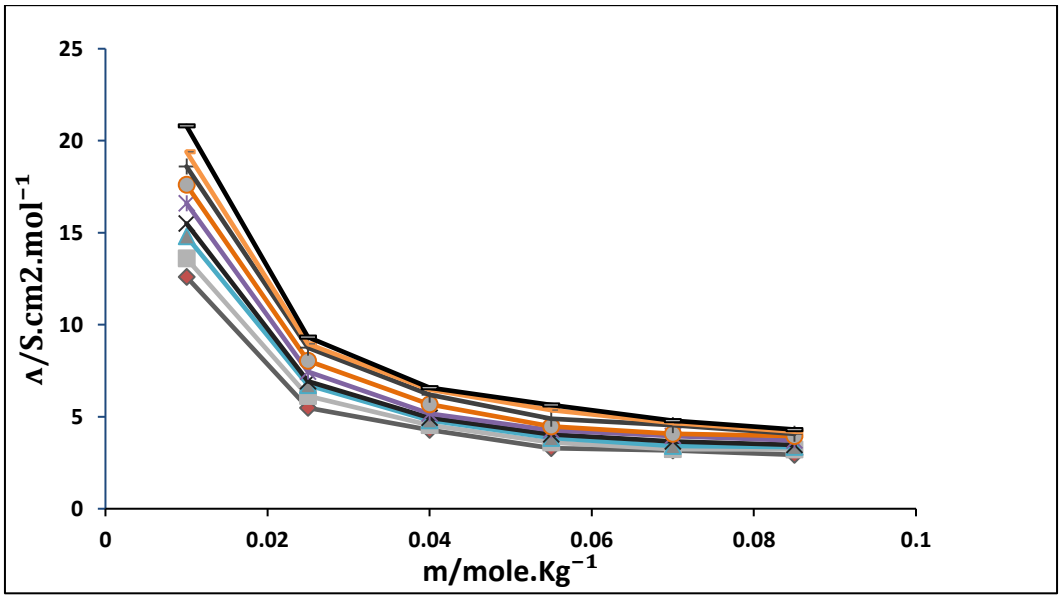


Figure 6. Variation of molar conductance (*Λ*) plot as a function of the concentration of L-Arginine (amino acid) in different concentrations aqueous TBMS solutions at different temperatures (*T*/K) (-◊- concentration(IL)0.001m/mol.kg^{-1} at 298.15K; -□-concentration(IL) 0.001m/mol.kg^{-1} at 303.15K; -Δ-concentration(IL)0.001m/mol.kg^{-1} at 308.15K, -x-concentration (IL) 0.003m/mol.kg^{-1} at 298.15K; -✳- concentration (IL) 0.003m/mol.kg^{-1} at 303.15K; -●- concentration (IL) 0.003m/mol.kg^{-1} at 308.15K; ─ concentration (IL) 0.005 at 298.15K; ─ concentration (IL) 0.005m/mol.kg^{-1} at 303.15K and ─ concentration (IL) 0.005m/mol.kg^{-1} at 308.15K.

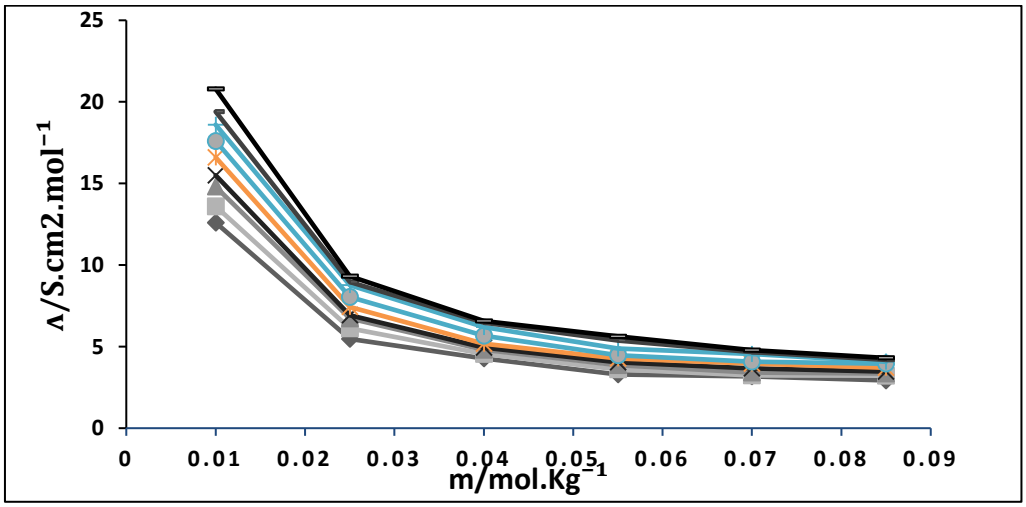


Figure 7. Variation of molar conductance (*Λ*) plot as a function of the concentration of L-Histidine (Amino acid) in differentconcentrations aqueous TBMS solutions at different temperatures (*T*/K) (-◊- concentration(IL)0.001m/mol.kg^{-1} at 298.15K; -□-concentration(IL)0.001m/mol.kg^{-1} at 303.15K;-Δ-concentration(IL)0.001m/mol.kg^{-1} at 308.15K, -x- concentration (IL) 0.003m/mol.kg^{-1} 0.003 at 298.15K; -✳- concentration (IL) 0.003m/mol.kg^{-1} at 303.15K; -●- concentration (IL) 0.003m/mol.kg^{-1} at 308.15K; ─ concentration (IL) 0.005m/mol.kg^{-1} at 298.15K; ─ concentration (IL) 0.005m/mol.kg^{-1} at 303.15K and ─ concentration (IL) 0.005m/mol.kg^{-1} at 308.15K.

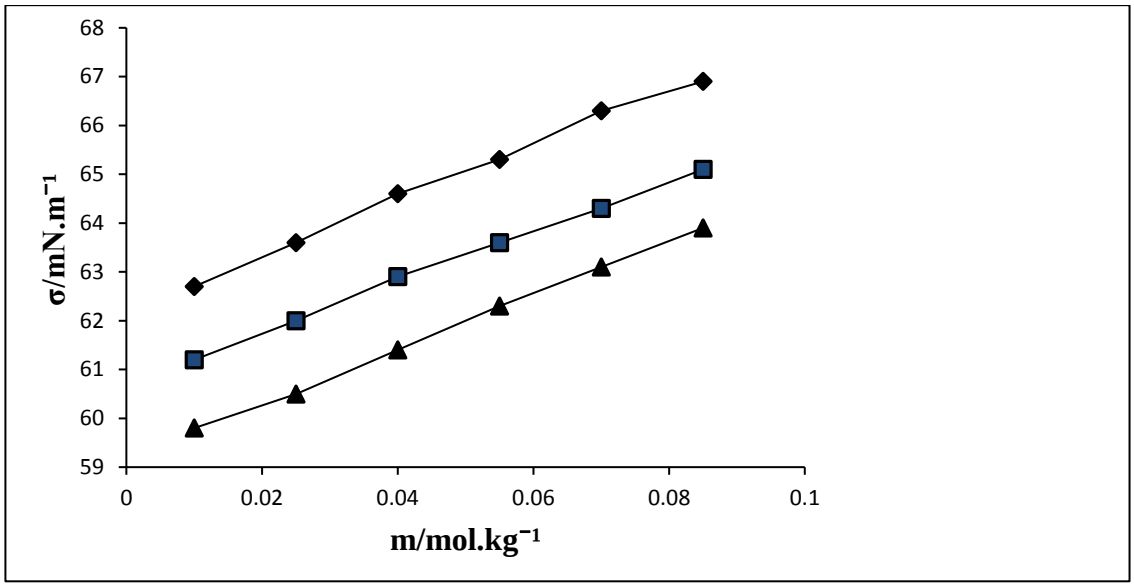


Figure 8. Variation of surface tension (σ) plot of L-Arginine as a function of different concentrations (-▲- 0.001m/mol.kg^{-1}; -■- 0.003m/mol.kg^{-1}; -♦- 0.005m/mol.kg^{-1}) of aqueous TBMS solutions at 298.15 K.

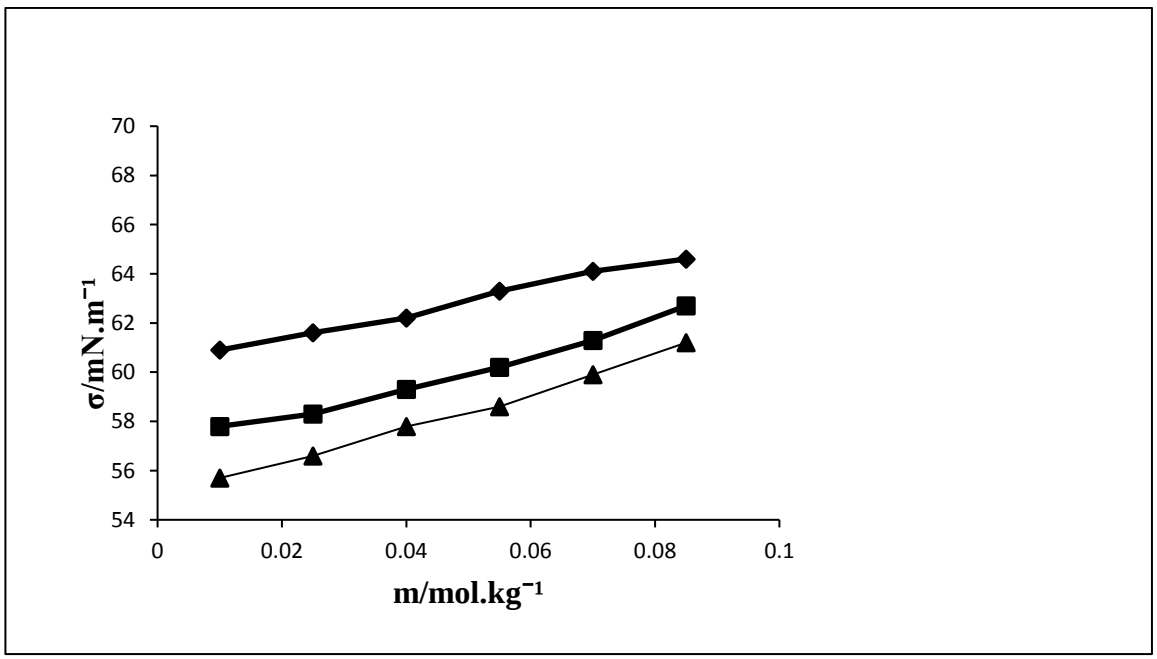


Figure 9. Variation of surface tension (σ) plot of L-Histidine as a function of different concentrations (-▲- 0.001m/mol.kg^{-1}; -■- 0.003m/mol.kg-^{1}; -♦- 0.005m/mol.kg^{-1}) of aqueous TBMS solutions at 298.15 K.

Supporting figures

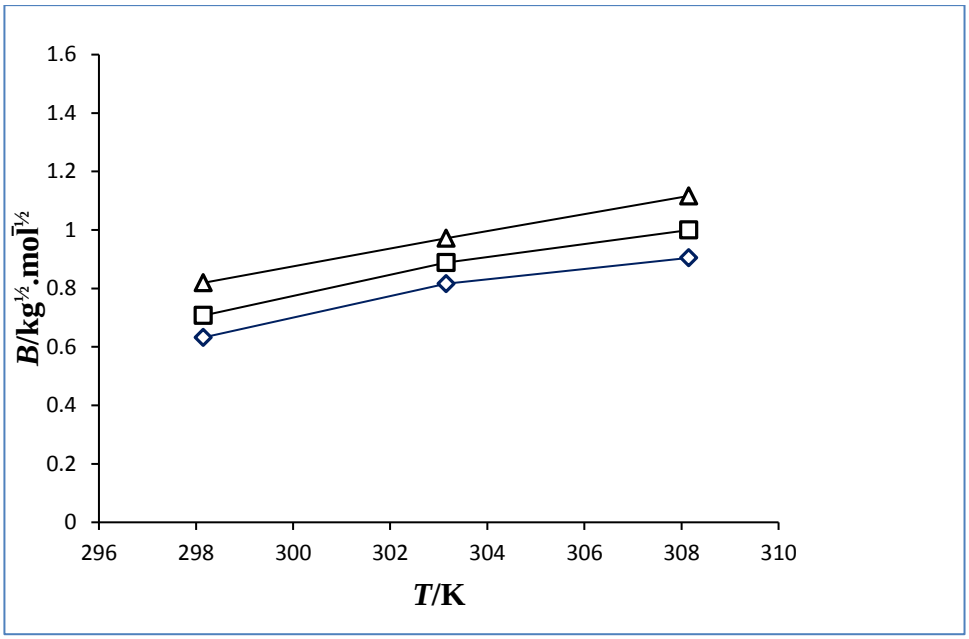


Figure S1. Variation of viscosity *B*-coefficient of L-Arginine against temperature in different concentrations (-◊- 0.001m/mol.kg^{-1}; -□- 0.003m/mol.kg^{-1}; -Δ- 0.005m/mol.kg^{-1}) of aqueous IL Solution.

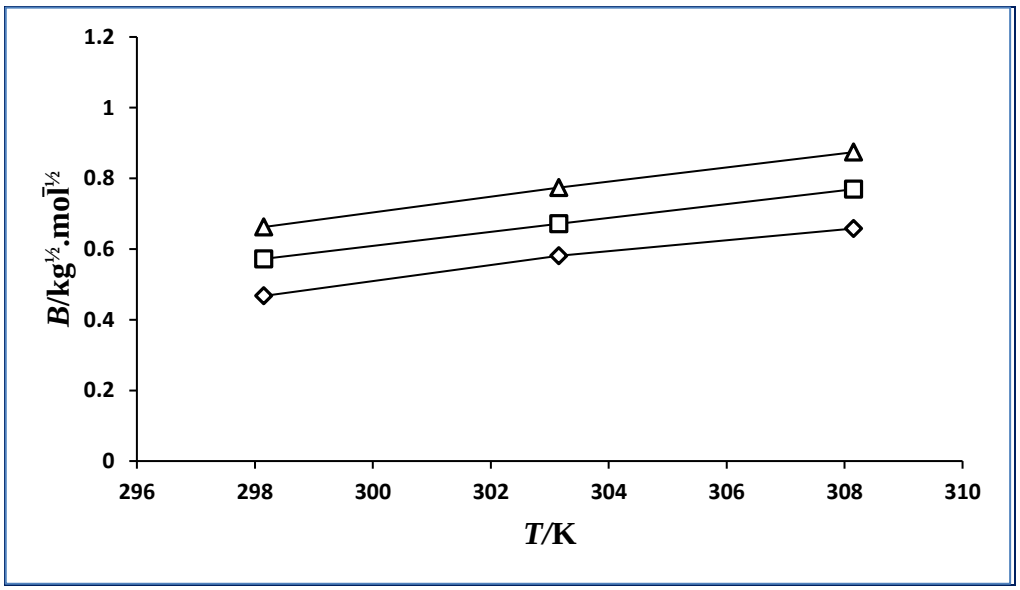


Figure S2. Variation of viscosity *B*-coefficient of L-Histidine solution against temperature in different concentrations (-◊- 0.001m/mol.kg^{-1}; -□- 0.003m/mol.kg^{-1}; -Δ- 0.005m/mol.kg^{-1}) of aqueous solutions of IL.

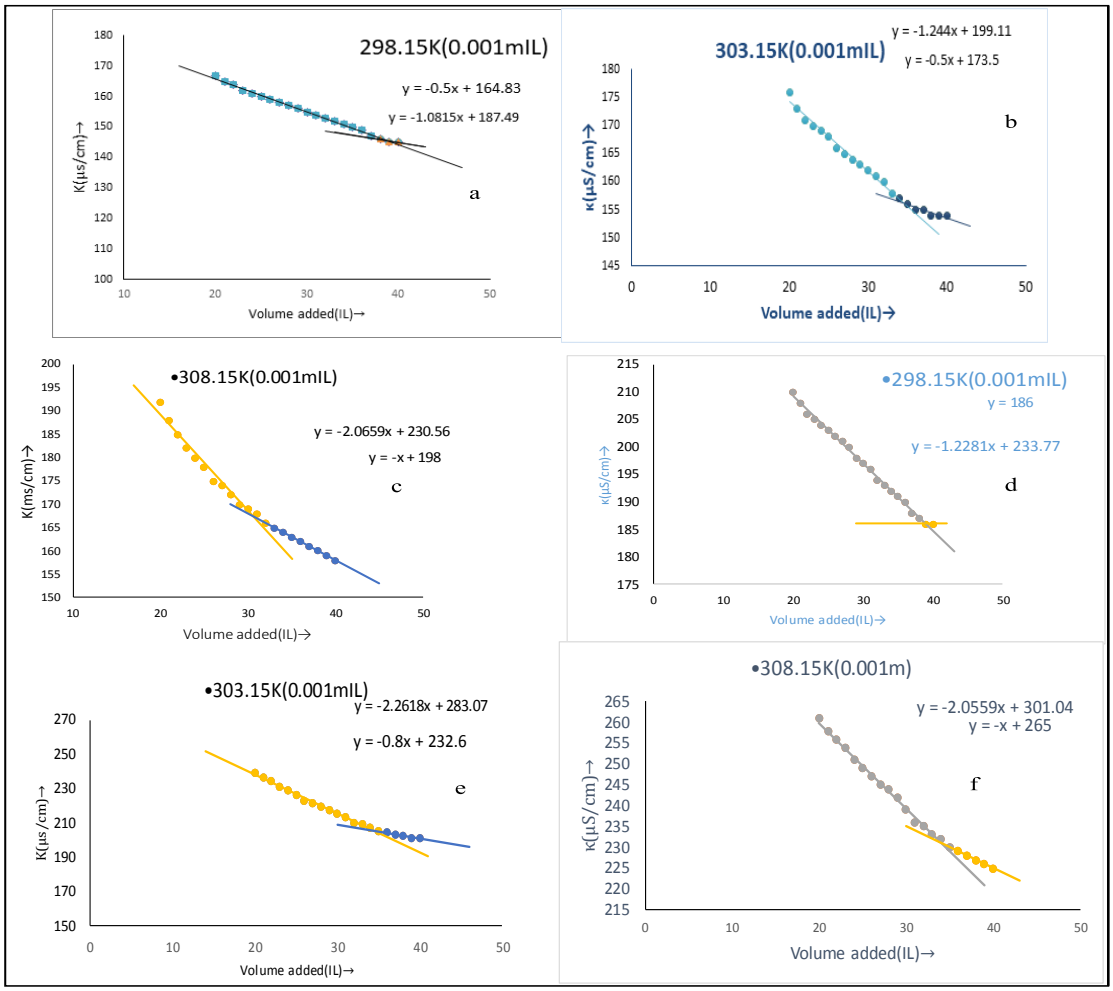


Figure S3. CMC plot of conductance of L-Arginine (a, b, c) and L-Histidine (d, e, f) with addition of 0.001 m aqueous solution of TBMS IL.

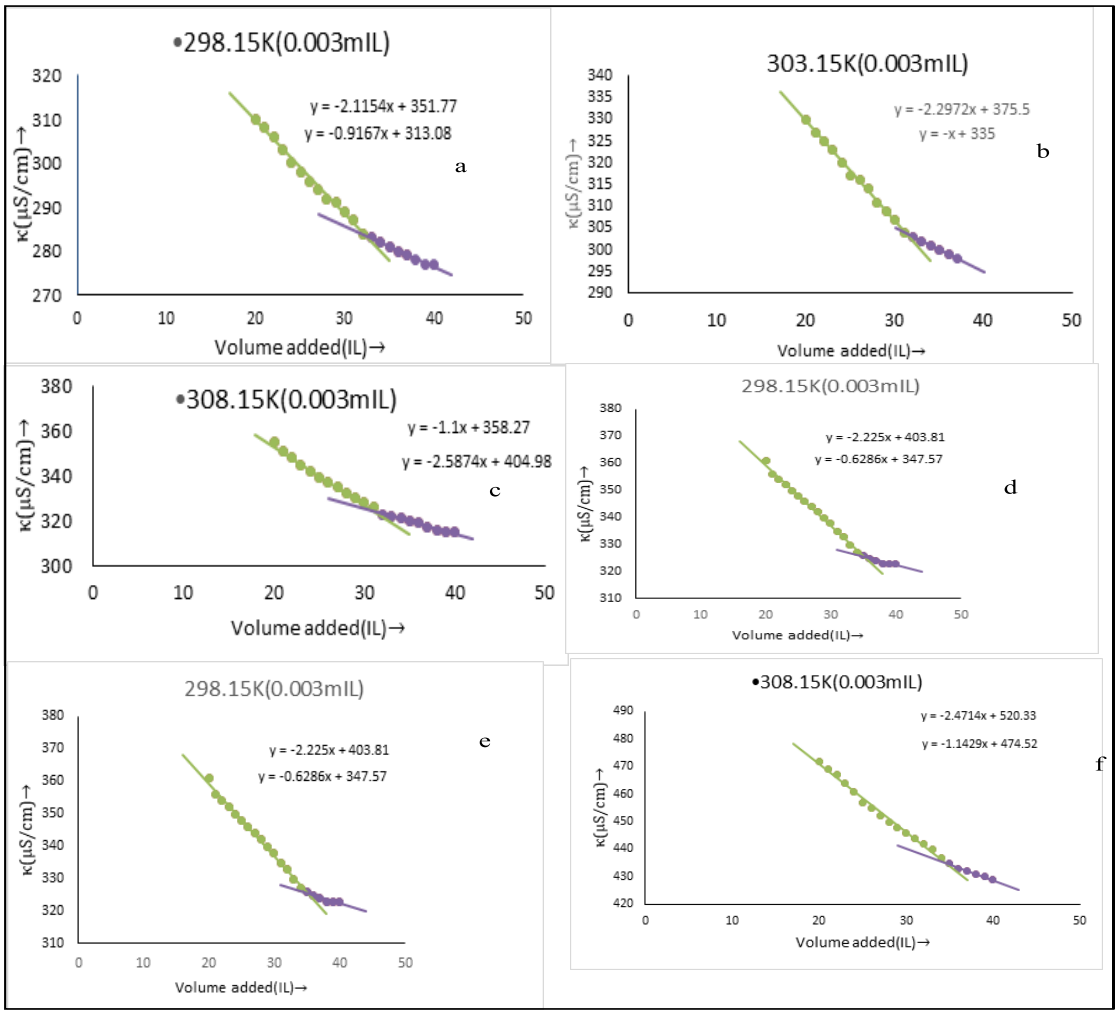


Figure S4 .CMC plot of conductance of L-Arginine (a, b, c) and L-Histidine (d, e, f) with addition of aqueous solutions of IL (0.003 m) at different temperatures.

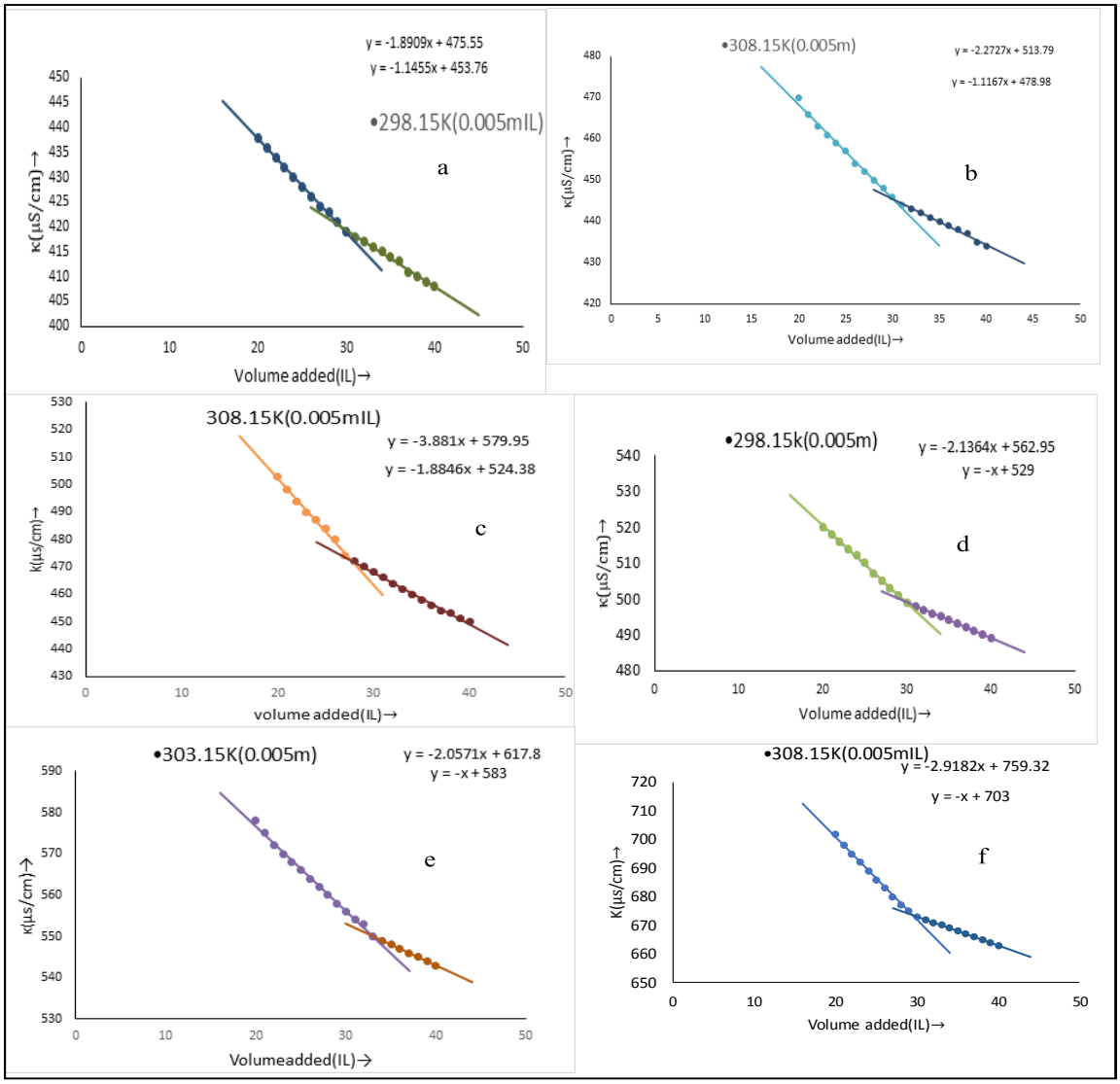
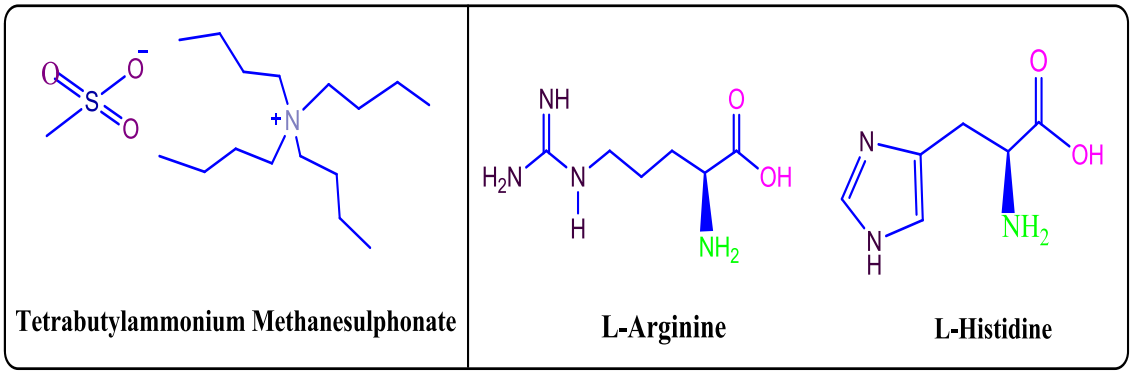
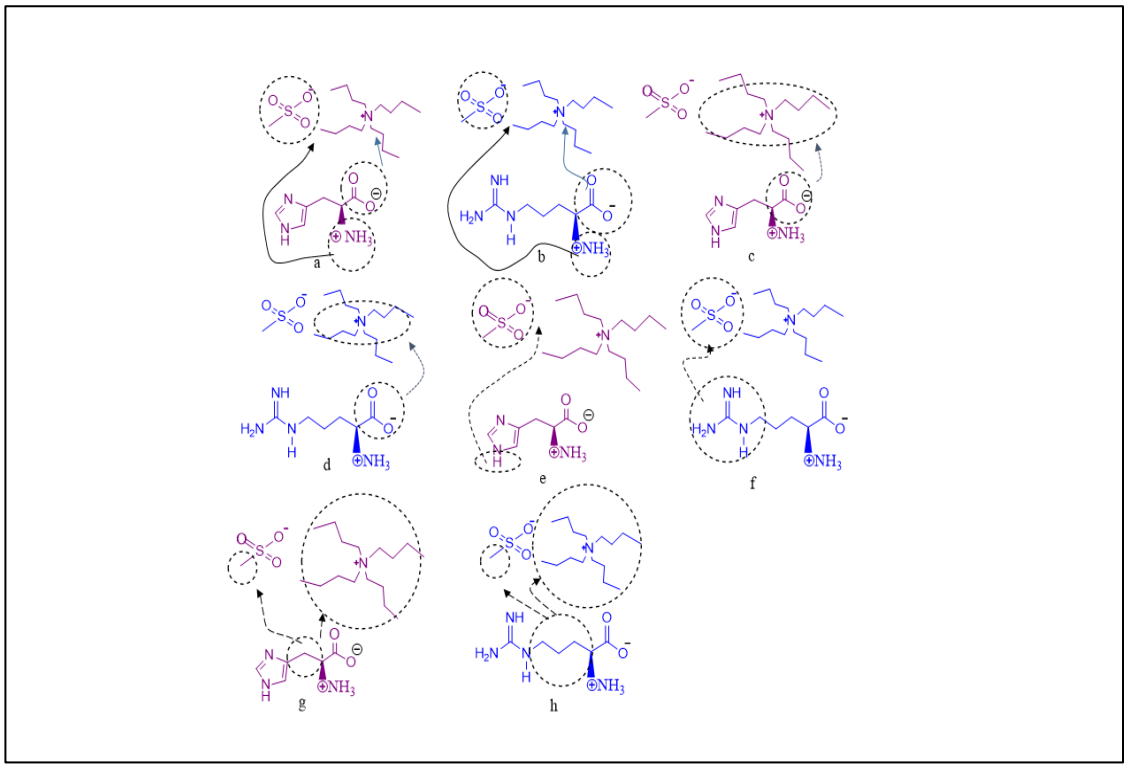


Figure S5. CMC plot of conductance of L-Arginine (a, b, c) and L-Histidine (d, e, f) with addition 0.005 m aqueous solution of IL (TBMS).

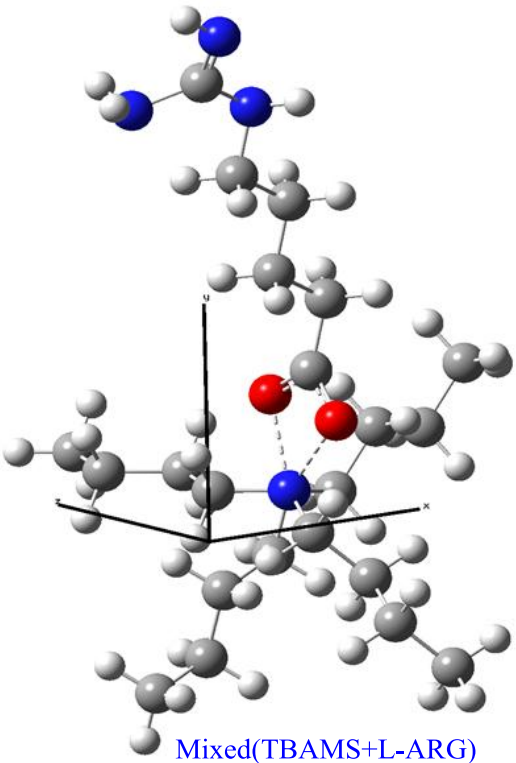
Schemes



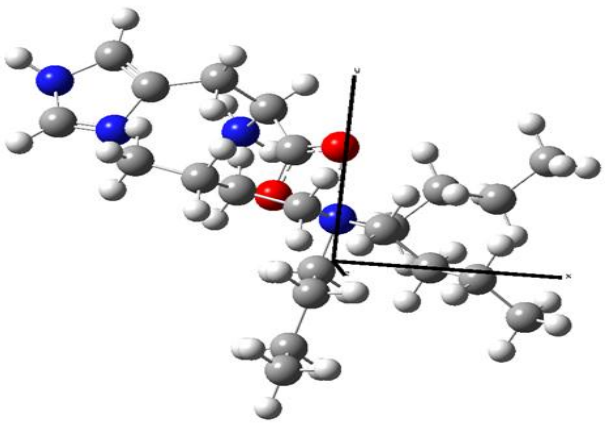
Scheme 1. Molecular Structure of Tetrabutylammonium Methanesulphonate and L-Arginine and L-Histidine.



Scheme 3. Schematic representation of plausible molecular interactions between amino acid and ionic liquid, a & b ion-ion interactions (→); c & d ion-hydrophobic interactions (⇢); e & f hydrogen bonding interactions (⇢); g & h hydrophobic-hydrophobic interactions (⇢).



Mixed(TBAMS+L-ARG)
Fig-a



Mixed(TBAMS+L-HIS)

Fig-b

Scheme 2 (a, b) Optimized geometry of (a) (TBMS+ L-ARG) and(b) TBMS+ L-HIS Systems.