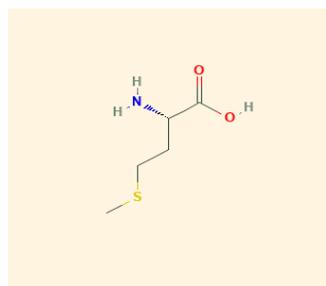


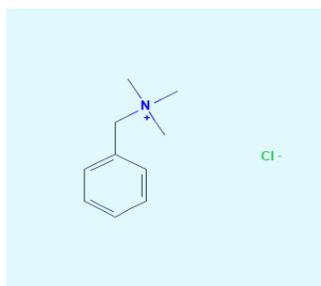
CHAPTER-VIII

EXPLORATION OF DIVERSE INTERACTIONS OF L-METHIONINE IN AQUEOUS SIGNIFICANT MIXED IONIC LIQUID SOLUTIONS OPTIMIZED BY COMPUTATIONAL THEORY

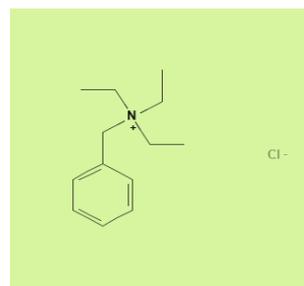
ABSTRACT: Solution behaviour prevailing in L-methionine in two aqueous ionic liquid solutions (Benzyl tri-methyl ammonium chloride and Benzyl tri-ethyl ammonium chloride) have been studied by investigation of some physico-chemical parameters namely density, viscosity, refractive index, conductance and surface tension. The nature of interactions occurring in the solution have been elucidated on the basis of apparent molar volume, viscosity A and B-coefficient, molar refraction at different temperatures and concentrations from density, viscosity, refractive index, surface tension measurements, respectively. Molecular interactions has also been explained based on Molar conductance (Λ) measurement. The experimental slopes and the limiting apparent molar volumes obtained from Masson equation, viscosity parameters, A and B coefficients obtained from Jones-Doles equation, Molar refraction from the Lorentz-Lorenz equation and specific conductance obtained, so, describe the nature of solute-solute and solute-solvent interactions in the solution. Spectroscopic techniques such as FTIR, $^1\text{H-NMR}$, UV-Vis also gives the supportive information for the interactions associated among two ionic liquid with L-methionine in aqueous medium.. Furthermore, density functional theory has been employed to evaluate adsorption energies and type of interactions which is concordant with the experimental observations.



L-Methionine



Benzyl tri-methyl ammonium chloride



Benzyl tri-ethyl ammonium chloride

Keywords: L-Methionine; Benzyl tri-methyl ammonium chloride; Benzyl tri-ethyl ammonium chloride; solute-solvent interaction; solute-solute interaction; Amino acids; Ionic liquid, structure-breaker solutes.

1. INTRODUCTION

The thermodynamic data of aqueous solutions of small amino acids chain are important for pharmaceuticals and food industries to improve the design and operation of the unit operations, as surface tension and volumetric properties are vital for understanding the multiplied phase transport processes.¹ Thermodynamic properties of amino acids in aqueous electrolyte solutions can provide valuable information regarding the conformation stability of proteins in these solutions, their solubility, denaturation, dissociation into subunits, the activity of enzymes,

separation and purification, solute–solvent and solute–solute interactions.^{2-5 6-9} Consequently, the study of the volumetric properties of amino acids in aqueous ionic liquid solutions will be very useful for obtaining information about various kinds of interactions occurring in these solutions, which are mostly hydrophobic and electrostatic. Studying these interactions can provide important insight into the conformational stability and unfolding behaviour of globular proteins.

Thermodynamic properties of amino acids in aqueous solutions containing salts can provide valuable information about solute–solute and solute–solvent interactions. The conformational properties of amino acids containing salts affect in aqueous solutions and cause denaturation of proteins which is an important biological phenomenon. Therefore, keeping the importance and applicability in view, the systematic thermodynamic investigation of mixtures containing IL and amino acids is undertaken to understand the solvation behaviour of these biomolecules.¹⁰ Study of transport properties of electrolytes in aqueous media is extremely very useful to obtain information regarding the solvation and association behaviour of ions in solutions. The electrical conductivity of electrolytes in solvents mainly depends on the concentration of the electrolyte and also the viscosity of the solvent. From the study of ionic solvation the application of salt is well understood.

The physicochemical and as well as the thermodynamic both properties of amino acids are of considerable interest, as these bio molecules are the building blocks of all living organisms, and are found to provide valuable information that leads to a better understanding of proteins. Therefore, one useful approach is to investigate interactions of the model compounds of proteins, e.g., amino acids, in aqueous solutions. It has also been recognized that in the absence of experimental thermodynamic data of proteins, amino acids can serve as useful models in estimating their properties. The choice of water for preparing mixed solvent stems from its important and unique role in determining the structure and stability of protein since its presence give rise to hydrophobic forces, which are of prime importance in stabilizing native globular structure of protein.¹¹

An ionic liquid, IL¹² is a salt in the liquid state of melting point below some arbitrary temperature such as 373 K. They have specific intrinsic properties, such as negligible vapour pressure, high thermal stability, large liquid range, ability of dissolving a variety of chemicals, large electrochemical window. Ionic liquids are used as “designer solvents” and “green” substitutes for volatile organic solvents used in reactions involving inorganic and biocatalytic reactions, etc. For processing biomass, ionic liquids are also utilized as heat transfer fluids. It can also utilized as electrically conductive liquids in electrochemistry (batteries and solar cells). They are used in analytical equipment. They make up electrolytes in lithium-ion batteries, super capacitors and metal plating baths.¹³⁻¹⁹

The chemicals used in this investigation find wide industrial usage. Benzyl tri-methyl ammonium chloride or BTMAC is soluble in water and has lyophilic and hydrophilic group. BTMAC can also be used as a corrosion inhibitor in oilfield. L-Methionine or L-Met is an essential amino acid in humans because it takes a critical role in the case of metabolism and health of many species. It is found in meat, fish and dairy products and is involved in many cell functions. It is also applied for increasing the acidity level of urine, treating as liver disorders and improving wound healing. Methionine can be synthesized from all plants and some forms of bacteria. Cobalamine enzyme is used to synthesize mammalian tissues and many bacteria whereas all the plants and some bacteria synthesize it from homocysteine. Cerebrospinal fluid levels of Methionine, cystathionine and homocysteine were very carefully investigated in patients with psychotic disorders.²⁰

In the modern technology, the application of the salt is well known from the study of ionic solvation or ion association. Ionic association of electrolytes in solution depends on the mode of solvation of its ions that in turn depends on the nature of the solvent/solvent mixtures.²¹⁻²⁴ The association and solvation behaviour of ions in solution is obtained from the conductance measurement. Moreover, viscosity and the relative permittivity as solvent properties help in determining the degree of ion association and the solvent-solvent interactions. The volumetric, viscometric, refractometric, conductometric and surface tension parameters of solutes has been found to be very useful in elucidating the various interactions occurring in solutions.

In continuation of our investigation, the present work deals with the transport and thermodynamic properties of L-Methionine in aqueous Benzyl tri-methyl ammonium chloride and Benzyl tri-ethyl ammonium chloride at 298.15K, 303.15K and 308.15K supported spectroscopically.

2. EXPERIMENTAL DETAILS

2.1. Materials. The studied ILs, Benzyl tri-methyl ammonium chloride, $C_{10}H_{16}ClN$ (M.W. 185.69 g/mole), Benzyl tri-ethyl ammonium chloride, $C_{13}H_{22}ClN$ (M.W. 227.77 g/mole) and amino acid, L-Methionine, $C_5H_{11}NO_2S$ (M.W. 149.21 g/mole) of puriss grade were purchased from Sigma Aldrich India, Germany and Japan, respectively and was used as purchased. The purity of mass of taken salts was nearly 0.97 to 0.99 in mass fraction. The ionic liquids and amino acid were taken for experiment without further purification. The Specification of the chemical samples are given in **Table 1**. The chemicals were dried in vacuum over blue silica gel for at least 72 h at room temperature before use.

2.2. Experimental Procedures. The vibrating-tube Anton Paar Density-Meter (DMA 4500M) was used to measure the density (ρ) with a precision of $0.00001 \times 10^{-3} \text{ (kg}\cdot\text{m}^{-3})$. The double-distilled water and dry air was used to calibrate the density meter.²⁵ The temperature was kept constant within range $\pm 0.01 \text{ K}$ with the help of an automatic built-in Peltier device.

The viscosity was measured with the help of suspended Ubbelohde viscometer which was calibrated at room temperature (298.15K) using doubly distilled water. It was purified with methanol and using viscosity, density data from literature.^{26, 27} The viscometer was dried and cleaned perfectly through hot thermostat and then filled with experimental solution, vertically placed in a glass-walled thermostat (Bose–Panda instruments Pvt.Ltd.) This instrument was maintained to 0.01K. At thermal equilibrium the flow-time were recorded with the help of a stop watch with an accuracy of $\pm 0.01 \text{ s}$. The uncertainty for the measurement of viscosity was $\pm 0.2 \times 10^{-3} \text{ mPa}\cdot\text{s}$.

Measurement of refractive index has been done with the help of a Digital Refractometer Mettler Toledo instrument. The accuracy for the refractive index measurement was ± 0.0002 units approximately. The refractometer was calibrated twice using distilled water for measurement of the refractive indices of experimental solutions. The calibration of instrument was made after few seconds of each measurement.²⁵ The light source was light-emitting diode, $\lambda = 589.3 \text{ nm}$. The temperature of the solution was maintained during the experiment in a Brookfield Digital TC-500 Thermostatic water bath.

The conductivity measurement was done by Mettler Toledo Instrument (In Lab730 probe cell). The specification of the cell has measurement of conductivity range (0.01-1000 mS/cm). The cell type 4 graphite having a cell constant 0.56 cm^{-1} . The calibration of the cell has been done with 0.01N (NaCl solution). The accuracy of the conductance measurement was $\pm 0.5\%$. The specific conductance of the experimental solution having concentration (0.0010, 0.0025, 0.0040, 0.0055, 0.0070, 0.0085) m was reported at 298.15 K, 303.15K, 308.15 K (Where the symbol “m” represents molality of the solution of amino acid & ionic liquid mixture and unit was given by $\text{kg}\cdot\text{mol}^{-1}$) and was converted into molar conductance by the following equation, $\Lambda = 1000 \kappa / c$ (where c is the molar concentration of the amino acid solutions in the ionic liquids. κ is the specific conductance of the specified solutions.^{28, 29}

Surface Tension measurements of the solutions were carried out by a digital K9 Tensiometer (Kruss, Germany) using the platinum ring detachment technique at 298K. The temperature of this device was maintained by circulating auto-thermostatic water through the solution in a double-wall glass vessel with an accuracy of $\pm 0.1 \text{ mNm}^{-1}$. The calibration of the digital K9 Tensiometer (Kruss, Germany) was carried out with doubly distilled water.

FTIR (Fourier Transformation Infrared) spectra were taken by using a PerkinElmer spectrometer with resolution of 4 cm^{-1} by disk method at room temperature.

Solution-state Nuclear Magnetic Resonance (NMR) measurements were performed in D_2O solvent using Bruker AVANCE DRX 400 NMR spectrometer operating at 400MHz for obtaining the ^1H NMR spectra at 298K. Signals were symolised as δ values in ppm using residual protonated solvent signals as internal standard (D_2O : 4.79 ppm). The differences in chemical shifts were recorded to analyze the interaction between the amino acid and ILs molecules. The chemical shift values of protons are reported as δ units (ppm). The chemical shift values of peaks of interest were get by using peak pick facility. The uncertainty of δ units was estimated to be better than 0.0005 ppm.¹⁴

JASCO V-530 UV–Vis spectrophotometer was used to record the UV-visible spectra of experimental solutions of different concentration. The accuracy of wavelength of this spectrophotometer was $\pm 0.5\text{ nm}$. During the experiment the cell temperature was maintained from 298.15K to 308.15K with a digital thermostat.

Adequate precautions of measurements were taken to minimize evaporation losses during the actual measurements. Mass measurements for stock solutions were done on a Mettler AG-285 electronic balance with a precision of $\pm 0.0003 \times 10^{-3}\text{ kg}$. The combined standard uncertainty in molality according to mass purity of the samples is estimated to be $\pm 0.0095\text{ mol. kg}^{-1}$.

The conversion of molarity into molality was accomplished using experimental density values using the following formula:³⁰

$$m = \frac{1}{\left\{ \left(\frac{\rho}{c} \right) - \left(\frac{M}{1000} \right) \right\}} \quad (1)$$

2.3 Computational Details. All the density functional theory (DFT) calculations were performed utilizing the Gaussian 16 program.³¹ Ground state geometry optimization of the L-methionine, ionic liquids, and the composites were done at B3LYP/6-31+G(d) level of theory. In the course of ground state optimization, solvent effects (water) were introduced employing the Polarizable Continuum Model (PCM) using the integral equation formalism variant by Gaussian 16 package. To check whether the energy minimized geometries correspond to the true ground state geometries, vibration frequency analysis were performed at the same level of theory. No imaginary frequency confirms that the geometries are minima on the potential energy surfaces. Meanwhile the different kinds of weak forces like Van der Waals interactions, H-bonding, steric interactions were investigated by Non-Covalent Interaction (NCI) index plots of the reduced

density gradient (RDG)³² using the Multiwfn 3.7suite.³³ Furthermore, molecular electrostatic potential (MESP) maps were visualized at the ground state geometries to understand the type and the moieties involved in the interactions. Finally, by the utilizing the formula, adsorption energies (ΔE_{ads}) for all the composite systems were analysed:

$$\Delta E_{ads} = E_{IL-L-methionine} - E_{IL} - E_{L-methionine}$$

Where $E_{IL-L-methionine}$, E_{IL} , $E_{L-methionine}$ are the total energy of the geometry optimized complexes, free IL and the L-methionine molecules, respectively.

3. RESULTS AND DISCUSSION

Experimental values of density (ρ), viscosity (η) and molar refraction (R_M) of different molality (m) of aqueous ionic liquids (BTMAC and BTEAC) solutions at 298.15 K, 303.15 K and 308.15 K and at pressure at 1.013bar are shown in **Table S1** and **Table S2** whereas **Table S3** and **Table S4** gives the experimental values of refractive index (n_D) and specific conductance (κ) of different molality (m) of the aqueous ionic liquids (BTMAC and BTEAC) solutions at 298.15K, 303.15K and 308.15K. Also the density (ρ), viscosity (η) and molar refraction (R_M) of L-Methionine solutions in different molality of aqueous ionic liquids solutions at different temperature at pressure 1.013bar are shown in **Table S5** and **S6**.

3.1. Density

The limiting apparent molar volumes (Φ_v^0), limiting molar refraction (R_M^0), experimental slopes (S_v^*), viscosity A, B-coefficients of L-Methionine solution in ILs (BTMAC and BTEAC) at different temperatures and pressure at 1.013bar are presented in **Table 2** and **Table 3**, respectively. The apparent molar volumes (Φ_v) were determined from the solution densities using the following equation³⁴ the result are provided in **Table S7** and **S8**.

$$\Phi_v = M / \rho_0 - (\rho - \rho_0) / m \rho_0 \quad (2)$$

where, M is the molar mass of the solute, m is the molality of the solution, ρ and ρ_0 are the densities of the solution and solvent, respectively. For the analysis of the interactions occurring here, the knowledge of the limiting apparent molar volumes are important. The limiting apparent molar volumes (Φ_v^0) were calculated using a least-squares treatment to the plots of (Φ_v) versus \sqrt{m} using the following Masson equation:³⁵

$$\Phi_v = \Phi_v^0 + S_v^* \sqrt{m} \quad (3)$$

where, Φ_v^0 is the limiting apparent molar volume at infinite dilution and S_v^* is the experimental slope. Here, we observe the variation of Φ_v^0 values of L-Methionine solutions at 0.001m, 0.003m and 0.005m concentration of the ILs at 298.15K, 303.15K and 308.15K. The Φ_v^0 values are positive and seem to increase with the increase in concentration of the solutions

which were in good agreement with the previous literature values⁸⁸ and also with the increase in temperature whereas BTEAC has higher values than BTMAC. But S_V^* values are negative and decreases with the increase in concentration of the solutions and also with the rise in temperature. Also it is observed that BTEAC have lower S_V^* values than BTMAC.

Φ_V^0 values indicate the extent of solute-solvent interaction. A perusal of **Table 2** and **Table 3** along with **Figure 1** and **Figure 2** reveals that the Φ_V^0 values are positive and is maximum for L-Met in 0.005m BTEAC at 308.15K indicating highest solute-solvent interaction here and minimum for L-Met in 0.001m BTMAC at 298.15K, indicating that the solute-solvent interaction is the least here. This is probably due to the release of a number of the solvent molecules from loose solvation layers during the solute-solvent interactions.³⁶ Also the higher Φ_V^0 values of L-Met in BTEAC indicates that the interaction is more with BTEAC than in BTMAC under any conditions. On the contrary, the S_V^* indicates the extent of solute-solute interaction. The values of S_V^* show that the extent of solute-solute interaction is highest in L-Met 0.001m BTMAC solution at 298.15K and minimum in 0.005m BTEAC solution at 308.15K. Here again the higher values of S_V^* in BTMAC indicates that it exhibits better interaction among itself than BTEAC molecules under any conditions.

Possible reasons for this behaviour could be the structural orientation of the larger alkyl group of BTEAC than BTMAC as depicted by their molecular structures in **Scheme 1**. A quantitative comparison of the magnitude of Φ_V^0 values shows that it is much greater in magnitude than S_V^* values for the solutions. This suggests that strong solute-solvent interactions dominate over the weak solute-solute interactions in all the solutions.^{37, 38} There is hydrophobic hydration, or the caging effect of water molecules³⁹ which reflects hydrophobic interactions in the amino acids that cause volume contractions in solutions. Similar linear correlations have been observed earlier for homologous series of amino acids in aqueous electrolytes.⁴⁰

Temperature dependency of the limiting apparent molar volume (Φ_V^0) were studied between the temperature range 298.15K to 308.15K and the results obtained were found to follow the following polynomial equation:⁴¹

$$\Phi_V^0 = a_0 + a_1T + a_2T^2 \quad (4)$$

where, a_0 , a_1 and a_2 are the empirical coefficients depending on the nature of solute and mass fraction (W) of co-solvent whereas T is the temperature in Kelvin scale. **Table 4** shows the empirical coefficient values (a_0 , a_1 and a_2) of L-Met in different concentration of the ILs, BTMAC and BTEAC at 298.15K, 303.15K, 308.15K and pressure at 1.013bar. First derivative of Equation(4) gives the values of limiting apparent molar expansibilities (Φ_E^0) which have been calculated for various temperatures and listed in **Table 5** and **Table 6** for L-Met in BTMAC and BTEAC solutions, respectively at pressure 1.013bar.

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

Limiting apparent molar expansibilities (Φ_E^0) for all the systems are found positive except for 0.005m IL at 308.15K in BTMAC. It signifies the absence of caging or packing effect in the other solutions except this one. The solute–solvent interaction studied so far is now at a state that, it may be structure-breaker or synergistic structure-maker interaction. In this connection, Hepler developed a way to examine the nature of the solute–solvent interaction taking place in the solution phase.⁴² According to Hepler, values of $(\delta\Phi_E^0/\delta T)_P$ in the expression given below, determines whether, it is structure-breaker or structure-maker interaction:⁴³

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

On the basis of this expression, it has been deduced that structure-making solutes should have positive value, whereas structure-breaking solutes should have negative values. Here, the negative values listed in **Table 7** and **Table 8** respectively for L-Met in BTMAC and BTEAC solutions at different temperatures confirms the mode of solute–solvent interaction is structure-breaking and the structure-breaking effect is strongest in 0.001m aqueous BTMAC solution with highest packing or caging effect.

3.2. Viscosity

In aqueous electrolytic solutions the extent of ionic hydration and structural interactions⁴⁴⁻⁴⁶ within the ionic hydration co-spheres⁴⁷ can be explored easily by studying viscosity coefficient with varying concentration and temperature of the aqueous solution. The results in **Table S1** and **Table S2** show that the viscosity of the solutions increases with increasing molality of the ILs. The number of collisions among the molecules also increases upon increasing the molality of the ionic liquid, resulting in a loss of kinetic energy. Consequently, the molecules tend to stick together with increasing viscosity.

Viscosity data so obtained were analysed with the help of Jones-Dole equation:⁴⁸

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

where, η and η^0 are viscosities of solution and solvent respectively, c is the concentration of solution in molarity. This is possibly due to stronger hydrophobic–hydrophobic interactions for longer alkyl chains of BTEAC.

Rearrangement of the above Equation (7) gives following:

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

Here, viscosity A-coefficient is a constant, also known as Falkenhagen coefficient,³⁴ stands for long-range coulombic forces, so represents the solute-solute interaction in solution, while B-coefficient is an adjustable parameter, which is the measure of the effective hydrodynamic volume that reflects the solute-solvent interaction. The value of viscosity B-coefficient which depends on the shape, size and partial molar entropies of the ions involving in solutions. According to the Jones-Dole equation from the plots of $(\eta_r-1) / \sqrt{c}$ vs \sqrt{c} , the viscosity A, B-coefficients obtained by linear least-square analysis, are reported in **Table 2** and **Table 3** for L-Met solutions in BTMAC and BTEAC at (298.15, 303.15 and 308.15)K and pressure at 1.013bar, respectively. **Figure 3** shows the variation of B values of L-Methionine in BTMAC and BTEAC respectively, against 0.001m IL, 0.003m IL and 0.005m IL solutions at different temperatures which were in good agreement with the previous literature values.⁸⁸

The viscosity B-coefficient is an empirical constant which depends on size and shape effects as well as structural effects induced by (solute+solvent) interactions.⁸ In all cases the viscosity B-coefficients are larger compared to A-coefficients in the aqueous ionic liquid solutions which indicates promotion of the liquid structure in the presence of an ionic liquid, thus supporting the conclusions obtained from volumetric properties. It is observed From **Table 2** and **Table 3**, that the values of the B-coefficient are positive, thereby suggesting the presence of strong solute-solvent interactions in solution, that strengthened with an increase in the solvent viscosity value, in accordance with the results obtained from Φ_v^0 values explained earlier. The values of the A-coefficient are found to very small as compared to B-coefficients. The above obtained results of A-coefficient indicate the presence of very weak solute-solute interactions. These results are in outstanding agreement with those obtained from S_v^* values. The extent of solute-solvent interaction obtained from the B-coefficient occurs into the local vicinity of the solute molecules in the solutions. 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 associated molecule by solute-solvent interactions.⁴⁹

Furthermore, these types of interactions are strengthened with rise in temperatures. It shows that the solute-solvent interaction increases with increase in temperature and the concentration of the IL solutions with more interaction between L-Met and aqueous BTEAC solutions. There placement of water molecules by more co-solvent molecules from the solvation sphere brings solute and co-solvent closer thereby increasing viscosity B-coefficients and accounts for the higher solute-solvent interaction. The overall viscometric studies show that, viscosity B-coefficients are positive and greater than viscosity A-coefficient, suggesting solute-solvent interaction is predominant over the solute-solute interaction.

Extensively study of the viscosity B-coefficient such that, its first derivative over temperature is an upgradation of viscosity B-coefficient in predicting the nature of solute–solvent interaction as structure-maker or structure-breaker. The value of dB/dT is a measure of activation energy required for the viscous flow in solution. This is the reason, why the measure of dB/dT is indicative towards the structure making or structure breaking ability than sign or magnitude of the B-coefficient.⁵⁰⁻⁵² Viscosity B-coefficients of L-Met solutions along with dB/dT values in different concentrations of the ILs, BTMAC and BTEAC at (298.15, 303.15 and 308.15) K and pressure at 1.013bar are given in **Table 7** and **Table 8**, respectively. The negative value of dB/dT indicates as a structure-making (kosmotropic) properties of the system whereas the positive value signifies it as structure-breaking (chaotropic) properties of the system. Here the positive dB/dT values indicate the amino acid, L-Met to behave as structure-breaker in the aqueous ionic liquid solutions, BTMAC and BTEAC.

According to theory of Eyring and co-workers,⁵³ $\Delta\mu_1^{0\#}$, the free energy of activation per mole of the solvent of viscous flow can be obtained by using the following equation:

$$\eta_0 = \frac{hN}{V_1^0} \exp\left(\frac{\Delta\mu_1^{0\#}}{RT}\right) \quad (9)$$

where h signify as Planck constant, N denotes Avogadro's number and V_1^0 indicates the solvent's partial molar volume. Rearranging the above equation, we get the following form:

$$\Delta\mu_1^{0\#} = RT \ln (\eta_0 V_1^0 / hN) \quad (10)$$

Feakins et al. have suggested the following expression based on the transition state treatment of the relative viscosity of electrolyte solution.^{54, 55}

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

Following equation can be obtained from the above equation(11):

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

According to the theory of transition state, solvent molecules passes to the transition state by the viscous flow. The $\Delta\mu_2^{0\#}$ is the involvement of free energy transfer of ionic liquid from ground state to transition state. It was observed from **Table 9** that the values of $\Delta\mu_2^{0\#}$ are all positive and which are much higher than that of $\Delta\mu_1^{0\#}$ representing in the ground state, which designates that the interaction between the amino acid (L-Met) with two aqueous ionic liquids, BTMAC and BTEAC mixture is stronger in the ground state than that in the transition state which were in good agreement with the previous literature values.⁸⁸ In the ground state the solute and solvent molecules are held together strongly than that in the transition state. Later on, in the transition state distortion and breaking of intermolecular bond take place frequently. Besides the

value of $\Delta\mu_1^{0\#}$ increase with increasing the molality of the ionic liquids in the presence of amino acid (L-Met) which indicate that with increasing the molality, ionic liquids in the ground state become more structured. The following equation has been used for determination of entropy for activation, $\Delta S_2^{0\#}$ in the experimental mixture of solutions:⁵⁶

$$d(\Delta\mu_2^{0\#})/dT = -\Delta S_2^{0\#} \quad (13)$$

From the plot of $\Delta\mu_2^{0\#}$ versus T, using the least-squares method, the value of $\Delta S_2^{0\#}$ has been attained from the negative slope of the plot.

Enthalpy of activation ($\Delta H_2^{0\#}$) has been calculated from the following relation:⁵⁶

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

The value of $\Delta H_2^{0\#}$, $\Delta S_2^{0\#}$ are shown in **Table 9**. The value of $\Delta\mu_2^{0\#}$ depend on both viscosity B-coefficient and limiting molar volume ($\bar{v}_1^0 - \bar{v}_2^0$) of the solution in the presence of ionic liquid.

In view of Feakins et al.,⁵⁴ for positive viscosity B-coefficient, $\Delta\mu_2^{0\#} > \Delta\mu_1^{0\#}$ 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} For positive values of $\Delta S_2^{0\#}$ and $\Delta H_2^{0\#}$ recommend that the formation of transition state is related 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.⁵⁸ Finally, according to Feakins et al. model, as $\Delta\mu_2^{0\#} > \Delta\mu_1^{0\#}$, the amino acid (L-Met) performs as structure breakers that again supports the dB/dT characteristics in an aqueous BTMAC and BTEAC mixture.

3.3. Refractive Index

Optical data of refractive index of the studied systems has provided interesting information allied to molecular interactions, structure of solutions in these assay. The refractive index of mixing can be interrelated by the application of a composition dependent polynomial equation and molar refraction, R_M in solution. The refractive index of amino acid (L-Methionine) solutions in both ionic liquid are provided in **Table S9**, **Table S10** and **Table S11**.

The molar refraction R_M can be evaluated from the Lorentz–Lorenz relation:⁵⁸

$$R_M = \{(n_D^2 - 1) / (n_D^2 + 2)\} (M/\rho) \quad (15)$$

where R_M , n_D , M and ρ are the molar refraction, the refractive index, the molar mass and the density of the solution, respectively. The refractive index of a substance is

well-defined as the ratio of the speed of light in vacuum to that in the medium. Stated the definition of refractive index more simply, the refractive index of a compound describes its ability to refract light as it moves from one medium to another medium and thus, the higher the refractive index of a compound, the more the light is refracted.⁵⁹ As stated by Deetlefs et al. the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser.⁶⁰ Generally, refractive index of a system is the capability to refract light and hence it can simultaneously measure the compactness of that system.

Hence, it is observed that the refractive index (n_D) **Table (S3-S4) and Table (S9-S11)** decrease but the molar refraction (R_M) (**Table S1 and Table S2**) increases with increase in temperature. However, both the parameters show an increase with increase in concentration of the amino acid and IL solutions. Again L-Met in BTEAC have higher values than in BTMAC solutions. This is in good agreement with the volumetric and viscometric results attained here. The higher refractive index shows that the molecules are more tightly packed in the solution.

The limiting molar refraction, (R_M^0) listed in **Table 1 and Table 2** can be calculated using the following equation:

$$R_M = R_M^0 + R_S \sqrt{m} \quad (16)$$

where, 'm' is the molality of solution and R_M^0 is the limiting molar refraction that signifies solute-solvent interaction. So, this measurement of molar refraction operates as an expensive tool for studying the molecular interaction in solution. Gradual increase in the values of R_M^0 as shown in **Figure 4 and Figure 5** with rise in mass fraction of co-solvent and temperature also signifies that solute-solvent interaction predominant over solute-solute interactions.

3.4. Electrical Conductance

The specific conductance of L-Methionine in two ionic liquid solutions at different concentration are shown in the **Table (S9-S11). Table 10** shows Molar conductance (Λ) of L-Methionine solutions in aqueous BTMAC & BTEAC ionic liquid solution in (0.001m, 0.003m, 0.005m) at 298.15K, 303.15K and 308.15K and pressure at 1.013bar. **Figure 6 and Figure 7** shows the variation of molar conductance (Λ) of L-methionine in aqueous IL(BTMAC) and IL (BTEAC) solutions, respectively at 298.15K(0.001m), 303.15K(0.003m), 308.15K(0.005m). The molar conductance (Λ) values increase with increase in temperature and increase in concentration of aqueous IL solution but decrease with the increase in concentration of amino acid solutions. However, the values are lesser in L-Met BTEAC solutions under all conditions. The molar conductance (Λ) has been obtained from the specific conductance (κ) value using the following equation:⁶¹

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

Linear conductivity curves (Λ vs. \sqrt{c}) were obtained for the amino acid in ILs solutions and extrapolation of $\sqrt{c} = 0$ was used to evaluate the limiting molar conductance for the ILs. ILs has benzyl trimethyl ammonium cation, benzyl triethyl ammonium cation and chloride anion. The terminal $-\text{COO}^-$ functional group of the amino acid interact with the N^+ centre of benzyl trimethyl and triethyl ammonium ring through ion–dipole interaction (**Scheme 1**).

Another contributing factor in the amino acids is the carboxylic ($-\text{O}-$) atom. The lone pair donating tendency of carboxylic oxygen increases with the increase in $+I$ effect of alkyl group of the studied ionic liquids. Thus $+I$ effect in BTEAC is greater than in BTMAC. Hence, the interaction is more prominent in L-Met BTEAC solution due to the presence of more lone pair availability of oxygen atom, making the interaction strong with IL. So the free ions are more available in L-Met BTMAC solution giving higher conductance values than L-Met BTEAC solution.

3.5. Surface Tension

Surface Tension (γ) values of L-Methionine solutions in IL (BTMAC) and L-Methionine solutions in IL(BTEAC) at different concentration (0.001m,0.003m,0.005m) at room temperature and pressure at 1.013bar* are given in **Table 11**. A liquid is always in contact with its vapour in a closed vessel. A molecule in the bulk of the liquid is subjected to forces of attraction from all directions by the surrounding molecules and is practically in a uniform field of force. But for a molecule at the surface, the net attraction towards the bulk of the liquid is much greater than that towards the vapour where the attracting molecules are more widely dispersed. This means that the molecules at the surface are pulled inwards. The result is liquid surfaces in absence of other forces tend to contract to minimum areas. The surface layer seems to behave as a stretched membrane and this pseudo-membrane tends to contract. Now, since the surface is in a state of tension, an attempt to make a penetration along any line in the surface will require an application of force to hold the separate portions of the surface together.⁶²

Figure S5 and **Figure S6** shows the variation of the surface tension with different concentration of L-Met in BTMAC and BTEAC, respectively at room temperature. The values increase with increase in concentration of the amino acid in both the ILs. However, surface tension decreases then increases with increase in concentration of the ionic liquids. Further, it was observed that surface tension is more for molecules in L-Met BTEAC solution compared to L-Met BTMAC solution.

The lower surface tension values is attributed to the hydrophobicity of the amino acids. The increase in surface tension values shows a significant amount of molecular association is present between adjacent molecules as the concentration shows an increasing trend, producing a robust surface film.⁶³

The hydrophobic and hydrophilic nature of solute with respect to the concentration depend upon the sign and magnitude of slopes ($\partial\sigma/\partial m$) of surface tension as it reflects the type of interactions that predominate on the surface of solute.^{64, 65} The limiting slope obtained from surface tension data were determined in very dilute region and area that are shown in the listed **Table 12**.

It was found that the values of ($\partial\sigma/\partial m$) are positive for L-methionine solutions in both aqueous solution of ionic liquid (BTMAC&BTEAC) are typical for electrolyte and very hydrophilic compounds⁶⁶ and this can be determined from the result of favorable interaction between the Zwitterionic group of amino acid (L-methionine) and an ionic group of two ionic liquid (BTMAC and BTEAC). Since L-Methionine contain hydrophobic part as a result it readily migrates to the liquid–air interface where it can be absorbed.

The cosphere overlap model⁶⁰ can explain the above effect. According to this model four types of possible interactions can exist in the ternary systems containing amino acid, ionic liquid and water (a) hydrophilic-ionic interactions between ions of IL and hydrophilic group (NH_3^+ , COO^-) of amino acid; (b) hydrophobic-ionic interactions between hydrophobic part of amino acid and ions of IL; (c) hydrophobic–hydrophobic interactions between the hydrophobic groups of amino acid and alkyl groups of IL; (d) hydrophilic–hydrophobic interactions between hydrophilic groups of amino acid and the hydrophobic parts of ILs.^{50, 67}

3.6. FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) spectra have been used to study the hydrogen bond formation through molecular interactions between the amino acid, L-Methionine (L-Met) and the two ionic liquids, Benzyl tri-methyl ammonium chloride (BTMAC) and Benzyl tri-ethyl ammonium chloride (BTEAC) aqueous solutions. Every pure substance has its own characteristic infrared spectrum different from that of any other substance. The spectral picture thus helps in confirming and identifying the sample of pure variety.

The FTIR spectra of pure ILs and pure Amino acid (**Figure A1**) show some common absorption peaks at frequencies such as 3431.6 cm^{-1} , 3403.5 cm^{-1} and 3428.2 cm^{-1} , respectively for aliphatic C-H groups present in these molecules. Besides this the presence of water in a sample is detected by these characteristic absorption bands in this region along with additional peaks at 1609.2 cm^{-1} , 1614.6 cm^{-1} and 1610.7 cm^{-1} for BTMAC, BTEAC and L-Met, respectively.

The bands observed at 520 cm^{-1} , 452 cm^{-1} for BTMAC, 529.7 cm^{-1} , 471.8 cm^{-1} for BTEAC and 543.2 cm^{-1} , 449.6 cm^{-1} for L-Met confirms the presence of water as lattice water with these molecules.⁶⁸

When L-Met and BTMAC are mixed in the ratio 1:3, 2:2 and 3:1, the absorption peaks obtained for the mixtures are shown in the FTIR spectra, **Figure A2**. When L-Met and BTEAC are mixed in the ratio 1:3, 2:2 and 3:1, the absorption peaks obtained for the mixtures are shown in the FTIR spectra, **Figure A3**. The spectra show that the common bands for the amino acid and ILs are retained in the figures.

Above 2500 cm^{-1} nearly all fundamental vibrations involve a hydrogen stretching mode. Hydrogen bonding O-H lowers the frequency and broadens the band. The N-H stretch occurs in the $3300\text{-}3400\text{ cm}^{-1}$ region. These bands often overlap the hydrogen bonded O-H bands but the N-H peaks are usually sharper. The N-H stretch in ammonium and alkylammonium ions occurs at lower frequencies, $2900\text{-}3200\text{ cm}^{-1}$. The C-H stretch occurs in the region $2850\text{-}3000\text{ cm}^{-1}$ for the aliphatic compound, L-Met and in the region $3000\text{-}3100\text{ cm}^{-1}$ for the aromatic compounds, BTMAC and BTEAC. Absorptions corresponding to S-H occur at 2500 cm^{-1} . The $2000\text{-}1600\text{ cm}^{-1}$ region contains stretching vibrations for doubly-bonded molecules and bending vibrations for the O-H, C-H and N-H groups.

The region below 1600 cm^{-1} is referred to as the fingerprint region for these organic compounds studied here. This is the single bond region and it is very common to get coupling of individual single bonds which have similar force constants and connect similar masses, like C-O, C-C and C-N stretches often couple. The absorption bands in this region for a given functional group occur at different frequencies depending upon the skeleton of the molecule, because each vibration often involves oscillation of a considerable number of atoms of the molecular skeleton.

Table A: The characteristic frequencies of some of the groups:⁵⁷

GROUPs	BAND FREQUENCIES, $\bar{\nu}\text{ cm}^{-1}$
C-H	2880-3030
=C-H	3000-3120
C=O	1660-1870
C=C	1600-1680
O-H	3500-3700
N-H	3300-3500
C-C	750-1300
C-N	700-1400
C-O	950-1300
S-H	2500-2600

The regular recurrence of some absorption bands when certain groups are present in the molecule points to the fact that these bands are characteristic of those groups. All compounds having a C-H bond exhibit bands in the region 3200-3500 cm^{-1} . The exact position of the band is somewhat influenced by the rest of the molecule. In the ionic liquids and amino acid aqueous solution mixtures, the C-H band is observed around 3250 cm^{-1} , N-H bonds have bands at 2900-3000 cm^{-1} and O-H at 2700-2800 cm^{-1} . This is very useful as it confirms the presence of a group in a molecule. In a mixture, the positions and intensities of the bands for a particular substance are not affected by the presence of other components. So, in a mixture of closely related compounds, the identification as well as the quantitative estimation of a particular component can be spectroscopically ascertained.

The broad peaks around 3427.5 cm^{-1} in 1:3 L-Met and BTMAC aqueous mixture is likely to be due to the overlap of O-H and N-H stretching vibrations, indicating the presence of both surface free hydroxyl groups and chemisorbed water. The peaks around 2929.7 cm^{-1} in 3:1 L-Met and BTMAC solution and 1386.6 cm^{-1} in 2:2 L-Met and BTEAC solution correspond to the C-H symmetric stretch of the methylene groups ($-\text{CH}_2$) and deformation vibration of methyl groups ($-\text{CH}_3$). The peak at 1252.7 cm^{-1} in 3:1 L-Met and BTMAC solution can be attributed to C=O stretching vibration of carboxylate ($-\text{COO}^-$) groups. Some shifts in wave numbers result from change in bonding energy in the corresponding functional groups.⁶⁹

The peak at 1609.4 cm^{-1} and 1597.9 cm^{-1} in 2:2 and 3:1 L-Met and BTEAC solution is indicative of an asymmetric $-\text{COO}^-$ stretching bond (carboxylate) and the peak at 1413.1 cm^{-1} and 1406.9 cm^{-1} in 2:2 L-Met and BTMAC solution indicates a symmetric $-\text{COO}^-$ stretching bond.⁷⁰ In addition, there was a new peak at 3231.2 cm^{-1} in 1:3 L-Met and BTEAC aqueous solution due to N-H stretch after absorption.⁷¹

Absorption bands are clearly observed at 600–700 cm^{-1} in 2:2 and 3:1 L-Met and BTMAC solution due to OH out-of-plane bending. Therein, peculiar stretching of C-O and C-C bonds, rocking of CH_2 and other skeletal modes, not easily encountered in other organic molecules, give their unique IR signatures. The peaks at 1272.5 cm^{-1} and 1319.1 cm^{-1} in L-Met are related to stretching, bending, and rocking of $-\text{CH}_2$ groups. As expected, the most prominent features are due to the IR absorption from the carboxyl group around 1600 cm^{-1} in the L-Met and BTEAC solutions.⁷²⁻⁷⁴

So from the above observations and nature of the spectra it may be concluded that the aqueous mixture of L-Methionine and Benzyl tri-ethyl ammonium chloride when mixed in the ratio 3:1 (**Figure A3**) indicates highest interactions and that in the ratio 1:3 of L-Methionine and Benzyl tri-methyl ammonium chloride exhibits the lowest interactions (**Figure A2**). Thus, the

FTIR spectroscopy has been found to be one of the most convenient method for investigating the molecular interactions in solutions.⁷⁵

3.7. ¹H NMR studies

We thus see that Nuclear Magnetic Resonance studies⁷⁶⁻⁷⁹ reveal the presence of particular functional groups, relative number of nuclei present in the group and the relative positions of these groups from the multiplicities of the lines. Hence, NMR provides means for the investigation of intimate details of the internal structure of molecules not available through other methods. The NMR phenomenon has significance to the chemist because the energy of the resonance is dependent upon the electronic environment about the nucleus.

The chemical shift, δ gives the difference in the shielding constants of the sample and reference. The chemical shift of a solute molecule in a solvent will be not only influenced by shielding of electrons but also by the volume diamagnetic susceptibility of the solvent. The diamagnetic contributions to the shielding of the solute would depend upon the average number of solute and solvent molecules, i.e., the number of solvent and solute neighbours. Consequently, the chemical shift will be concentration dependent. There is more intermolecular interactions associate with concentrated solutions than in dilute solutions. The effect of this interaction is to reduce the screening of the proton, causing a shift to lower field.⁸⁰

As the nucleus is being examined, the static component of another nucleus causes a slight variation in the effective field at this nucleus. The contribution to the effective magnetic field

A variation in the environments of nuclei undergoing the NMR transition exists because of the random arrangements of neighbouring molecules. Thus^{81, 82} Nuclear magnetic resonance (NMR) is an effective tool to study the changes of the electronic environment around the different protons of IL in presence amino acids. The chemical shifts of the amino acids and the IL studied depends on the electron density present in their surrounding area.

Here, ¹H NMR spectroscopy of pure BTMAC, BTEAC, L-Met and also in the mixture of amino acid with ILs has been done. The chemical shift value of various protons (δ_1 to δ_3) of BTMAC and (δ_1 to δ_4) BTEAC in D₂O solvent are shown in **Figure B1 & Figure B2**, respectively. The results obtained from ¹H NMR spectrum of [BTMA]⁺ ion has three characteristic peaks corresponding to the terminal -CH₃ (δ_1) protons of the alkyl chain at 3.022 ppm, benzyl-CH₂ (δ_2) protons at 4.401 ppm, and -C₆H₅ protons (δ_3) at 7.497 ppm. In addition, the [BTEA]⁺ ion has four characteristic peaks corresponding to terminal-CH₃ (δ_1) protons at 1.320 ppm of ethyl chain, -CH₂ (δ_2) protons at 3.149 ppm of ethyl chain, benzyl-CH₂ (δ_3) protons at 4.329 ppm, and -C₆H₅ protons (δ_4) at 7.527 ppm. The chemical shift of different protons of L-Met in D₂O solvent is shown in **Figure B3**. In the ¹H NMR spectrum of L-Methionine there are

four characteristic peaks observed corresponding to terminal $-\text{CH}_3$ (δ_1) protons at 2.054ppm, CH_2 (δ_2) protons at 2.552 ppm, CH_2 (δ_3) protons at 2.096 ppm, Methane($-\text{CH}$) proton (δ_4) directly attached to $-\text{NH}_2$ group resonates at 3.753ppm.

The chemical shift (δ) values of protons of any compound are greatly influenced by the nature of moieties present in their close vicinity. The change in chemical shift values of (L-Met + BTMAC) and (L-Met + BTEAC) system in the ratio 4:1 in D_2O are shown in **Figure B4** and **Figure B5**, respectively. It is well-known fact that the δ values shift upfield (lower frequency) or downfield (higher frequency) depending upon the shielding and deshielding effects of the surrounding groups. In our present study, the results point out that the chemical shifts of BTMAC protons move to lower frequency when it interacts upon addition of amino acids. It has also been found that there are upfield chemical shift (δ) values of protons for the amino acid (L-Met). An upfield shift is indicative of an increase in electron density around the protons of BTMAC, BTEAC and the amino acid, which may be owing to the intermolecular interactions.

Figure B4 and **Figure B5** shows the change in chemical shifts of each proton of BTMAC, BTEAC and L-Met in the presence of each other (AA: IL = 4:1) by comparing with their corresponding pure BTMAC, BTEAC and pure amino acid. It has been found that the terminal $-\text{CH}_3$ (δ_1) protons (moved from 3.022 ppm to 3.010ppm), benzyl- CH_2 (δ_2) protons (moved from 4.401 ppm to 4.405 ppm), and the phenyl ring (δ_3) protons (moved from 7.497 ppm to 7.494 ppm) of BTMAC and it has also been found that the terminal $-\text{CH}_3$ (δ_1) protons (moved from 1.320 ppm to 1.214ppm), $-\text{CH}_2$ (δ_2) protons (moved from 3.149 ppm to 3.130 ppm), benzyl- CH_2 (δ_3) protons (moved from 4.329ppm to 4.310 ppm), and the phenyl ring (δ_4) protons (moved from 7.527 ppm to 7.464 ppm) of BTEAC. But it has been noticed that an upfield shift with much higher magnitude of BTEAC is shown compared with BTMAC in presence of L-Me. On the other hand, the chemical shifts of protons of terminal- CH_3 (δ_1) (moved from 3.022 ppm to 3.010 ppm), benzyl- CH_2 (δ_2) protons (shifted from 4.401ppm to 4.405ppm) of BTMAC and also the chemical shift of protons of terminal- CH_3 (δ_1) (moved from 1.320 ppm to 1.214 ppm), ethyl chain- CH_2 (δ_2) (moved from 3.149 ppm to 3.130 ppm), benzyl- CH_2 (δ_4) protons (shifted from 4.329 ppm to 4.310ppm) of BTEAC give the smallest changes and the significant change in chemical shifts of terminal- CH_3 (δ_1) protons attached with S atom (shifted from 2.054 ppm to 1.993ppm), $-\text{CH}_2$ (δ_2) protons attached with S atom (shifted from 2.552 ppm to 2.548ppm) and $-\text{CH}_2$ (δ_3) protons (shifted from 2.096 ppm to 1.301ppm) and $-\text{CH}$ (δ_3) protons directly attached with $-\text{NH}_2$ group (shifted from 3.753 ppm to 3.759ppm) of L-Met is observed in case of (L-Met + BTMAC) system and also the significant chemical change is observed of nearer S- CH_3 (δ_1) protons (shifted from 2.054 ppm to 2.062ppm), $-\text{CH}_2$ (δ_2) protons (shifted from 2.552 ppm to 2.541ppm) and $-\text{CH}_2$ (δ_3) protons shifted from 2.096 ppm to 1.336 ppm, $-\text{CH}_2$ (δ_4) directly attached with $-\text{NH}_2$ group (shifted from 3.753 ppm to 3.766 ppm). However, if we compare the

change of chemical shift between two system (L-Met + BTMAC) and (L-Met + BTEAC), higher chemical shift of protons has been found in case of L-Met + BTEAC system.

The above results suggest that the hydrophobic interactions may primarily be between the hydrophobic part of alkyl chains and phenyl group of ILs, BTMAC and BTEAC and hydrophobic portion (-CH₃ group attached with sulphur atom, -CH₂ group attached with sulphur atom, one -CH₂ group and one -CH group of L-Met attached with -NH₂ group.^{52, 82, 83} It can be also found that the hydrophobic interaction is more stronger in (BTEAC + L-Met) system (as more up field shifts of terminal -CH₃ (δ1), -CH₂ (δ2), phenyl ring (δ3), phenyl ring (δ4), protons of BTEAC and -CH₃(δ1), attached with S atom-CH₂ (δ2) attached with S atom, -CH(δ3) protons of L-Met compared to (BTMAC + L-Met) system .

The nature of the spectra, number, intensity and broadness of the peaks obtained by proton NMR spectroscopy of the systems mixed in the ratio of (4:1)(AA:IL) shows that the aqueous mixture of L-Methionine and Benzyl tri-ethyl ammonium chloride (**Figure B5**) exhibits more interactions compared to the aqueous mixture of L-Methionine and Benzyl tri-methyl ammonium chloride (**Figure B5**)

Thus, the NMR data provide a conclusion about the plausible contributing factors such as ion-dipole, ion-ion interactions between amino acid and ILs as well as the hydrophobic interactions.^{43,50} All the possible type of interactions between ionic liquids (ILs) and amino acid (AA) are presented in **Scheme 1**. The conclusion from NMR measurements is in good agreement with the results obtained by FTIR studies of the Ionic liquids and the Amino acid studied here.

3.8. UV-Visible Spectra Measurement

The binding affinity and stability of the molecular association between the amino acid, AA (L-Met) with two ionic liquids, ILs (BTMAC & BTEAC) exhibited in the solution mixture due to manifestation of solute-solvent interaction were measured by the association or stability constant (K_a) with the help of UV-Vis spectroscopic technique.⁸⁴ The data obtained in the solution mixture from the above mentioned technique helps to determine the stability constant or association constant. The association constant (K_a) can be determined by observing the changes in absorbance (ΔA) of BTMAC and BTEAC at λ_{max} = 208 nm (**Figure C1** and **Figure C2**, respectively) with increasing the concentration of L-Methionine at 298.15 K.

The Benesi-Hildebrand method which represents one of the popular and most renowned technique to measure the association constant (K_a), the double reciprocal plots were obtained using the following equation⁸⁵ and the plots were found to be linear in nature (**Figure C3** and **Figure C4**) that usually states about the solute:solvent ratio in solution.⁸⁶

$$1/\Delta A = 1/\Delta \epsilon [\text{IL}] \cdot 1/[\text{AA}] + 1/\Delta \epsilon [\text{IL}] \quad (18)$$

where ΔA denotes the difference in absorbance of ILs in absence or presence of AA. [IL] denotes the concentration of BTMAC and BTEAC. [AA] denotes the concentration of L-Methionine. The value of association constant of the system (BTMAC+L-Met) and (BTEAC+L-Met) were obtained from the slope/intercept of the plots using the equation of Benesi–Hildebrand and the result of the K_a value are listed in **Table 12** and **Table 13**.⁸⁷

The change of free energy for the molecular assemble taking place between amino acid with ionic liquid can be obtained by the following association constant-free energy relationship:

$$\Delta G = -RT \ln K_a \quad (19)$$

where, ΔG is the change in free energy, K_a denotes the association constant, R refer to the universal gas constant, T stands for temperature in Kelvin scale.

3.9. Theoretical study of solute-solvent (amino acid and IL) interaction

Optimized geometries of L-Met-BTMAC and L-Met-BTEAC composites are illustrated in the **Figure C5 (a-b)**. In both the composites, L-Met and ionic liquids strongly interacted by H bonds within a range of 2.28-3.34 Angstrom. L-Met-BTMAC composite experiences higher adsorption energy ($E_{ads} = -13.61$ kJ/mole) than the corresponding L-Met-BTEAC composite ($E_{ads} = -7.39$ kJ/mole). This data clearly indicates that H bonding is more prominent in L-Met-BTMAC than L-Met-BTEAC which is confirmed from the shorter H bonding distance for the former than the later.

To gain insight on the hydrophobic and electrostatic interactions between L-Met and ionic liquids, we have plotted molecular electrostatic maps (ESP), as illustrated in **Figure C6**. From the ESP maps it is clear that interaction is purely electrostatic (red region) and offer by the interactions between the carboxylic groups and the hydrogen of the methyl group attached to the nitrogen atom of the ionic liquids.

The presence of hydrogen bonding in the composites has also been confirmed by the scattered area of the negative region of the RDG plot (0.01-0.02 region) for both the composite systems **Figure C7**.

4. CONCLUSIONS

Density, viscosity, refractive index, conductance and surface tension measurements of aqueous solution of amino acid, L-Methionine in the ionic liquids, Benzyl tri-methyl ammonium chloride and Benzyl tri-ethyl ammonium chloride supported by FTIR, $^1\text{H-NMR}$ and UV-Vis spectroscopy provided the information that strong solute-solvent interactions dominate over the weak solute-solute interactions in the studied compounds. Further, L-Met in 0.005m BTEAC at 308.15K indicates highest solute-solvent interaction whereas, L-Met in 0.001m BTMAC at

298.15K shows the lowest. Again, mode of solute–solvent interaction is structure-breaking and the structure-breaking effect of L-Met is strongest in 0.001m aqueous BTMAC solution with highest packing or caging effect. The free energy of activation of viscous flow indicated 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. Due to larger alkyl group, +I effect in BTEAC is greater than in BTMAC making the interaction more prominent in L-Met BTEAC solution as there is presence of more lone pair availability of oxygen atom, making the interaction strong with the Ionic liquid.

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Declaration of competing Interest: The authors declare that they have no known competing for any financial interests or personal relationships among the groups that could have appeared to affect the work in this manuscript.

Tables

Table 1. Specification of chemical samples

SL. No.	Name of Chemicals	CAS NO.	Abbreviation	Supplier	Purity (mass fraction)	Molar mass(g/mole)
1	Benzyl tri-methyl ammonium chloride (C ₁₀ H ₁₆ ClN)	56-37-1	BTMAC	SigmaAldrich (India)	≥ 0.99	185.69
2	Benzyl tri-ethyl ammonium chloride (C ₁₃ H ₂₂ ClN)	56-93-9	BTEAC	Sigma Aldrich (Germany)	≥ 0.97	227.77
3	L-Methionine (C ₅ H ₁₁ NO ₂ S)	63-68-3	L-Met	Sigma Aldrich (Japan)	≥ 0.98	149.21

Table 2. Limiting apparent molar volumes (Φ_V^0), Limiting molar refraction (R_M^0), experimental slopes (S_V^*), viscosity A, B-coefficients of L-Methionine solution in IL (BTMAC) at different temperatures and pressure at 1.013bar*

Temperature (K)	$\Phi_V^0 \times 10^6$ (m ³ .mol ⁻¹)	R_M^0	$S_V^* \times 10^6$ (m ³ .mol ^{-3/2} .kg ^{1/2})	B (kg ^{1/2} .mol ^{-1/2})	A (kg.mol ⁻¹)
0.001m IL					
298.15	112.80±0.02	30.5990	-125.26±0.01	4.456±0.034	0.109±0.001
303.15	115.24±0.04	30.5690	-150.91±0.05	5.220±0.016	0.090±0.003
308.15	117.02±0.03	30.5840	-176.65±0.07	6.474±0.013	0.052±0.004
0.003m IL					
298.15	128.14±0.02	30.5750	-288.55±0.01	4.658±0.033	0.071±0.002
303.15	130.10±0.02	30.5790	-298.40±0.06	5.632±0.027	0.049±0.004
308.15	130.87±0.03	30.6000	-301.94±0.09	6.825±0.040	0.016±0.003
0.005m IL					
298.15	137.84±0.02	30.5840	-398.45±0.08	4.975±0.064	0.029±0.003
303.15	140.70±0.04	30.5930	-405.47±0.04	5.927±0.053	0.017±0.004
308.15	141.68±0.03	30.6090	-445.11±0.03	7.037±0.035	0.013±0.003

*Standard uncertainties values of u are: $u(T) = 0.01\text{K}$, $u(R_M^0) = \pm 0.0002$ (0.68 level of confidence)

#Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol. kg⁻¹*molality has been expressed per kg of (IL + water) solvent mixture.

Table 3. Limiting apparent molar volumes (Φ_V^0), Limiting molar refraction (R_M^0), experimental slopes (S_V^*), viscosity A, B-coefficients of L-Methionine solution in IL (BTEAC) at different temperatures and pressure at 1.013bar*

Temperature (K)	$\Phi_V^0 \times 10^6$ (m ³ .mol ⁻¹)	R_M^0	$S_V^* \times 10^6$ (m ³ .mol ^{-3/2} .kg ^{1/2})	B (kg ^{1/2} .mol ^{-1/2})	A (kg.mol ⁻¹)
0.001m IL					
298.15	113.42±0.02	30.5690	-137.64±0.03	4.630±0.039	0.085±0.004
303.15	115.83±0.05	30.6070	-153.49±0.03	5.530±0.067	0.055±0.005
308.15	117.30±0.05	30.6440	-184.96±0.01	6.751±0.020	0.019±0.007
0.003m IL					
298.15	128.76±0.05	30.5830	-300.93±0.05	4.789±0.052	0.049±0.005
303.15	130.79±0.04	30.6230	-307.04±0.03	5.760±0.038	0.028±0.007

308.15	131.56±0.05	30.6720	-310.61±0.04	7.079±0.034	0.012±0.004
0.005m IL					
298.15	140.20±0.05	30.6120	-400.22±0.01	5.113±0.059	0.011±0.005
303.15	143.87±0.04	30.6510	-455.31±0.00	6.018±0.054	0.001±0.006
308.15	145.45±0.05	30.6950	-463.77±0.02	7.213±0.071	0.009±0.002

*Standard uncertainties values of u_{ρ} : $u(T) = 0.01\text{K}$ $u(R_M) = \pm 0.0002$ (0.68 level of confidence)

#Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol. kg^{-1} *molality has been expressed per kg of (IL + water) solvent mixture.

Table 4. The empirical coefficient values (a_0 , a_1 and a_2) of L-Methionine solution in different concentration of the ILs (BTMAC) & (BTEAC) (0.001m,0.003m,0.005m) at 298.15K, 303.15K and 308.15K and pressure at 1.013bar*

Conc. of aq. ILs (BTMAC) & (BTEAC) solns. in molality (mol.kg ⁻¹)	$a_0 \times 10^6$ (m ³ .mol ⁻¹)	$a_1 \times 10^6$ (m ³ .mol ⁻¹ .K ⁻¹)	$a_2 \times 10^6$ (m ³ .mol ⁻¹ .K ⁻²)	$a_0 \times 10^6$ (m ³ .mol ⁻¹)	$a_1 \times 10^6$ (m ³ .mol ⁻¹ .K ⁻¹)	$a_2 \times 10^6$ (m ³ .mol ⁻¹ .K ⁻²)
	L-Methionine in BTMAC			L-Methionine in BTEAC		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
0.001	-1224.5	8.4212	-0.0132	-1727.7	11.781	-0.0188
0.003	-2137.7	14.696	-0.0238	-2267.6	15.551	-0.0252
0.005	-3427.7	23.170	-0.0376	-3852.8	25.856	-0.0418

*standard uncertainty in density $u(\rho) = \pm 0.0066$ g.cm⁻¹, *Standard uncertainties values of u_{ρ} : $u(T) = 0.01\text{K}$ (0.68 level of confidence) #

#Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol. kg^{-1} *molality has been expressed per kg of (IL + water) solvent mixture.

Table 5. Values of limiting molar expansibilities (Φ_E^0) for L-Methionine solutions in IL (BTMAC) at different temperatures and pressure at 1.013bar*

Conc. of aq. IL soln. in molality (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)
	298.15K	303.15K	308.15K	
0.001	0.55004	0.41804	0.28604	-0.0264
0.003	0.50406	0.26606	0.02806	-0.0476
0.005	0.74912	0.37312	-0.00288	-0.0752

*standard uncertainty in density $u(\rho) = \pm 0.0066$ g.cm⁻¹, *Standard uncertainties values of u_{ρ} : $u(T) = 0.01\text{K}$ (0.68 level of confidence) #

#Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol. kg^{-1} *molality has been expressed per kg of (IL + water) solvent mixture.

Table 6. Values of limiting molar expansibilities (Φ_E^0) for L-Methionine solution in IL (BTEAC) at different temperatures and pressure at 1.013bar*

Conc. of aq. IL soln. in molality (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)
	298.15K	303.15K	308.15K	
0.001	0.57056	0.38256	0.19456	-0.0376
0.003	0.52424	0.27224	0.02024	-0.0504
0.005	0.93066	0.51266	0.09466	-0.0836

*standard uncertainty in density $u(\rho) = \pm 0.0066$ g.cm⁻¹, *Standard uncertainties values of $u_{are}:u(T) = 0.01$ K(0.68 level of confidence) #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol. kg⁻¹*molality has been expressed per kg of (IL + water) solvent mixture.

Table 7. Viscosity B-coefficients of L-Methionine solution along with dB/dT values in different concentrations of IL (BTMAC) at (298.15, 303.15 and 308.15) K and pressure at 1.013bar*

Temperature (K)	0.001m IL		0.003m IL		0.005m IL		dB/dT
	B		B		B		
298.15	4.456		5.220		6.474		0.052
303.15	4.658		5.632		6.825		0.071
308.15	4.975		5.927		7.037		0.056

*Standard uncertainties values of $u_{are}:u(T) = 0.01$ K(0.68 level of confidence) #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol. kg⁻¹,*molality has been expressed per kg of (IL + water) solvent mixture

Table 8. Viscosity B-coefficients of L-Methionine solution along with dB/dT values in different concentrations of IL (BTEAC) at (298.15, 303.15 and 308.15) K and pressure at 1.013bar*

Temperature (K)	0.001m IL		0.003m IL		0.005m IL		dB/dT
	B		B		B		
298.15	4.630		5.530		6.751		0.048
303.15	4.789		5.760		7.079		0.049
308.15	5.113		6.018		7.213		0.046

*Standard uncertainties values of $u_{are}:u(T) = 0.01$ K(0.68 level of confidence) #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol. kg⁻¹*molality has been expressed per kg of (IL + water) solvent mixture

Table 9. Values of $(\bar{V}_1^0 - \bar{V}_2^0)$, $\Delta\mu_1^{0\#}$, $\Delta\mu_2^{0\#}$, $T\Delta S_2^{0\#}$, $\Delta H_2^{0\#}$ for L-Methionine in different molality(m) of aqueous solution of IL(BTMAC&BTEAC) mixture at different temperatures and atmospheric pressure 0.1MPa

parameters	0.001m			0.003m			0.005m		
	T=298.15K	303.15K	308.15K	T=298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
L-Met + BTMAC									
$(\bar{V}_1^0 - \bar{V}_2^0)$ /m ³ .mol ⁻¹	-94.79	-97.82	-97.29	-110.13	-112.09	-112.86	-119.82	-122.68	-123.66
$\Delta\mu_1^{0\#}$ /KJ.mol ⁻¹	8.91	9.03	9.07	8.95	9.06	9.17	9.01	9.14	9.17
$\Delta\mu_2^{0\#}$ /KJ.mol ⁻¹	634.10	758.47	944.49	665.33	817.07	996.17	710.11	861.49	1027.66
$T\Delta S_2^{0\#}$ /KJ.mol ⁻¹	9254.57	9409.74	9564.97	9863.99	10029.41	10194.83	9467.75	9626.52	9785.30
$\Delta H_2^{0\#}$ /KJ.mol ⁻¹	9888.67	10168.21	10509.46	10529.32	10846.48	11191.00	10177.86	10488.01	10812.96
L-Met + BTEAC									
$(\bar{V}_1^0 - \bar{V}_2^0)$ /m ³ .mol ⁻¹	-95.41	-97.83	-99.29	-110.75	-112.78	-113.55	-122.18	-125.85	-127.43
$\Delta\mu_1^{0\#}$ /KJ.mol ⁻¹	8.94	9.07	9.10	8.98	9.12	9.16	9.01	9.14	9.17
$\Delta\mu_2^{0\#}$ /KJ.mol ⁻¹	659.65	802.21	988.98	683.55	836.57	1031.31	729.43	874.52	1053.32
$T\Delta S_2^{0\#}$ /KJ.mol ⁻¹	9664.83	9826.91	9988.99	10368.46	10542.34	10716.22	9653.50	9815.39	9977.28
$\Delta H_2^{0\#}$ /KJ.mol ⁻¹	10324.48	10629.11	10977.97	11052.01	11378.91	11747.53	10382.93	10689.91	11030.60

*Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol. kg⁻¹. Standard uncertainty in temperature $u(T) = \pm 0.01$ K

Standard uncertainty in pressure $u(P) = \pm 0.01$ MPa* molality has been expressed per kg of (IL + water) solvent mixture.

Table 10. Molar conductance (Λ) of L-Methionine solutions in aqueous BTMAC & BTEAC ionic liquid solution in (0.001m, 0.003m, 0.005m) at 298.15K, 303.15K and 313.15K and pressure at 1.013bar*

Concentration of amino acid solutions in molality, m(mole/kg)	Molar Conductance of L-Methionine in BTMAC solutions $\Lambda \times 10^{-4}(\text{S.m}^2.\text{mol}^{-1})$			Molar conductance of L- Methionine in BTEAC solutions $\Lambda \times 10^{-4}(\text{S.m}^2.\text{mol}^{-1})$		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
0.001mIL						
0.0010	125.1	170.0	190.2	110.3	38.2	41.0
0.0025	52.0	73.0	79.0	18.1	19.4	20.9
0.0040	35.5	49.5	54.8	13.9	14.6	15.4
0.0055	27.3	37.2	45.2	11.6	12.6	12.9
0.0070	22.7	30.6	36.1	10.8	11.3	11.7
0.0085	19.9	26.3	31.1	9.9	10.5	10.6
0.003m IL						
0.0010	300.0	330.3	380.3	44.1	46.3	49.6
0.0025	135.0	140.0	158.0	21.7	22.8	23.9
0.0040	87.5	91.5	99.2	17.1	17.6	18.1
0.0055	64.5	68.0	75.1	14.3	14.9	14.9
0.0070	51.9	55.1	62.3	12.9	13.2	13.5
0.0085	44.0	47.7	53.6	11.5	12.1	12.4
0.005mIL						
0.0010	480.5	550.3	600.0	54.2	58.2	61.2
0.0025	196.0	225.4	245.1	25.6	26.8	27.6
0.0040	125.5	143.3	155.5	19.2	19.4	19.9
0.0055	93.5	107.0	115.3	15.8	15.9	16.5
0.0070	74.1	85.6	92.3	14.0	14.1	14.4
0.0085	62.6	72.1	77.8	12.5	12.7	12.8

*Standard uncertainties $u(\Lambda) = 0.5 \text{ Sm}^2 \text{ mol}^{-1}$, $u(T) = 0.01\text{K}$ (0.68 level of confidence)#Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol. kg⁻¹*molality has been expressed per kg of (IL + water) solvent mixture

Table 11. Surface Tension (γ) values of L-Methionine solutions in IL (BTMAC) and L-Methionine solutions in IL (BTEAC) at different concentration(0.001m,0.003m,0.005m) at room temperature and pressure at 1.013bar*

Concentration of amino acid solutions in molality(mole/kg)	Surface Tension of L- Methionine solutions in IL (BTMAC) γ (mN/m)	Surface Tension of L- Methionine solutions in IL (BTEAC) γ (mN/m)
0.001mIL		
0.0010	59.3	59.8
0.0025	60.3	60.6
0.0040	61.9	61.3
0.0055	62.3	62.5
0.0070	62.6	63.4
0.0085	64.3	64.8
0.003mIL		
0.0010	56.3	56.6
0.0025	57.8	60.2
0.0040	60.1	64.2
0.0055	60.3	66.4
0.0070	62.3	67.8
0.0085	63.2	69.2
0.005mIL		
0.0010	58.0	58.9
0.0025	58.6	61.2
0.0040	59.0	63.5
0.0055	59.6	64.9
0.0070	60.1	66.1
0.0085	60.8	69.5

*Standard uncertainties $u(Y)=\pm 0.1(mN/m)$ (0.68 level of confidence)#Combined standard uncertainty in molality according to mass purity of the samples is estimated to be $\pm 0.0095 \text{ mol. kg}^{-1}$ *molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence).

Table 12. Limiting Slopes ($\partial\sigma/\partial m$) of the Surface Tension of the Aqueous Solutions of α -Amino acid

Aqueous Mixture	IL	$(\partial\sigma/\partial m) / \text{mN m}^{-1}.\text{Kg. mol}^{-1}$	
		L-Methionine+Aq.BTMAC	L-Methionine+Aq.BTEAC
0.001		61.90	68.76
0.003		76.57	106.67
0.005		88.57	117.14

*Standard uncertainties $u(Y)=\pm 0.1(mN/m)$ (0.68 level of confidence)#Combined standard uncertainty in molality according to mass purity of the samples is estimated to be $\pm 0.0095 \text{ mol. kg}^{-1}$ *molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence).

Table 13. UV-Vis Spectroscopic data for the Benesi-Hildebrand double reciprocal plot of BTMAC+L-Met system at 298.15K

BTMAC+L-Met											
Temp/K	IL/ μM	[AA] $/\mu\text{M}$	A_0	A	ΔA	$1/[\text{AA}]/\text{M}^{-1}$	$1/\Delta A$	Intercept	Slope	$K_a/\text{M}^{-1} \times 10^{-3}$	$\Delta G/\text{KJmol}^{-1}$
	300	20	0.56530	0.59036	0.02505	0.0500	39.1117	2.0918	759.25	2.75	-19.6
	300	40	0.56530	0.61686	0.04736	0.0250	21.1107				
298.15	300	60	0.56530	0.63080	0.06617	0.0166	15.1107	2.0918	759.25	2.75	-19.6
	300	80	0.56530	0.64903	0.08427	0.0125	11.8657				
	300	100	0.56530	0.66593	0.10090	0.0100	9.9108				
	300	120	0.56530	0.68707	0.12203	0.0088	8.1948				
	300	140	0.56530	0.70875	0.14375	0.0062	6.9589				

Table 14. UV-Vis Spectroscopic data for the Benesi-Hildebrand double reciprocal plot of BTEAC+L-Met system at 298.15K

BTEAC+L-Met											
Temp/K	IL/ μM	[AA] $/\mu\text{M}$	A_0	A	ΔA	$1/[\text{AA}]/\text{M}^{-1}$	$1/\Delta A$	Intercept	Slope	$K_a/\text{M}^{-1} \times 10^{-3}$	$\Delta G/\text{KJ mol}^{-1}$
	300	20	0.79716	0.82339	0.02623	0.0500	38.1242	2.8794	711.05	3.85	-20.4
	300	40	0.79716	0.84560	0.04844	0.0250	20.6406				
298.15	300	60	0.79716	0.85986	0.06270	0.0166	15.9489	2.8794	711.05	3.85	-20.4
	300	80	0.79716	0.87791	0.08070	0.0125	12.3915				
	300	100	0.79716	0.90063	0.10345	0.0100	9.6602				
	300	120	0.79716	0.91899	0.12093	0.0088	8.2695				
	300	140	0.79716	0.93426	0.13717	0.0062	7.2932				

Tables

Table S1. Experimental values of density (ρ), viscosity (η) and molar refraction (R_M) of different molality (m) of aqueous IL (BTMAC) solution at 298.15K, 303.15K and 308.15K and pressure at 1.013bar*

Conc. of Aq. IL(BTMAC) soln. in molality, m (mol.kg ⁻¹)	$\rho \times 10^{-3}$ (kg.m ⁻³)			η (mPa.s)			R_M		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
				308.15K					
0.001	.99713	.99574	.99413	0.810	0.781	0.765	30.5618	30.5711	30.5866
0.003	.99717	.99577	.99416	0.821	0.791	0.779	30.5777	30.5783	30.5950
0.005	.99720	.99581	.99421	0.831	0.803	0.785	30.6017	30.6108	30.6179

*standard uncertainty in density $u(\rho) = \pm 0.0066 \text{ g.cm}^{-3}$, *molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence). * Standard uncertainty in refractive index $u(n_D) = \pm 0.01528$ and $u(T) = 0.01\text{K}$, (0.68 level of confidence). #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be $\pm 0.0095 \text{ mol.kg}^{-1}$. *Standard uncertainty in viscosity (u) $\eta = \pm 0.0152 \text{ mPa. S}$.

Table S2. Experimental values of density (ρ), viscosity (η) and molar refraction (R_M) of different molality (m) of aqueous IL (BTEAC) solution at 298.15K, 303.15K and 308.15K. and pressure at 1.013bar*

Conc. of Aq. IL(BTEAC) soln. in molality, m (mol.kg ⁻¹)	$\rho \times 10^{-3}$ (kg.m ⁻³)			η (mPa.s)			R_M		
	298.15K 303.15K		308.15K	298.15K 303.15K		308.15K	298.15K 303.15K		308.15K
	308.15K			308.15K			308.15K		
0.001	.99711	.99572	.99410	0.819	0.793	0.774	30.5709	30.5883	30.6213
0.003	.99715	.99575	.99414	0.830	0.807	0.792	30.5864	30.6042	30.6366
0.005	.99720	.99579	.99420	0.840	0.816	0.795	30.6101	30.6198	30.6435

*standard uncertainty in density $u(\rho) = \pm 0.0066$ g.cm⁻¹, *molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence). * Standard uncertainty in refractive index $u(n_D) = \pm 0.01528$ and $u(T) = 0.01$ K, (0.68 level of confidence).# Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol.kg⁻¹. *Standard uncertainty in viscosity (u) $\eta = \pm 0.0152$ mPa. S.

Table S3. Experimental values of refractive index (n_D) and specific conductance (κ) of different molality (m) of aqueous IL (BTMAC) solution at 298.15 K, 303.15 K and 308.15 K and pressure at 1.013bar*

Conc. of Aq. IL (BTMAC) soln. in molality, m (mol.kg ⁻¹)	n_D			κ (mS/cm)		
	298.15K	303.15K	308.15K	298.15K	303.15K	313.15K
0.001	1.3304	1.3300	1.3296	0.107	0.160	0.175
0.003	1.3306	1.3301	1.3297	0.280	0.310	0.368
0.005	1.3309	1.3305	1.3302	0.469	0.520	0.580

*Standard Uncertainties of refractive index (u) are: $u(n_D) = \pm 0.01528$, *molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence). $u(\sigma) = \pm 0.01$ (mS cm⁻¹)
¹⁾ $u(Y) = \pm 0.1$ (mN/m) #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol.kg⁻¹

Table S4. Experimental values of refractive index (n_D) and specific conductance (κ) of different molality (m) of aqueous IL (BTEAC) solution at 298.15 K, 303.15 K and 308.15 K. and pressure at 1.013bar*

Conc. of Aq. IL (BTEAC) soln. in molality, m (mol.kg ⁻¹)	n_D			κ (mS/cm)		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
0.001	1.3305	1.3302	1.3300	0.100	0.112	0.131
0.003	1.3307	1.3304	1.3302	0.278	0.300	0.310
0.005	1.3310	1.3306	1.3303	0.459	0.500	0.529

*Standard Uncertainties in refractive index (u) are: $u(n_D) = \pm 0.01528$ *molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence). $u(\sigma) = \pm 0.01$ (mScm⁻¹) $u(Y) = \pm 0.1$ (mN/m) #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol. kg⁻¹

Table S5. Density (ρ), viscosity (η) and molar refraction (R_M) of L-Methionine in aqueous (BTMAC) ionic liquid solutions at 298.15K, 303.15K and 308.15K and pressure at 1.013bar*

Conc. of L- Methionine soln.in molality, m(mol.kg ⁻¹)	$\rho \times 10^{-3}$ (kg.m ⁻³)			η (mPa.s)			R_M		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
0.001m IL									
0.0010	0.99717	0.99578	0.99417	0.919	0.882	0.845	30.5774	30.5949	30.6022
0.0025	0.99724	0.99584	0.99423	0.925	0.888	0.851	30.5921	30.6098	30.6173
0.0040	0.99731	0.99592	0.99431	0.931	0.894	0.857	30.5983	30.6158	30.6235
0.0055	0.99738	0.99599	0.99438	0.936	0.899	0.863	30.6046	30.6305	30.6295
0.0070	0.99747	0.99606	0.99446	0.941	0.905	0.869	30.6105	30.6367	30.6358
0.0085	0.99754	0.99615	0.99455	0.946	0.910	0.875	30.6165	30.6424	30.6411
0.003mIL									
0.0010	0.99720	0.99580	0.99419	0.926	0.885	0.851	30.5933	30.6027	30.6185
0.0025	0.99726	0.99585	0.99424	0.932	0.892	0.858	30.6083	30.6176	30.6338
0.0040	0.99733	0.99593	0.99431	0.938	0.898	0.864	30.6145	30.6323	30.6401
0.0055	0.99741	0.99601	0.99440	0.943	0.904	0.870	30.6205	30.6386	30.6460
0.0070	0.99749	0.99608	0.99447	0.948	0.909	0.877	30.6264	30.6445	30.6520
0.0085	0.99757	0.99617	0.99456	0.954	0.915	0.883	30.6323	30.6502	30.6577
0.005mIL									
0.0010	0.99722	0.99583	0.99423	0.935	0.897	0.856	30.6095	30.6186	30.6341
0.0025	0.99729	0.99589	0.99429	0.941	0.903	0.862	30.6241	30.6335	30.6491
0.0040	0.99736	0.99595	0.99435	0.947	0.909	0.868	30.6304	30.6395	30.65.54
0.0055	0.99743	0.99602	0.99445	0.952	0.915	0.874	30.6450	30.6542	30.6695
0.0070	0.99750	0.99611	0.99452	0.958	0.921	0.880	30.6513	30.6601	30.6757
0.0085	0.99760	0.99620	0.99461	0.964	0.927	0.887	30.6566	30.6661	30.6814

*standard uncertainty in density $u(\rho) = \pm 0.0066$ g.cm⁻¹, $u(T) = 0.01$ K, *molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence). #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol. kg⁻¹ *Standard uncertainty in viscosity (u) $\eta = \pm 0.0152$ mPa. S.

Table S6. Density (ρ), viscosity (η) and molar refraction (R_M) of L-Methionine in aqueous (BTEAC) ionic liquid solutions at 298.15K, 303.15K and 308.15K. and pressure at 1.013bar*

Conc. of L- Methionine soln.in molality (mol.kg ⁻¹)	$\rho \times 10^{-3}(\text{kg.m}^{-3})$			$\eta(\text{mPa.s})$			R_M		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
0.001m IL									
0.0010	0.99715	0.99576	0.99414	0.921	0.884	0.849	30.6116	30.6375	30.6790
0.0025	0.99722	0.99582	0.99420	0.930	0.893	0.858	30.6263	30.6525	30.7025
0.0040	0.99728	0.99589	0.99427	0.939	0.902	0.867	30.6412	30.6672	30.7172
0.0055	0.99736	0.99597	0.99436	0.948	0.912	0.877	30.6556	30.6731	30.7231
0.0070	0.99744	0.99604	0.99443	0.956	0.921	0.887	30.6699	30.6878	30.7378
0.0085	0.99753	0.99613	0.99453	0.965	0.929	0.897	30.6842	30.6934	30.7515
0.003mIL									
0.0010	0.99718	0.99578	0.99418	0.929	0.888	0.853	30.6191	30.6538	30.6862
0.0025	0.99724	0.99583	0.99423	0.938	0.896	0.863	30.6425	30.6690	30.7015
0.0040	0.99730	0.99590	0.99429	0.947	0.906	0.872	30.6574	30.6837	30.7250
0.0055	0.99739	0.99599	0.99439	0.957	0.917	0.882	30.6711	30.6977	30.7387
0.0070	0.99747	0.99606	0.99446	0.967	0.926	0.894	30.6774	30.7037	30.7447
0.0085	0.99756	0.99615	0.99455	0.977	0.936	0.904	30.6914	30.7096	30.7506
0.005m IL									
0.0010	0.99722	0.99581	0.99422	0.939	0.899	0.859	30.6431	30.6697	30.7019
0.0025	0.99728	0.99586	0.99427	0.949	0.909	0.869	30.6664	30.6849	30.7172
0.0040	0.99735	0.99593	0.99433	0.960	0.919	0.880	30.6811	30.6909	30.7321
0.0055	0.99743	0.99602	0.99440	0.970	0.929	0.891	30.6870	30.6974	30.7381
0.0070	0.99749	0.99609	0.99451	0.980	0.939	0.901	30.7016	30.7028	30.7518
0.0085	0.99759	0.99619	0.99461	0.990	0.950	0.912	30.7073	30.7090	30.7581

*standard uncertainty in density $u(\rho) = \pm 0.0066 \text{ g.cm}^{-1}$, * $u(T) = \pm 0.01\text{K}$, *molality has been expressed per kg of (IL + water) solvent mixture (0.68 level of confidence). #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be $\pm 0.0095 \text{ mol.kg}^{-1}$ *Standard uncertainty in viscosity (u) $\eta = \pm 0.0152 \text{ mPa. S}$.

Table S7. Apparent molar volume, (Φ_v) and $(\eta/\eta^0 - 1)/\sqrt{m}$ of L-Methionine solution in 0.001m, 0.003m and 0.005m aqueous BTMAC solution at different temperatures 298.15K, 303.15K, 308.15K and pressure at 1.013bar*

Conc. of L-Methionine soln. in molality, m (mol.kg ⁻¹)	$\Phi_v \times 10^6$ (m ³ .mol ⁻¹)	$(\eta/\eta^0 - 1)/\sqrt{m}$ (kg ^{1/2} .mol ^{-1/2})	$\Phi_v \times 10^6$ (m ³ .mol ⁻¹)	$(\eta/\eta^0 - 1)/\sqrt{m}$ (kg ^{1/2} .mol ^{-1/2})	$\Phi_v \times 10^6$ (m ³ .mol ⁻¹)	$(\eta/\eta^0 - 1)/\sqrt{m}$ (kg ^{1/2} .mol ^{-1/2})
0.001mIL	298.15K		303.15K		308.15K	
0.0010	109.52±0.03	0.243±0.003	109.62±0.03	0.270±0.004	109.73±0.03	0.285±0.005
0.0025	105.51±0.03	0.334±0.003	109.62±0.03	0.340±0.004	109.73±0.03	0.347±0.005
0.0040	104.50±0.03	0.403±0.003	104.59±0.03	0.412±0.004	107.21±0.03	0.448±0.005
0.0055	104.05±0.03	0.434±0.004	104.13±0.03	0.446±0.004	104.23±0.03	0.527±0.005
0.0070	102.36±0.03	0.486±0.005	102.43±0.03	0.541±0.005	102.52±0.03	0.609±0.006
0.0085	101.26±0.03	0.512±0.005	101.33±0.03	0.578±0.005	100.23±0.03	0.659±0.007
0.003mIL	298.15K		303.15K		308.15K	
0.0010	119.54±0.03	0.218±0.004	119.67±0.03	0.241±0.005	119.81±0.03	0.248±0.007
0.0025	113.53±0.03	0.307±0.004	117.66±0.03	0.318±0.005	117.80±0.03	0.340±0.006
0.0040	109.52±0.03	0.361±0.005	109.61±0.03	0.403±0.005	112.25±0.03	0.440±0.006
0.0055	105.87±0.03	0.424±0.005	107.78±0.03	0.458±0.006	109.89±0.03	0.513±0.007
0.0070	103.79±0.03	0.463±0.005	105.30±0.03	0.534±0.007	105.40±0.03	0.600±0.008
0.0085	102.44±0.03	0.499±0.007	102.52±0.03	0.572±0.007	102.60±0.03	0.651±0.009
0.005mIL	298.15K		303.15K		308.15K	
0.0010	129.57±0.03	0.200±0.006	129.72±0.03	0.220±0.007	129.90±0.03	0.219±0.008
0.0025	113.52±0.03	0.261±0.006	117.65±0.03	0.302±0.007	117.79±0.03	0.295±0.009
0.0040	109.51±0.03	0.335±0.006	114.64±0.03	0.375±0.007	112.24±0.03	0.413±0.009
0.0055	107.69±0.03	0.411±0.006	111.44±0.03	0.452±0.007	106.05±0.03	0.487±0.010
0.0070	106.65±0.03	0.446±0.008	106.74±0.03	0.531±0.008	105.40±0.03	0.554±0.010
0.0085	102.44±0.03	0.491±0.010	103.70±0.03	0.566±0.010	102.60±0.03	0.643±0.010

*standard uncertainty in density $u(\rho) = \pm 0.0066$ g.cm⁻¹, *Standard uncertainties u are: $u(T) = 0.01$ K, *molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence). #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol. kg⁻¹ *Standard uncertainty in viscosity (u) $\eta = \pm 0.0152$ mPa. S.

Table S8. Apparent molar volume, (Φ_v) and $(\eta/\eta^0 - 1)/\sqrt{m}$ of L-Methionine solutions in 0.001m, 0.003m and 0.005m in aqueous (BTEAC) solution at different temperatures 298.15K, 303.15K, 308.15K and pressure at 1.013bar*

Conc. of L-Methionine soln. in molality (mol.kg ⁻¹)	$\Phi_v \times 10^6$ (m ³ .mol ⁻¹)	$(\eta/\eta^0 - 1)/\sqrt{m}$ (kg ^{1/2} .mol ^{-1/2})	$\Phi_v \times 10^6$ (m ³ .mol ⁻¹)	$(\eta/\eta^0 - 1)/\sqrt{m}$ (kg ^{1/2} .mol ^{-1/2})	$\Phi_v \times 10^6$ (m ³ .mol ⁻¹)	$(\eta/\eta^0 - 1)/\sqrt{m}$ (kg ^{1/2} .mol ^{-1/2})
0.001m IL	298.15K		303.15K		308.15K	
0.0010	109.52±0.05	0.230±0.005	109.62±0.05	0.251±0.006	109.73±0.05	0.259±0.007
0.0025	105.51±0.05	0.317±0.005	109.62±0.05	0.302±0.006	109.73±0.05	0.337±0.007
0.0040	104.51±0.05	0.387±0.005	107.10±0.05	0.410±0.006	107.21±0.05	0.424±0.007
0.0055	104.05±0.05	0.424±0.006	104.13±0.05	0.458±0.007	102.39±0.05	0.515±0.008
0.0070	102.36±0.05	0.475±0.006	102.43±0.05	0.521±0.008	102.52±0.05	0.596±0.009

0.0085	100.08±0.05	0.511±0.008	101.34±0.05	0.576±0.009	99.05±0.05	0.656±0.009
0.003mIL	298.15K		303.15K		308.15K	
0.0010	119.55±0.05	0.207±0.007	119.67±0.05	0.228±0.008	119.82±0.05	0.225±0.009
0.0025	113.53±0.05	0.292±0.007	117.66±0.05	0.303±0.008	117.80±0.05	0.303±0.010
0.0040	109.52±0.05	0.340±0.007	112.13±0.05	0.376±0.009	114.77±0.05	0.396±0.010
0.0055	105.87±0.05	0.401±0.008	105.96±0.05	0.455±0.010	106.06±0.05	0.489±0.010
0.0070	103.79±0.05	0.453±0.009	105.30±0.05	0.519±0.010	105.40±0.05	0.577±0.011
0.0085	101.26±0.05	0.500±0.010	102.52±0.05	0.568±0.010	102.61±0.05	0.642±0.011
0.005m IL	298.15K		303.15K		308.15K	
0.0010	129.57±0.05	0.191±0.008	129.72±0.05	0.207±0.009	129.90±0.05	0.198±0.010
0.0025	117.54±0.05	0.242±0.008	121.68±0.05	0.290±0.008	121.83±0.05	0.293±0.011
0.0040	114.53±0.05	0.326±0.009	114.64±0.05	0.368±0.009	117.29±0.05	0.355±0.011
0.0055	109.51±0.05	0.401±0.010	107.78±0.05	0.446±0.010	113.39±0.05	0.475±0.012
0.0070	108.08±0.05	0.445±0.011	106.74±0.05	0.515±0.011	105.40±0.05	0.561±0.012
0.0085	103.62±0.05	0.483±0.012	102.51±0.05	0.562±0.012	101.42±0.05	0.625±0.014

*Standard uncertainties u are: $u(T) = 0.01K$, *standard uncertainty in viscosity $u(\eta) = \pm 0.0152 \text{ mPa} \cdot S$, *molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence), #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be $\pm 0.0095 \text{ mol} \cdot \text{kg}^{-1}$

Table S9. Refractive index (n_D) and specific conductance (κ) of L-Methionine in aqueous IL (BTMAC) solution at 298.15K, 303.15K and 308.15K and pressure at 1.013bar*

Conc. of L-Methionine soln. in molality, m ($\text{mol} \cdot \text{kg}^{-1}$)	n_D			κ (mS/cm)		
	298.15K	303.15K	313.15K	298.15K	303.15K	313.15K
0.001Mil						
0.0010	1.3306	1.3303	1.3298	0.1251	0.170	0.190
0.0025	1.3308	1.3305	1.3300	0.130	0.182	0.197
0.0040	1.3309	1.3306	1.3301	0.142	0.198	0.219
0.0055	1.3310	1.3308	1.3302	0.149	0.204	0.248
0.0070	1.3311	1.3309	1.3303	0.158	0.213	0.252
0.0085	1.3312	1.3310	1.3304	0.169	0.223	0.264
0.003mIL						
0.0010	1.3308	1.3304	1.3300	0.300	0.330	0.380
0.0025	1.3310	1.3306	1.3302	0.337	0.350	0.392
0.0040	1.3311	1.3308	1.3303	0.350	0.366	0.396
0.0055	1.3312	1.3309	1.3304	0.354	0.374	0.412
0.0070	1.3313	1.3310	1.3305	0.362	0.386	0.435
0.0085	1.3314	1.3311	1.3306	0.374	0.405	0.455
0.005mIL						
0.0010	1.3310	1.3306	1.3302	0.481	0.550	0.600
0.0025	1.3312	1.3308	1.3304	0.490	0.563	0.612
0.0040	1.3313	1.3309	1.3305	0.502	0.573	0.622
0.0055	1.3314	1.3311	1.3307	0.513	0.588	0.633
0.0070	1.3316	1.3312	1.3308	0.518	0.598	0.645
0.0085	1.3317	1.3313	1.3309	0.532	0.612	0.660

*Standard uncertainties values of u are: $u(T) = 0.01K$ (0.68 level of confidence) #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be $\pm 0.0095 \text{ mol} \cdot \text{kg}^{-1}$ *molality has been expressed per kg of (IL + water) solvent mixture).

Table S10. Refractive index (n_D) and specific conductance (κ) of L-Methionine in aqueous IL (BTMAC) solution at 298.15K, 303.15K and 308.15K and pressure at 1.013bar*

Conc. of L-Methionine soln. in molality, m (mol.kg ⁻¹)	n_D			κ (mS/cm)		
	298.15K	303.15K	313.15K	298.15K	303.15K	313.15K
0.001Mil						
0.0010	1.3306	1.3303	1.3298	0.125	0.170	0.190
0.0025	1.3308	1.3305	1.3300	0.130	0.182	0.197
0.0040	1.3309	1.3306	1.3301	0.142	0.198	0.219
0.0055	1.3310	1.3308	1.3302	0.149	0.204	0.248
0.0070	1.3311	1.3309	1.3303	0.158	0.213	0.252
0.0085	1.3312	1.3310	1.3304	0.169	0.223	0.264
0.003Mil						
0.0010	1.3308	1.3304	1.3300	0.300	0.330	0.380
0.0025	1.3310	1.3306	1.3302	0.337	0.350	0.392
0.0040	1.3311	1.3308	1.3303	0.350	0.366	0.396
0.0055	1.3312	1.3309	1.3304	0.354	0.374	0.412
0.0070	1.3313	1.3310	1.3305	0.362	0.386	0.435
0.0085	1.3314	1.3311	1.3306	0.374	0.405	0.455
0.005mIL						
0.0010	1.3311	1.3305	1.3302	0.481	0.550	0.600
0.0025	1.3312	1.3307	1.3304	0.490	0.563	0.612
0.0040	1.3313	1.3308	1.3305	0.502	0.573	0.622
0.0055	1.3314	1.3309	1.3307	0.513	0.588	0.633
0.0070	1.3315	1.3311	1.3308	0.518	0.598	0.645
0.0085	1.3317	1.3312	1.3309	0.532	0.612	0.660

*Standard uncertainties values of u are: $u(T) = 0.01K$ (0.68 level of confidence), #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be ± 0.0095 mol. kg⁻¹*molality has been expressed per kg of (IL + water) solvent mixture

Table S11. Refractive index (n_D) and specific conductance (κ) of L-Methionine in aqueous IL (BTEAC) solution at 298.15K, 303.15K and 308.15K and pressure at 1.013bar*

Conc. of L-Methionine soln. in molality, m (mol.kg ⁻¹)	n_D			κ (mS/cm)		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
0.001Mil						
0.0010	1.3310	1.3308	1.3307	0.110	0.120	0.140
0.0025	1.3312	1.3310	1.3310	0.120	0.133	0.152
0.0040	1.3314	1.3312	1.3312	0.129	0.146	0.168
0.0055	1.3316	1.3313	1.3313	0.141	0.156	0.176
0.0070	1.3318	1.3315	1.3315	0.144	0.168	0.190
0.0085	1.3320	1.3316	1.3317	0.150	0.179	0.206
0.003Mil						
0.0010	1.3311	1.3310	1.3308	0.290	0.310	0.330
0.0025	1.3314	1.3312	1.3310	0.300	0.322	0.345
0.0040	1.3316	1.3314	1.3313	0.310	0.330	0.354
0.0055	1.3318	1.3316	1.3315	0.317	0.345	0.363
0.0070	1.3319	1.3317	1.3316	0.324	0.352	0.371
0.0085	1.3321	1.3318	1.3317	0.334	0.360	0.389

0.005mIL						
0.0010	1.3314	1.3312	1.3310	0.470	0.520	0.540
0.0025	1.3317	1.3314	1.3312	0.480	0.533	0.552
0.0040	1.3319	1.3315	1.3314	0.492	0.540	0.562
0.0055	1.3320	1.3316	1.3315	0.498	0.553	0.574
0.0070	1.3322	1.3317	1.3317	0.511	0.565	0.583
0.0085	1.3323	1.3318	1.3318	0.527	0.576	0.604

*Standard uncertainties values of u are: $u(T) = 0.01\text{K}$ (0.68 level of confidence), #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be $\pm 0.0095 \text{ mol. kg}^{-1}$ *molality has been expressed per kg of (IL + water) solvent mixture.

Figures

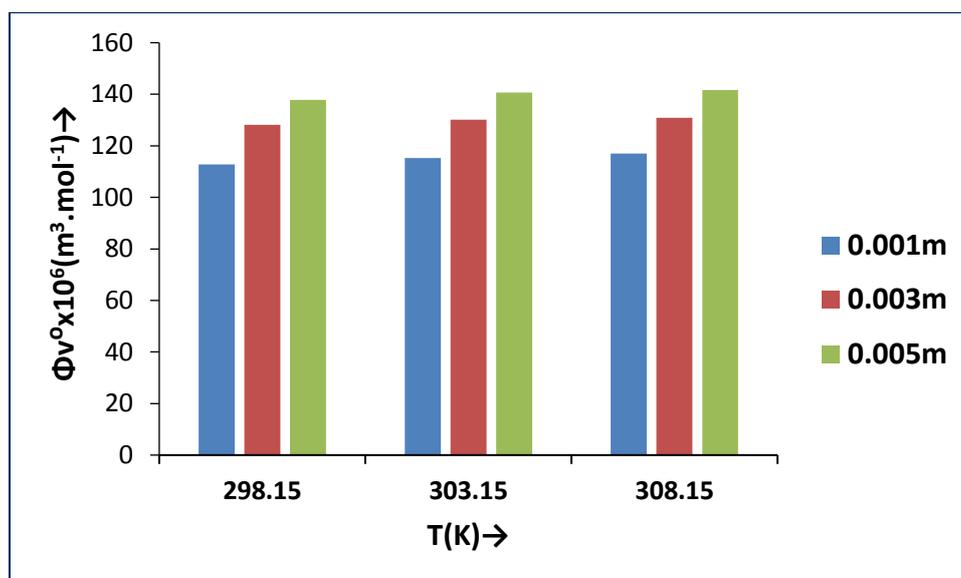


Figure 1 .Variation of limiting apparent molar volume (Φ_v^0) of L-methionine as a function of temperature (T/K) and different concentrations of(0.001,0.003,0.005)m aqueous BTMAC solutions

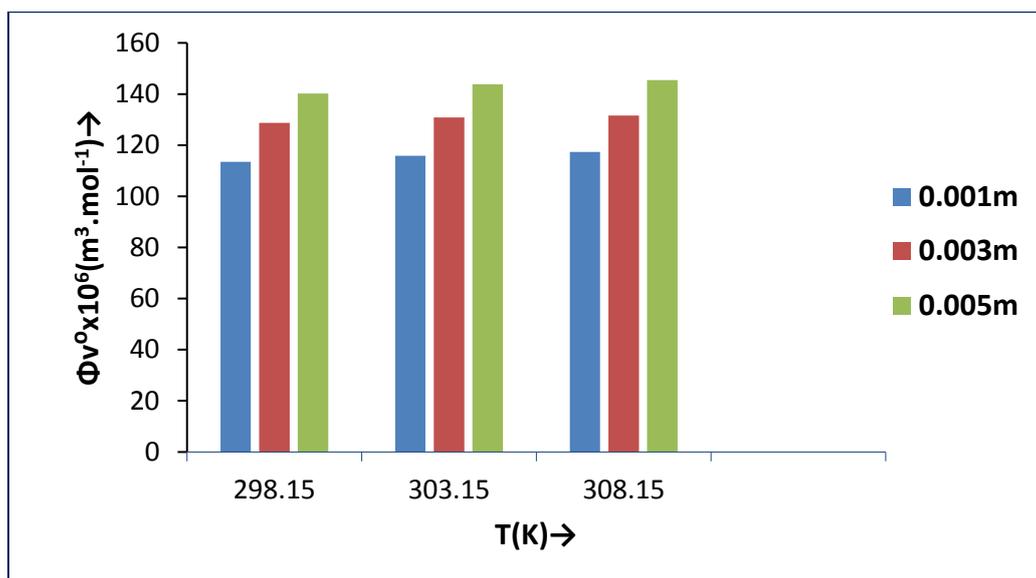


Figure 2 .Variation of limiting apparent molar volume (Φ_v^0) of L-methionine as a function of temperature (T/K) and different concentrations of(0.001,0.003,0.005)m aqueous BTEAC solutions

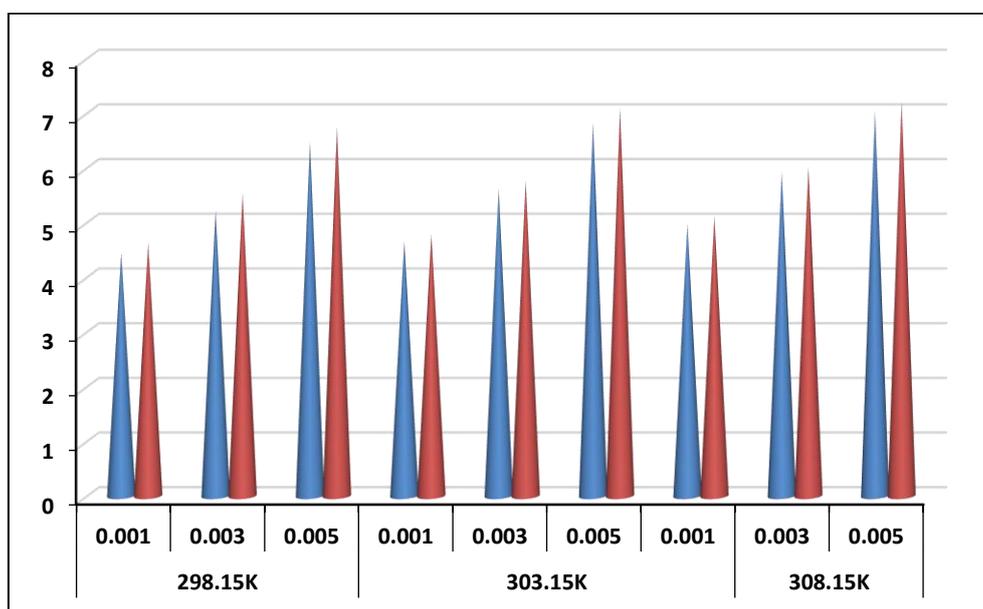


Figure 3.Variation of viscosity B-coefficient of L-methionine as a function of different temperature(T/K) and different concentrations of aqueous BTEAC (IL) and BTMAC (IL) solutions

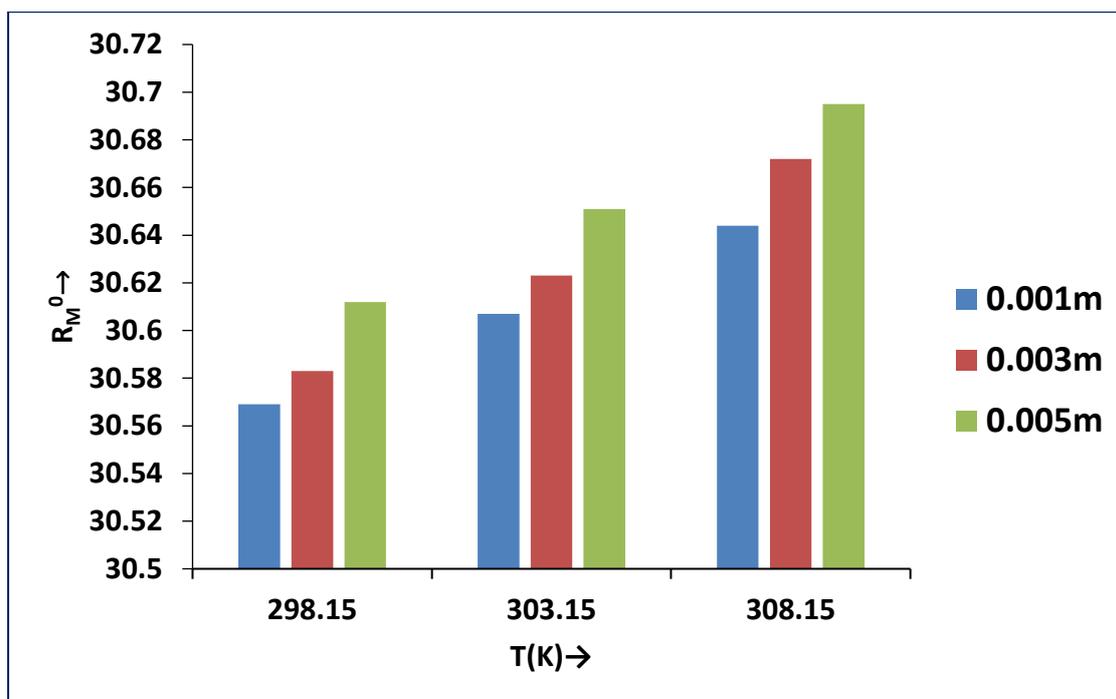


Figure 4. Variation of Limiting Molar refraction (R_M^0) of L-methionine as a function of temperature (T/K) and different concentrations of (0.001,0.003,0.005)m aqueous BTMAC solutions

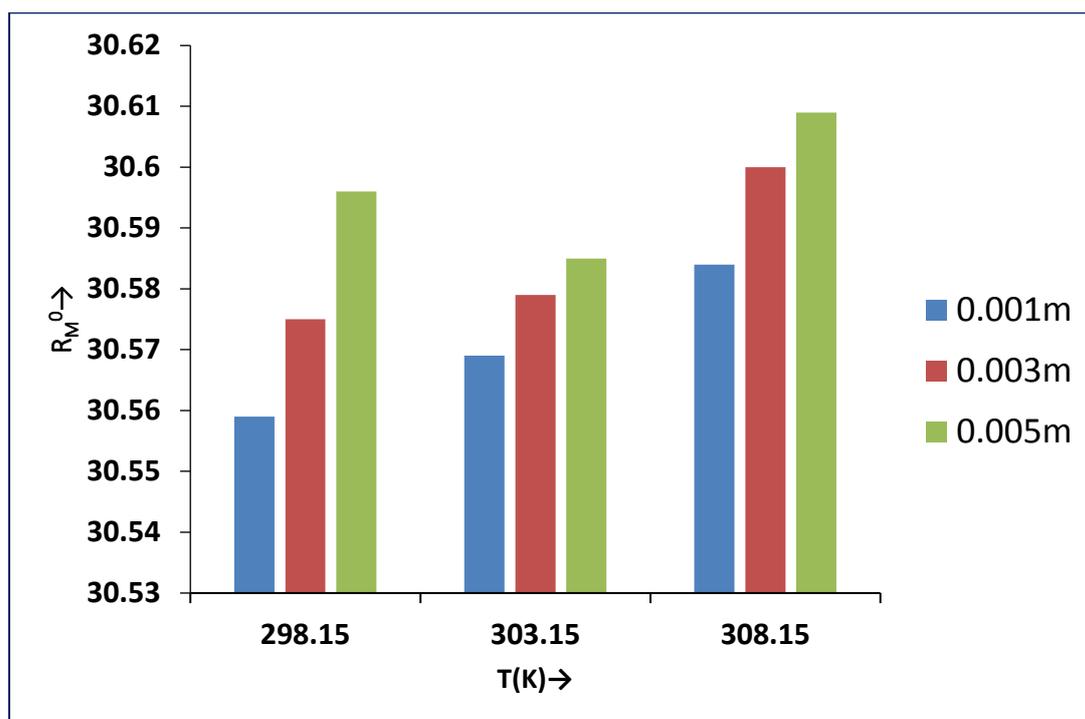


Figure 5. Variation of Limiting Molar refraction (R_M^0) of L-methionine methionine as a function of temperature (T/K) and different concentrations of (0.001,0.003,0.005)m aqueous BTEAC solutions

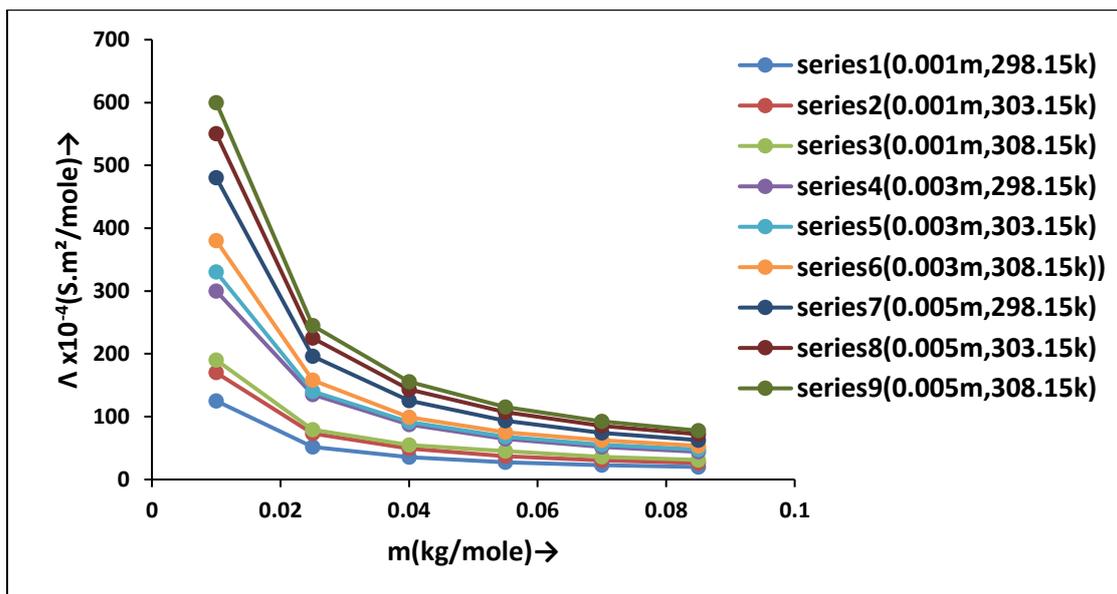


Figure 6. Variation of molar conductance (Λ) plot as a function of the concentration of L-Methionine (amino acid) in different concentrations of aqueous BTMAC solutions at different temperatures (T/K)

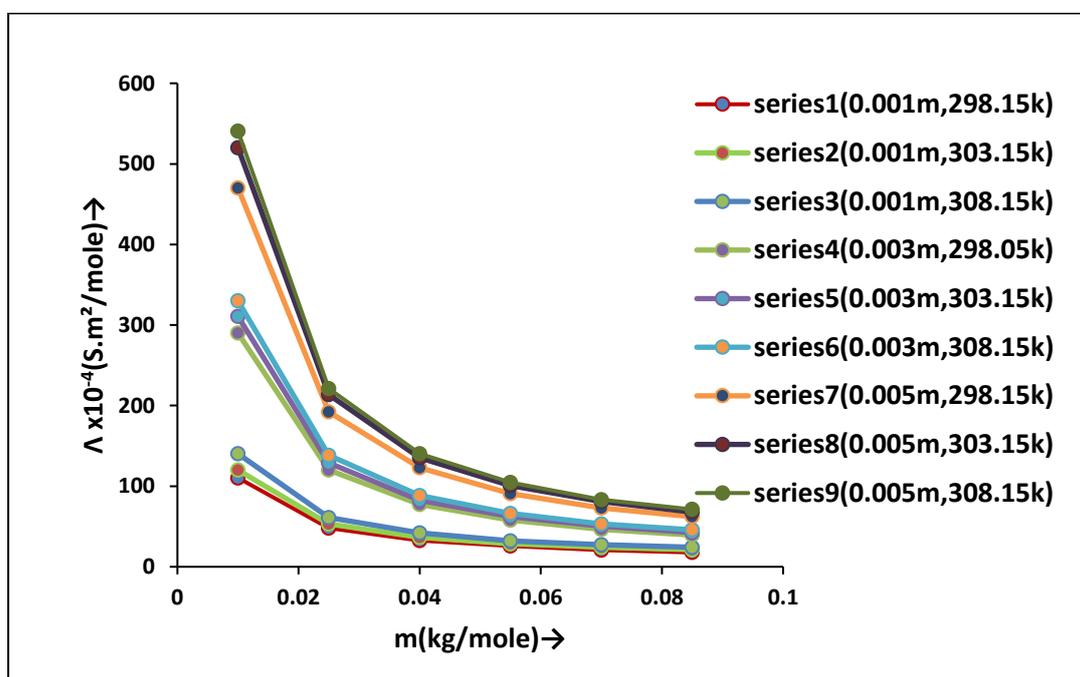


Figure 7. Variation of molar conductance (Λ) plot as a function of the concentration of L-Methionine (amino acid) in different concentrations of aqueous BTEAC solutions at different temperatures (T/K)

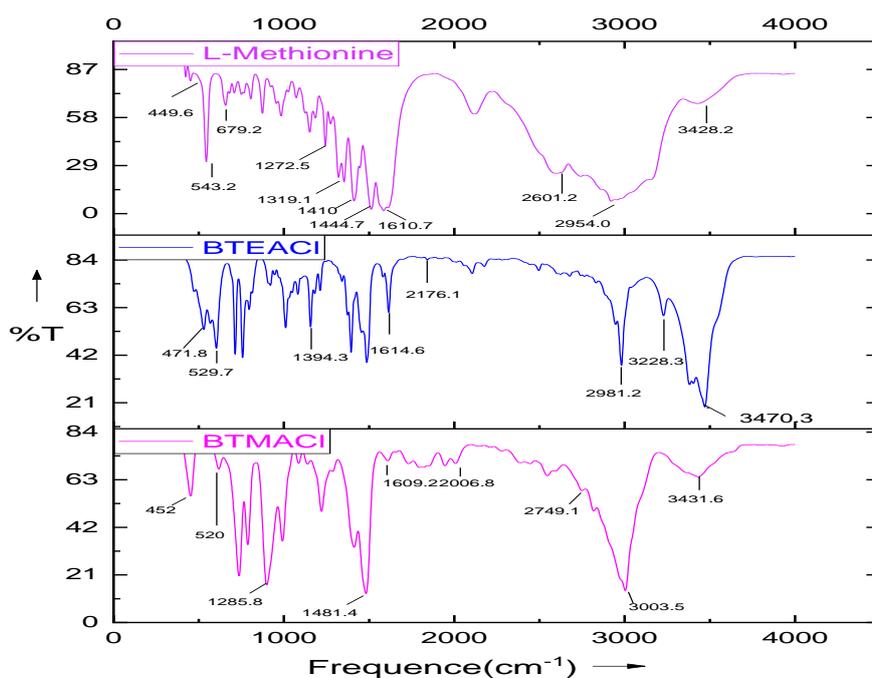


Figure A1. FTIR Spectrum of pure ILs (BTMAC & BTEAC) and AA (L-Met)

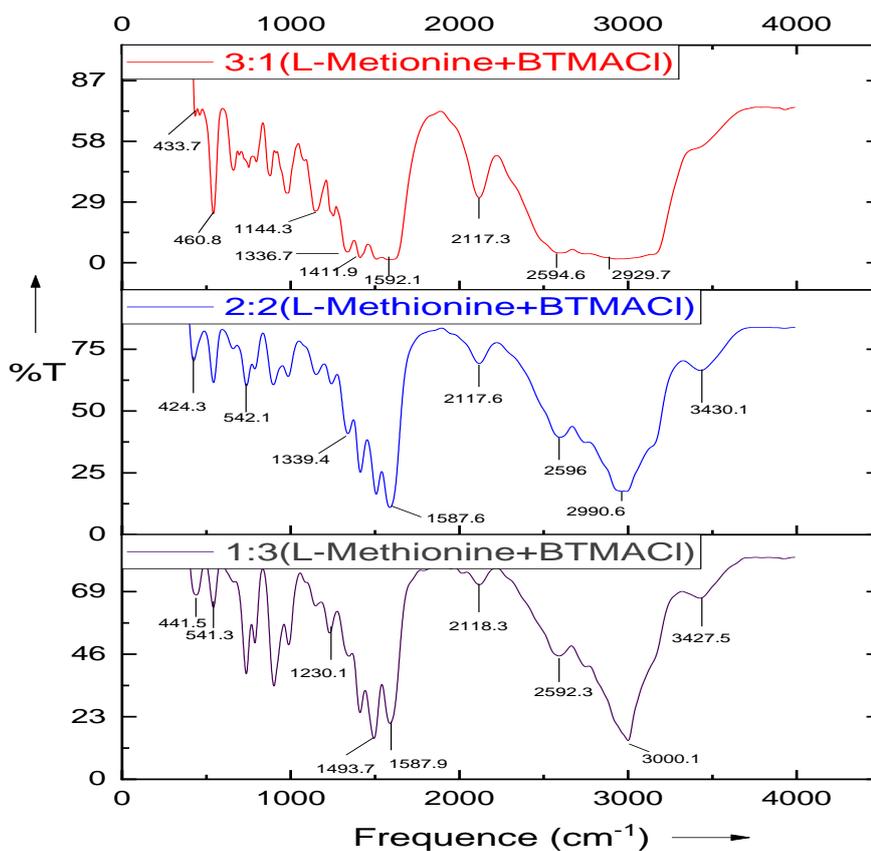


Figure A2. FTIR Spectrum of L-Met + BTMAC Mixture (AA:IL=1:3,2:2,3:1)

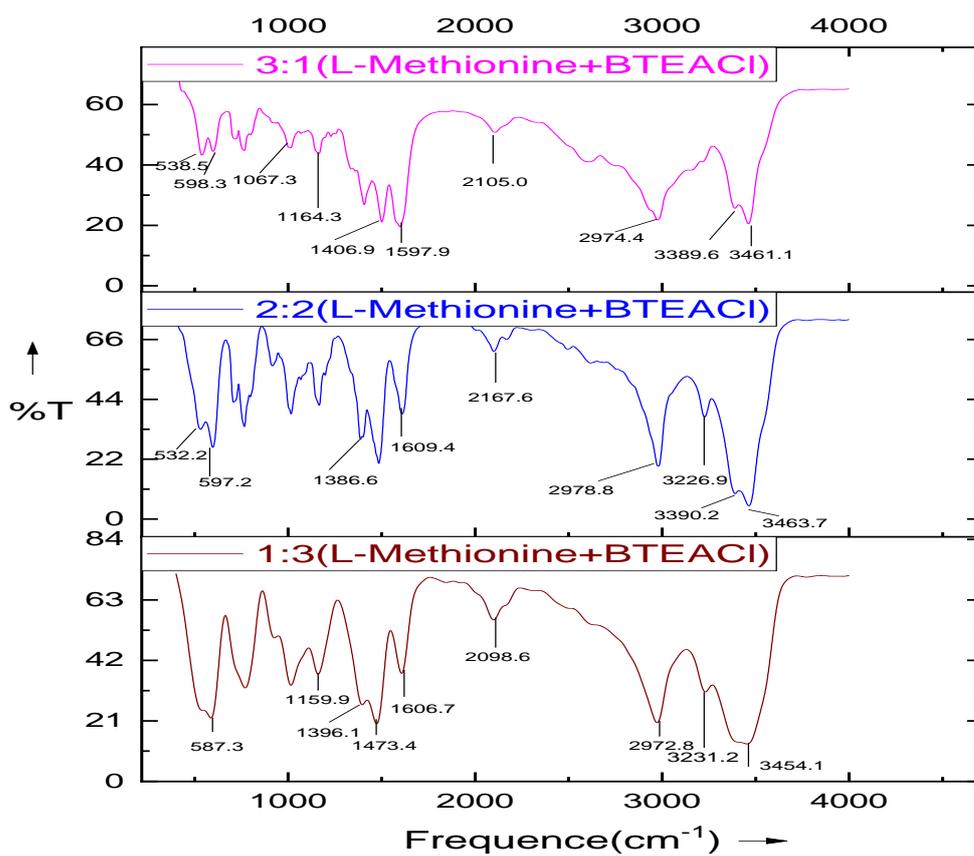


Figure A3. FTIR Spectrum of L-Met + BTEAC Mixture (AA:IL=1:3,2:2, 3:1)

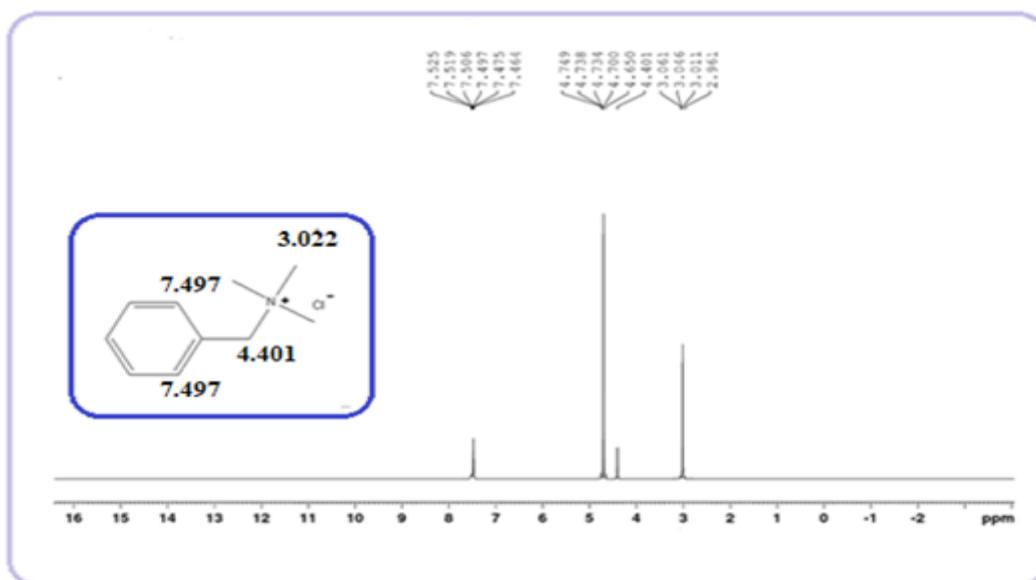


Figure B1. $^1\text{H-NMR}$ Spectrum of pure BTMAC in D_2O

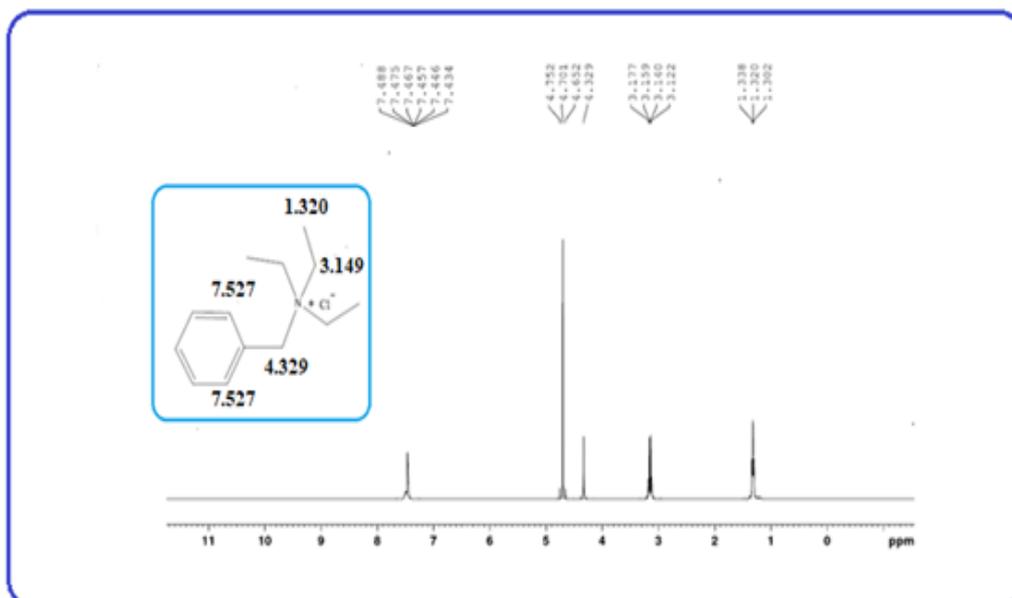


Figure B2. ¹H-NMR Spectrum of pure BTEAC in D₂O

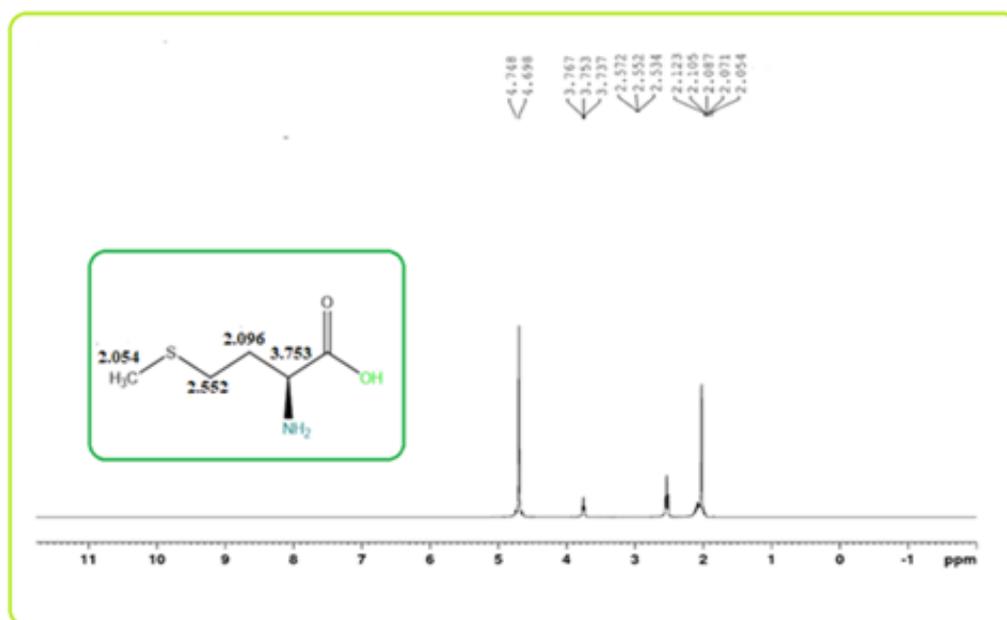


Figure B3. ¹H-NMR Spectrum of pure L-Methionine in D₂O

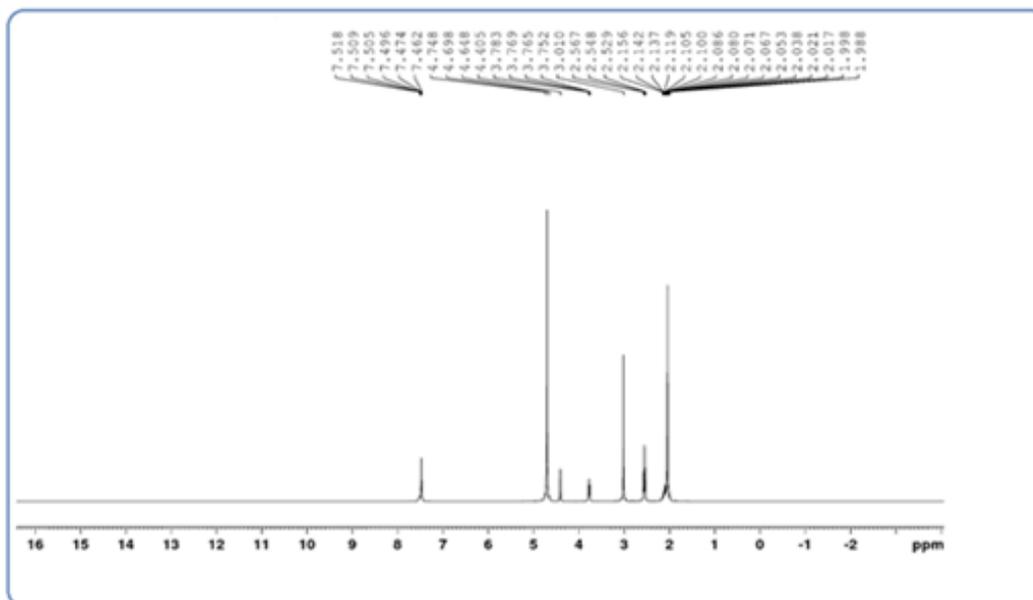


Figure B4. $^1\text{H-NMR}$ Spectrum of L-Met + BTMAC(AA:IL=4:1) in D_2O

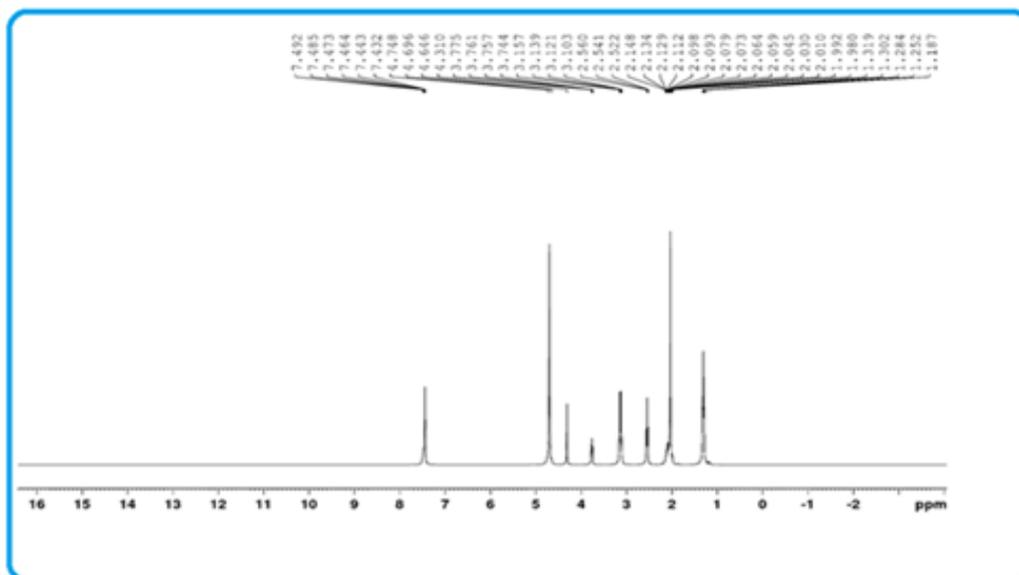


Figure B5. $^1\text{H-NMR}$ Spectrum of L-Met + BTEAC (AA:IL=4:1) in D_2O

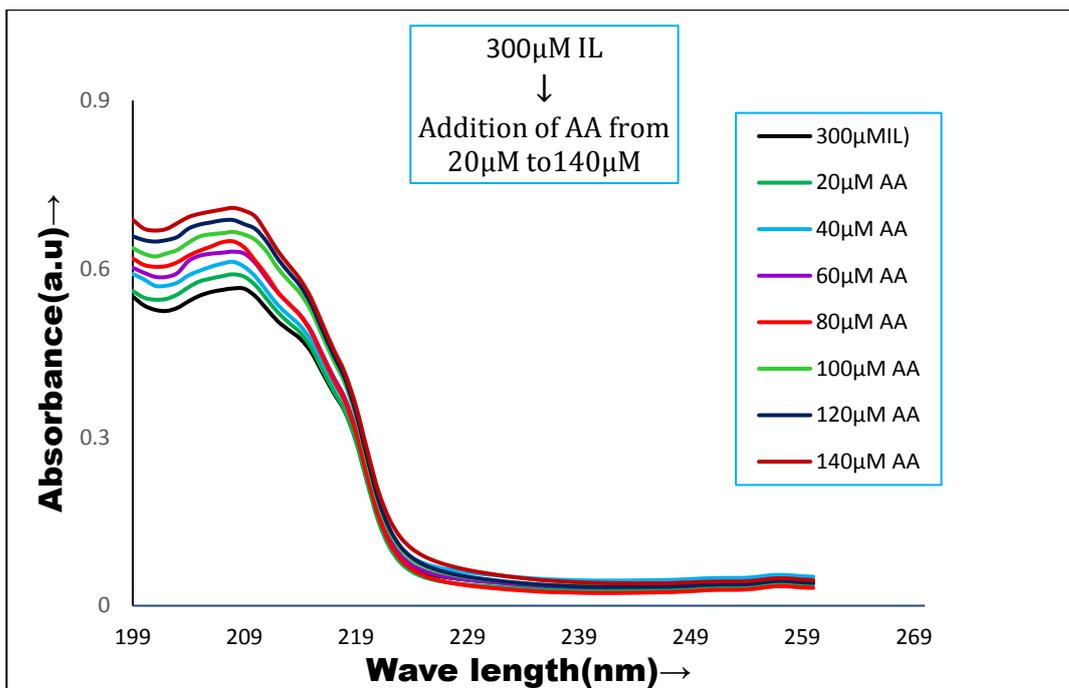


Figure C1. UV-Vis spectra of (BTMAC+L-Met) system

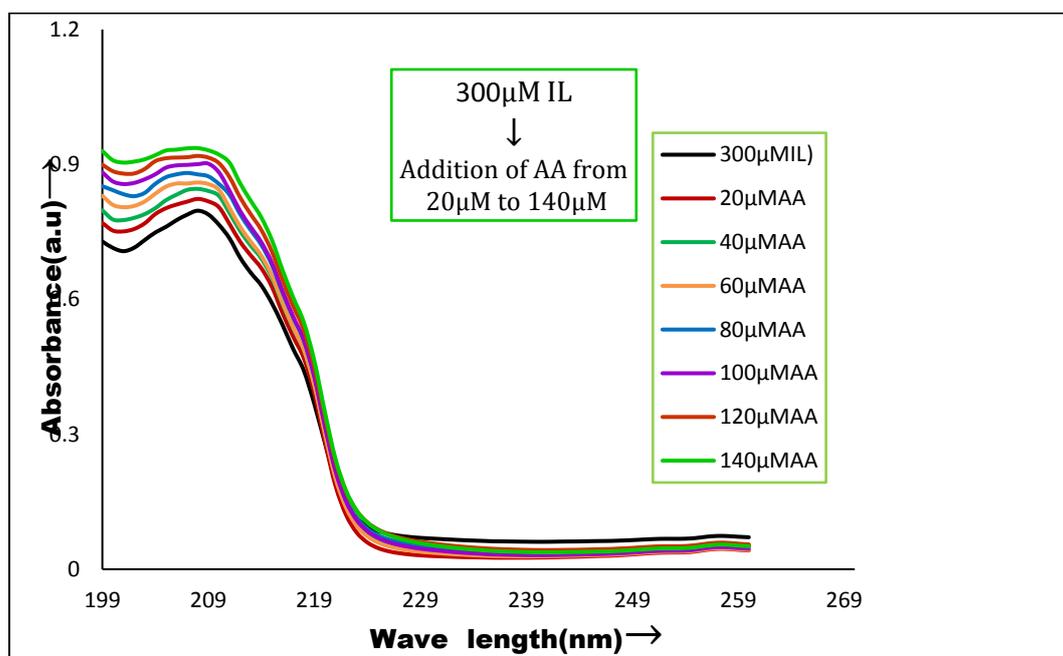


Figure C2. UV-Vis spectra of (BTEAC+L-Met) system

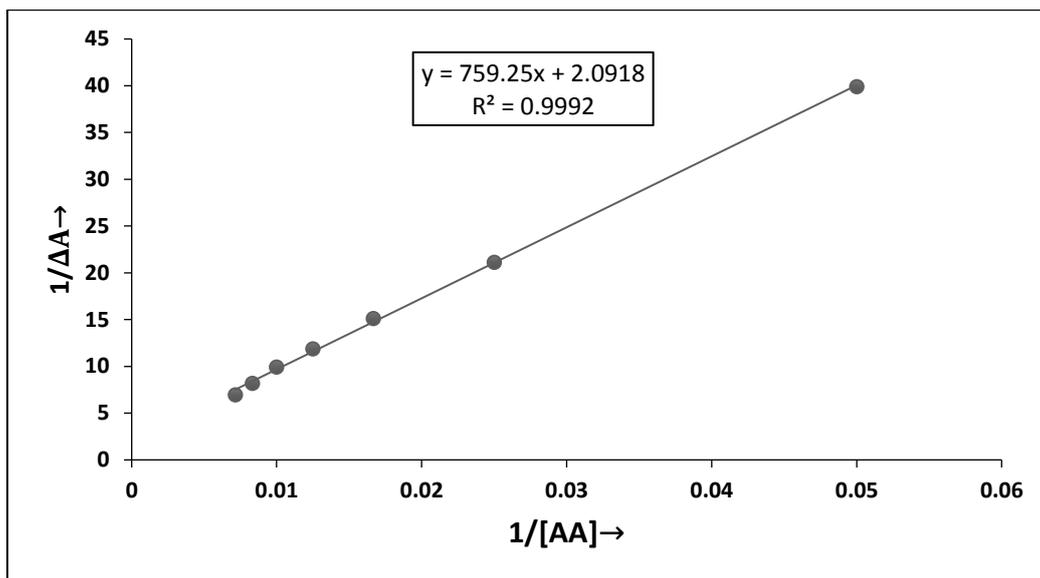


Figure C3. Benesi double reciprocal plot of BTMAC+L-Met system

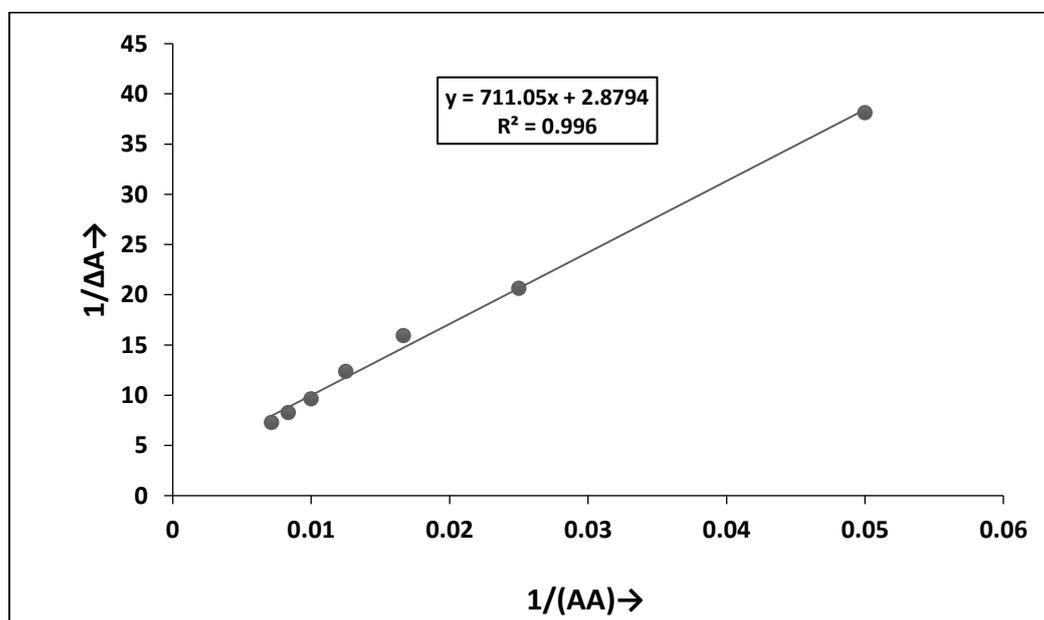


Figure C4. Benesi double reciprocal plot of BTEAC+L-Met system

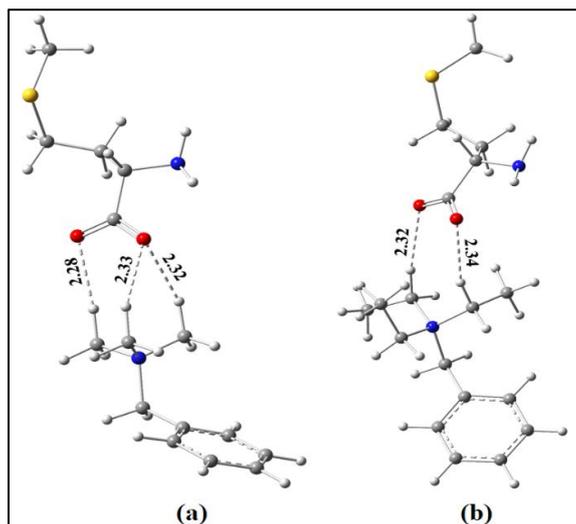


Figure C5: Optimized geometries of the (a) L-Met-BTMAC (b) L-Met-BTEAC in aqueous solution

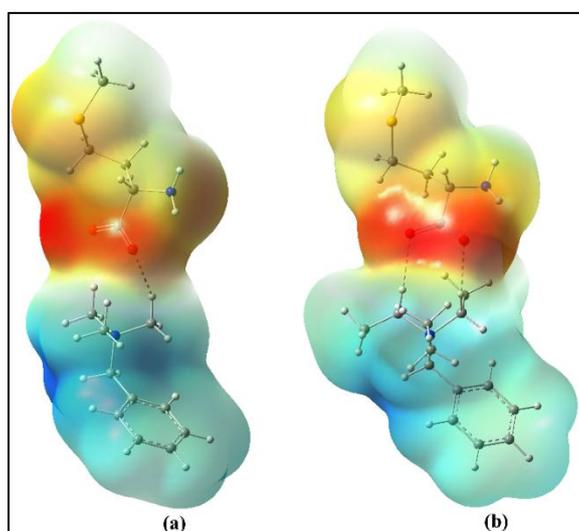


Figure C6: Electrostatic potential maps for (a) L-Met-BTMAC (b) L-Met-BTEAC in aqueous medium

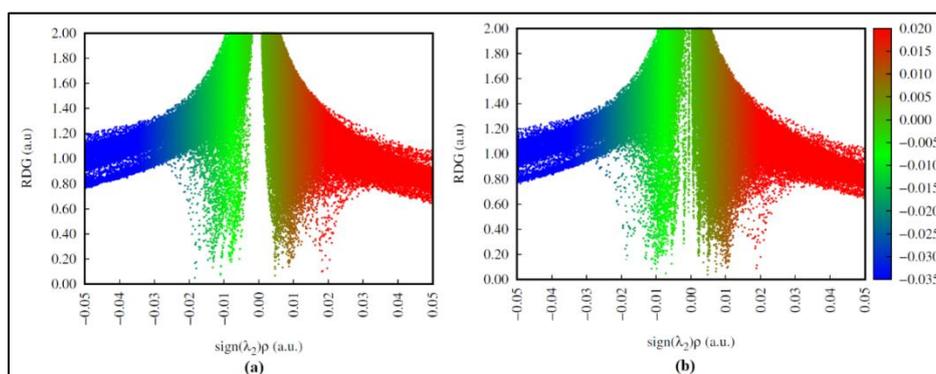


Figure C7: Plots of reduced density gradient (RDG) for (a) L-Met-BTMAC (b) L-Met-BTEAC composites

Supporting figures

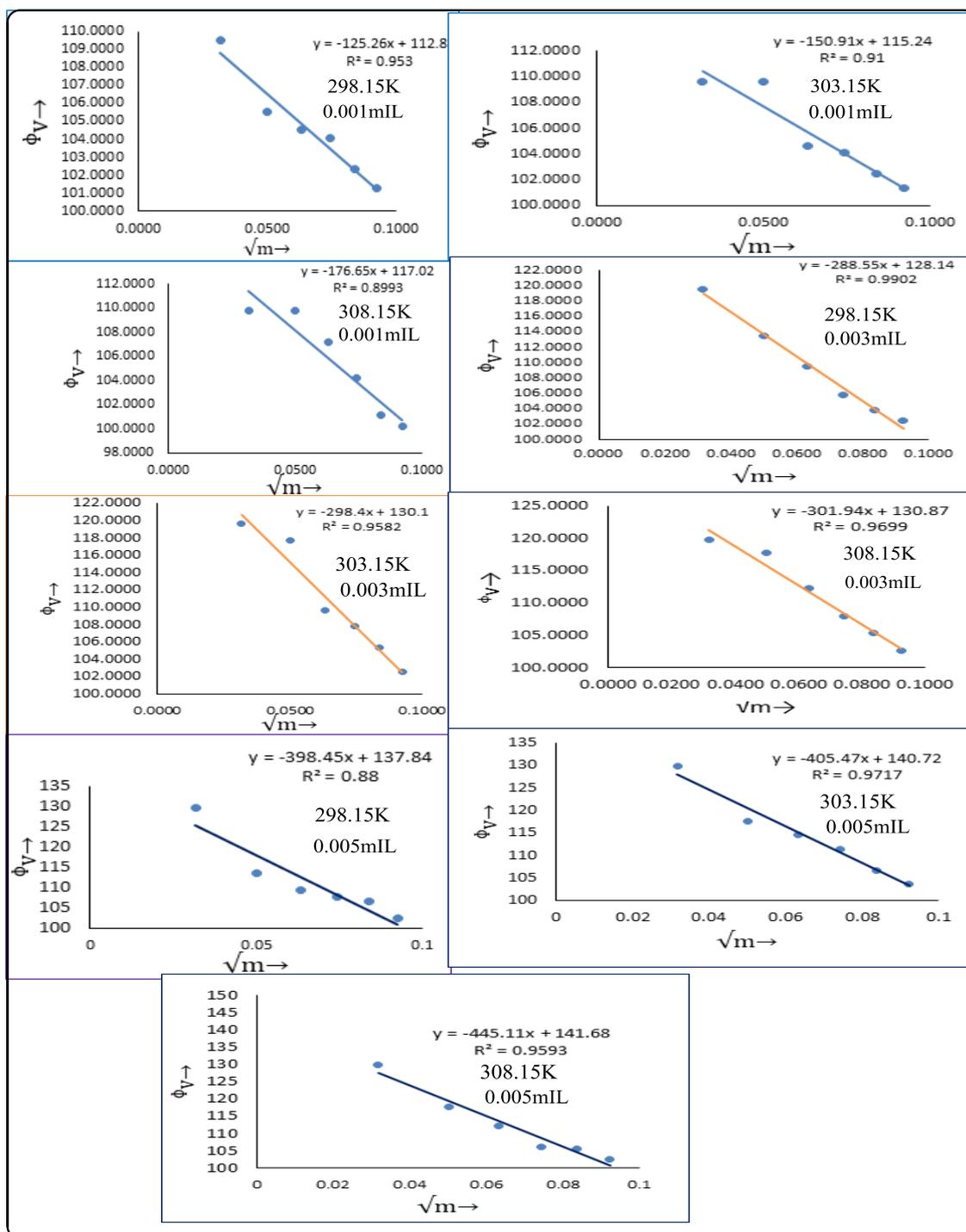


Figure S1. Variation of Apparent molar volume, Φ_v of L-methionine solutions with concentration, \sqrt{m} against different temperature in 0.001m, 0.003m, 0.005m aqueous IL (BTMAC) solutions

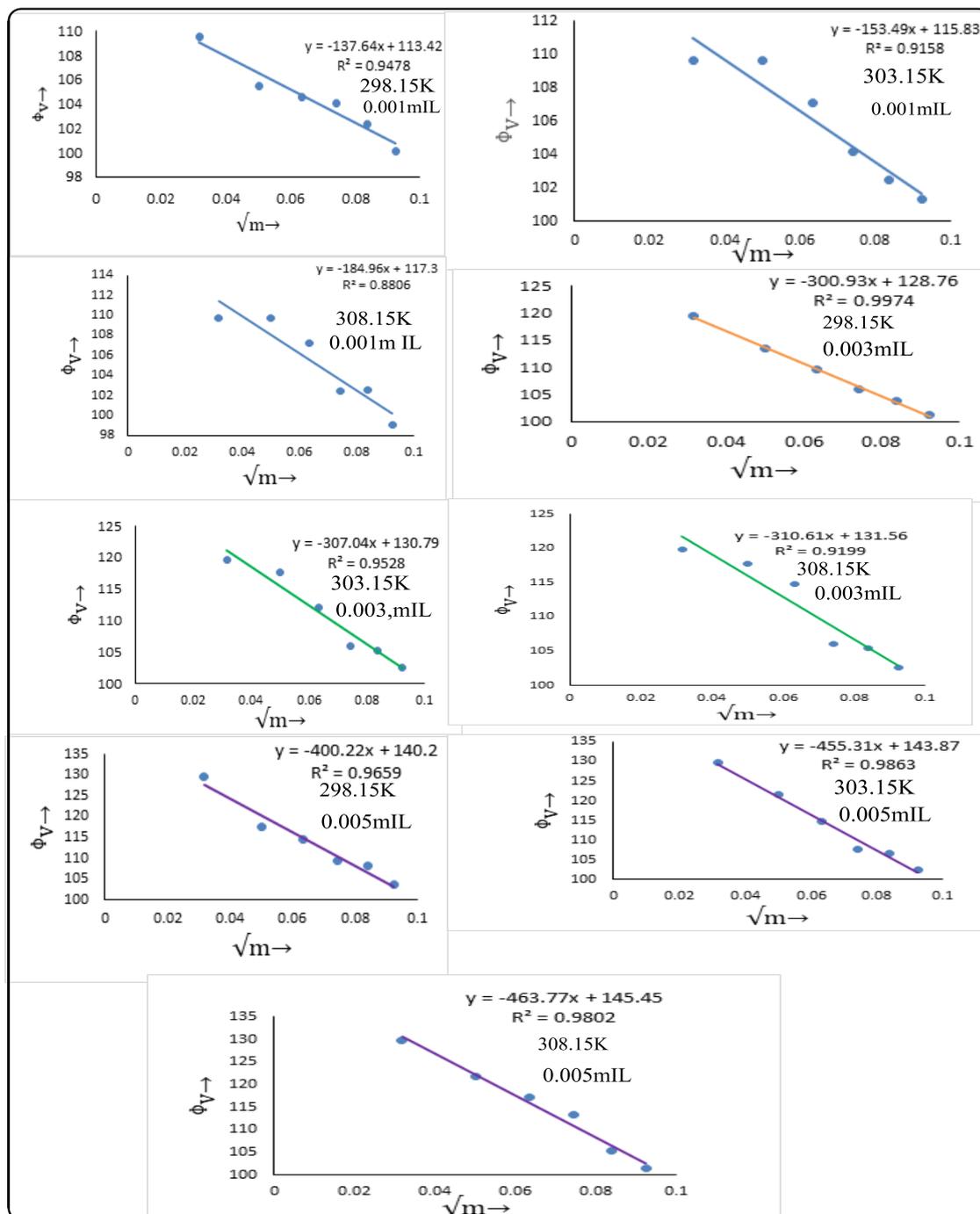


Figure S2. Variation of Apparent molar volume, Φ_v of L-methionine solutions with concentration, \sqrt{m} against different temperature in 0.001m, 0.003m, 0.005m aqueous IL (BTEAC) solutions

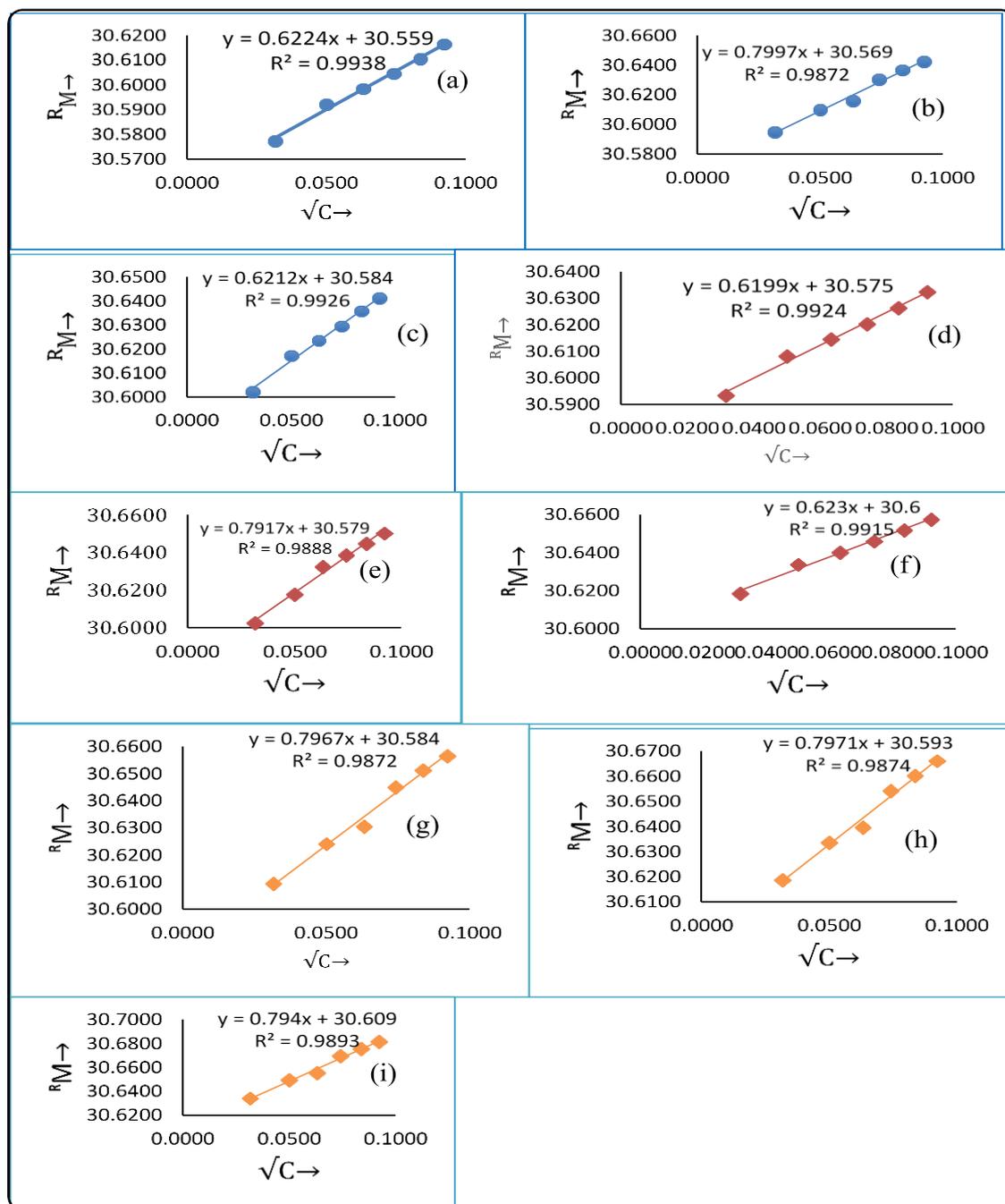


Figure S3. Variation of Molar refraction, R_M plot (a,b,c,d,e,f,g,h,i) of L-methionine against concentration, \sqrt{C} at different temperature in 0.001m, 0.003m, 0.005m aqueous solutions of IL(BTMAC)

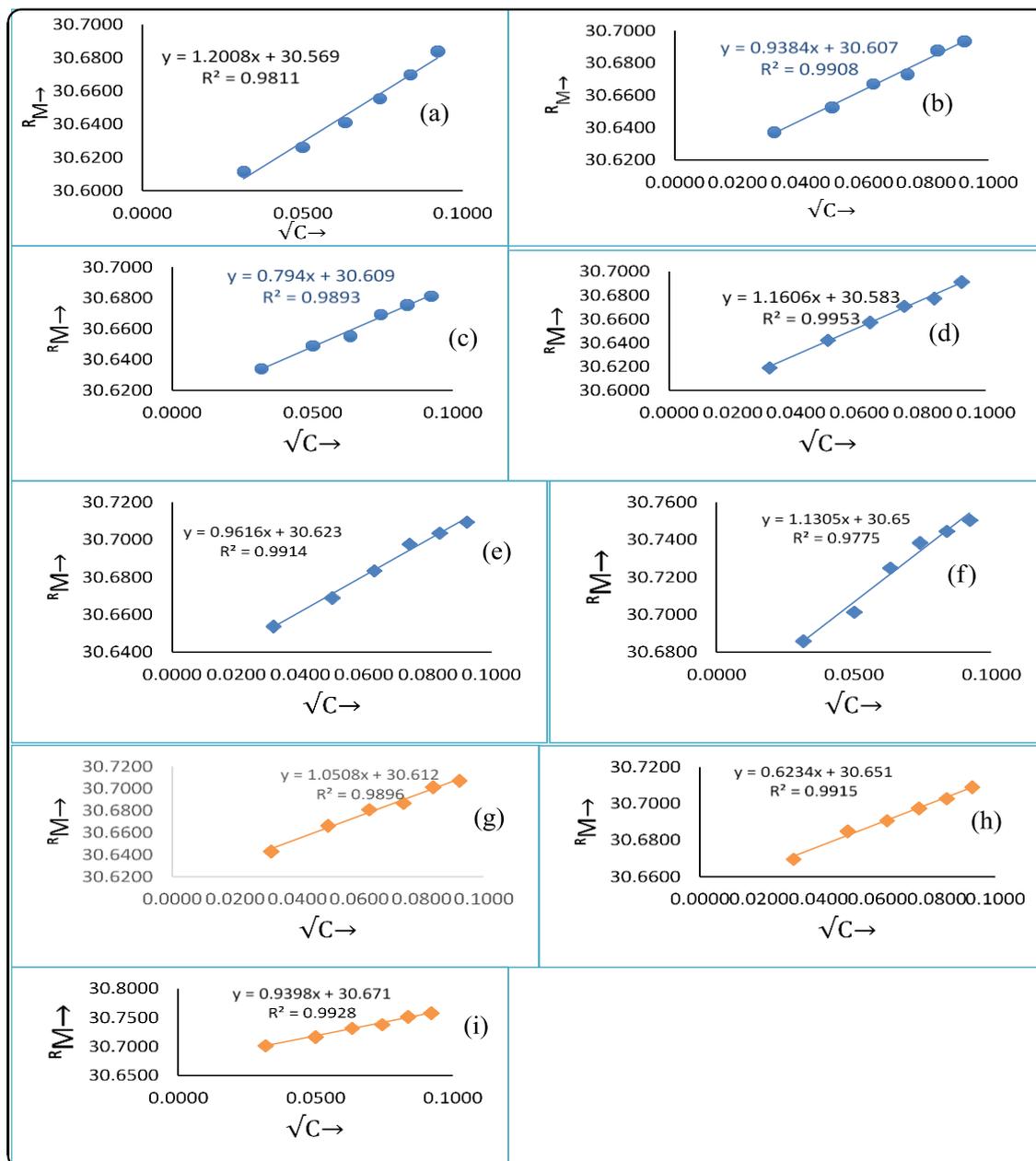


Figure S4. Variation of Molar refraction, R_M plot (a,b,c,d,e,f,g,h,i) of L-methionine against concentration, \sqrt{C} at different temperature in 0.001m, 0.003m, 0.005m aqueous solutions of IL (BTEAC)

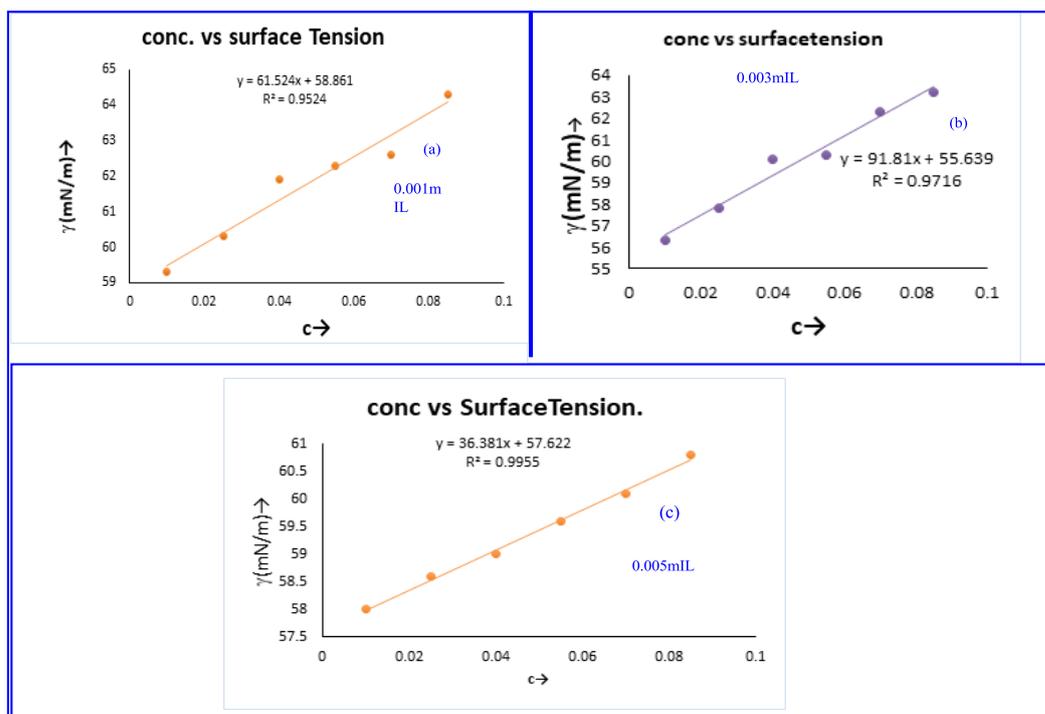


Figure S5. Variation of surface tension plot (γ) (a ,b , c) with different conc. of L-methionine at room temperature in 0.001m, 0.003m, 0.005m aqueous solutions of ionic liquid (BTMAC)

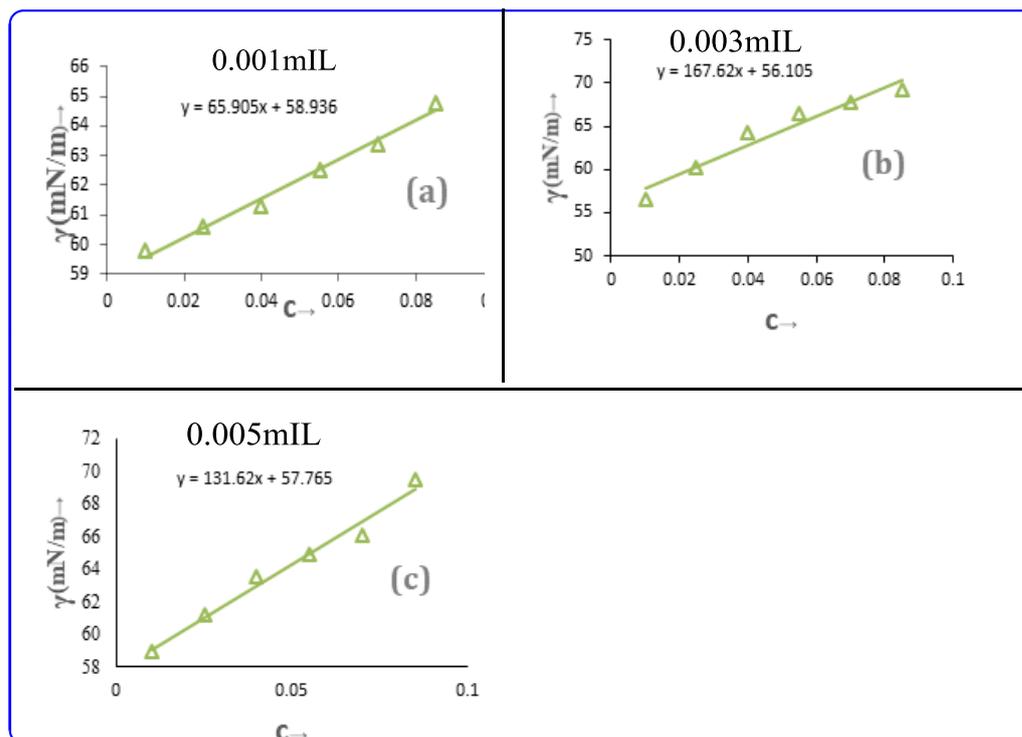
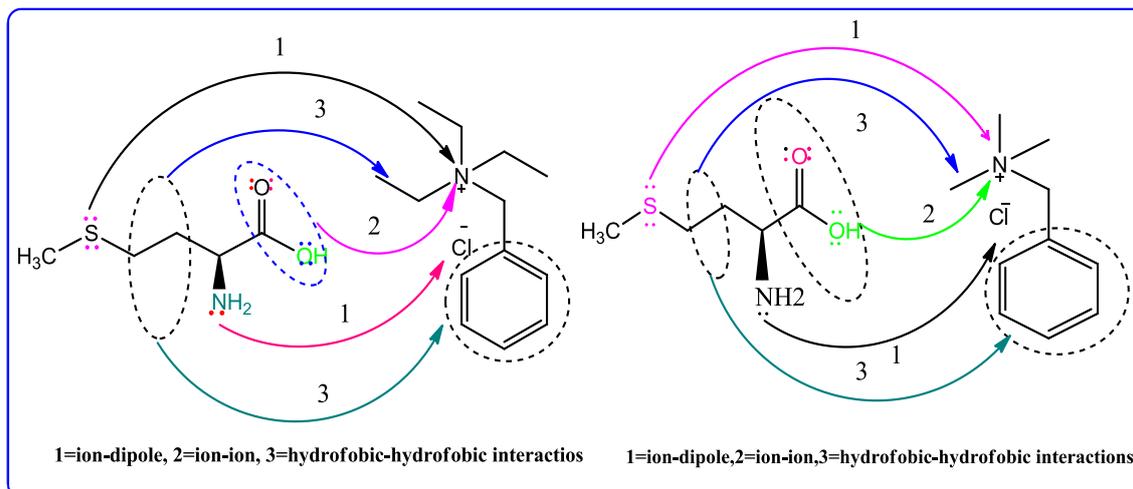


Figure S6. Variation of surface tension (γ) plot (a ,b , c) with different conc. of L-methionine at room temperature in 0.001m, 0.003m, 0.005m aqueous solutions of ionic Liquid(BTEAC)

Schemes

Scheme 1. Plausible molecular interactions between the ionic liquids, BTMAC and BTEAC with the amino acid, L-Methionine