CHAPTER-IX

SOLVATION BEHAVIOUR OF L-ASPARAGINE AND L-GLUTAMINE PREVAILING IN AQUEOUS IONIC LIQUID SOLUTION BY PHYSICOCHEMICAL AND COMPUTATIONAL INVESTIGATIONS

Abstract: Physicochemical properties (Density, viscosity, refractive index, conductivity and surface tension) of L-Asparagine and L-Glutamine in aqueous solution of an ionic liquid, benzyltributylammonium chloride, have been measured at 0.001m, 0.003m, 0.005m concentrations and at 298.15K, 303.15K and 308.15K temperatures.^{1}H-NMR Spectroscopy also applied to ascertain the molecular interaction in solute-solvent systems. There are some important physicochemical parameters that have been derived from the above physicochemical experiments namely as limiting apparent molar volume (φ_V^0) and viscosity *B*-coefficients using extended Masson equation and Jones-Dole equation respectively. The limiting molar refraction and molar refractive index (R_M) values obtained of the solutions by using the very popular equation(Lorentz-Lorenz equation).Specific Conductivity measurement of the experimental solution which applied to ascertain ionic nature of the system. Optimization energy calculation by the computational technique leads to the consequence of stability of ternary system (solute-solvent system) in molecular level.

Keywords: Solute-cosolute interactions, apparent molar volume, viscosity B-coefficient, molar refraction, conductivity, NMR spectroscopy, Computational study.

1. Introduction

Ionic liquids (ILs) are greener organic solvents that are large chemical window and liquids at or near room temperature in their pure form. They have been extensively used in a number of fields in both academia and industry and exhibit many useful advantages such as a low melting point (<373 K), are liquid over a wide temperature

range, and have suitable viscosity, thermal stability, and the ability to dissolve a diversity of chemicals, and most importantly, insignificant vapor pressure [1,2]. Ionic liquids have been proposed as green and benign replacements for traditional volatile organic solvents, and a rising number of applications in the fields of catalysis, chemical reactions, separations, electrochemistry, nanoscience and bioscience so far considered [3,4]. So the cationic ionic liquid Benzyltributylammonium chloride (BTBAC) having hydrophobic and hydrophilic part, attracted immense interest in the development of methods for separation, purification, extraction of DNA; and also been tested for gene delivery and gene transfection that involve in recent clinical trials based on gene therapy [5].

L-Glutamine is an amino acid commonly found as a component in total parenteral nutrition. L-Glutamine is the most plentiful free amino acid in the body. L-Glutamine is produced in the muscles and is distributed by the blood to the organs that need it. Glutamine might help intuitive function, the immune system, and other crucial processes in the body, especially in times of stress. L-asparaginase has been used extensively for the treatment of acute lymphoblastic leukemia on the supposition that the circulating L-asparagine is vital for leukemic cells which appear to lack the ability of creating L-asparagine. However, the use of L-asparaginase and L-glutamine involves several problems, such as hypersensitivity, antibody formation, rebound phenomenon due to the rapid induction of liver L-asparagine synthetase [6].

To overcome these biological problems, the enzyme was immobilized in solid drug carriers, such as microspheres and liposomes, giving a higher stability against denaturation and reduced immunogenicity. Also, it was reported that L-glutaminase used together with L-asparaginase reduced the rebound phenomenon. Here, we perform the physicochemical, computational and spectroscopic investigation of L-glutamine and L-aspargine with the cationic ionic liquid.

Measurements of density, viscosity and refractive index, conductivity, surface tension of aqueous IL solution with amino acids have not been made over significant temperature and concentration ranges. These measurements are important for elucidation of ion-solvent, ion-ion and solvent-solvent interactions in aqueous ternary (H_2O + IL+ amino acid) systems [6-9].

Therefore, in present study we have endeavoured to make ascertain nature of interaction of solute itself (amino acid) and with co-solute IL in w_1=0.001, 0.003 and

0.005 mass fraction of aqueous medium at different temperatures (298.15K, 303.15K and 313.15K) to explain various noncovalent interactions foremost in the ternary systems under investigation.

2. Experimental section

2.1 Source and purity of materials

Benzyltributylammonium chloride and L-Asparagine and L-Glutamine were purchased from Sigma-Aldrich, Germany. The mass fractions purity of these three chemicals were ≥0.98, ≥0.99 and ≥0.99 respectively. All the reagents were always stored in the desiccators over P_2O_5 to keep them in dry environment. These chemicals were then subsequently applied as received without further purification.

2.2 Apparatus and procedure

Aqueous (deionised, doubly distilled) solubility of the benzyltributylammonium chloride (IL) and L-Asparagine and L-Glutamine has been checked prior to start of the experimental work and perceived that all the reagent are freely soluble in all proportion of aqueous solution. The stock solution of 0.001m, 0.003m and 0.005m concertation of IL were prepared by mass (Mettler Toledo AG-285 with uncertainty 0.0003g) in doubly distilled water. L-Asparagine and L-Glutamine solutions were made by mass and then the working solutions (six sets) were prepared by mass dilution. The conversion of molarity into molality [10] has been done using experimental density values of respective solutions.

The densities (ρ) of the experimental solutions were measured by the vibrating u-tube Anton Paar digital density meter (DMA 4500M) having a precision of ±0.00005 $g.cm^{-3}$ with maintained at ±0.01 K of the anticipated temperature. Apparatus was calibrated by passing deionised, triply distilled water and then dry air [11].

The viscosities (η) of the studied solution were measured using a Brookfield DV-III Ultra Programmable Rheometer with fitted spindle size-42. The detail description of the instrument has already been described earlier [12].

Refractive indeces (n_D) were measured from the Digital Refractometer Mettler Toledo. The light source was LED, λ=589.3nm. The refractometer was calibrated twice using distilled water and then calibration was checked after every few measurements [13]. The uncertainty of refractive indices measurement was ±0.0002 units.

Specific conductivity of the solutions was measured through Systronics- 308 conductivity meter of working frequency 1 kHz with an accuracy of ±1%.The calibration of conductivity cell was done and determination of cell constant that proposed by the technique as suggested by Lind et al.[14]. The cell constant was carried out using freshly prepared 0.01 M aqueous KCl solution and it was maintained within the range 0.09–1.00 cm^{-1} during the experiment. All the solutions were placed in a dip-type immersion conductivity (CD-10) cell with a cell constant of about (0.1 ± 0.001) cm^{-1}. The cell was attached to a temperature-controlled water bath to sustain the investigational temperature.

K9 digital Tensiometer (KrussGmbH, Hamburg, Germany) instrument was used to determine the surface tension of different concentrations of mixed and pure experimental solutions. The accuracy of the instrument was ±0.1(mN/m). For the determination of surface tension(σ) the platinum ring detachment technique was used. The calibration of the K9 digital Tensiometer was carried out with doubly distilled water and the calibration value of surface tension(σ) was found to be 71.8 mN/m which is in good agreement with the literature values of surface tension 71.57 mN/m[15]. This tensiometer is a very good precision instrument that contains a solid and vibration-free base. This instrument puts on such a place that same demand on its neighbour as a laboratory balance with a resolution of 0.1 mg. In addition, a clean and dust-free atmosphere is needed for the measurements of surface tension. 1H NMR study, spectra were recorded at 600 MHz Bruker advance at T = 298.15 K in D2O for obtaining the 1H NMR spectra as well as chemical shifts for various protons.

3. Result and Discussion

The physical parameters of binary mixtures in different mass fractions (w_1=0.001, 0.003, 0.005) of aqueous ionic liquid(IL) solutions at three different temperatures (298.15K,303.15K,308.15K) and at 1.013 bar have been stated in table 1&2. The experimental measured values of density and viscosity of L-Asparagine and L-Glutamine as a function of concentration (molality), in different mass fractions of aqueous ionic liquid (IL) mixture at above mentioned temperatures have been given in **Table 3&4.**

3.1 Apparent molar volume

Calculation of apparent molar volume (φ_V) and the limiting apparent molar volume (φ_V^0) of solutions both were consider as a substantial tools for understanding of interactions taking place in tenary solution systems. Therefore, the apparent molar volumes (φ_V) determined from the solutions densities using the suitable equation [16] and the values are given in **Table 5&6.**

$$\varphi_V = M/\rho - (\rho - \rho_0)/m\rho\rho_0 \qquad (1)$$

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

The limiting apparent molar volumes (Φ_v^0), i.e. apparent molar volume at infinite dilution were determined using a least-squares fitting linear method as the plots of Φ_v versus square root of the molar concentration, √m using the Masson equation as follows [17] to analyse the different interactions taking place in the solutions:

$$\Phi_v = \Phi_v^0 + S_v^* \sqrt{m} \qquad (2)$$

φ_V^0 denotes as the apparent molar volume at infinite dilution, S_V^* is signify as the experimental slope. At infinite dilution solute molecule is enclosed only by the solvent molecules and remains infinite distant from each other. Consequently, that φ_V^0 is unaffected by itself interaction of L-Asparagine and L-Glutamine molecules and it is a measure only of the solute-cosolute interaction. limiting molar volume, values represented in **Table 7(a)&7(b)**

An inspection of **Table 7(a)&7(b)** shows that φ_V^0 are large and positive for L-Glutamine compared to L-Asparagine at all the studied temperatures, suggesting the occurrence of strong solute-cosolute interaction in L-Glutamine than that of L-Asparagine **(scheme 1).** Comparing φ_V^0 with S_V^* values show that the magnitude of φ_V^0 is greater than S_V^*, suggesting that solute-cosolute interactions predominates over itself

interaction of solute molecules in all solutions at all studied temperatures. Moreover, S_V^* values are negative at all studied temperatures indicates force of itself interaction of L-Asparagine and L-Glutamine molecules is very poor.

Dependency of temperature of the limiting apparent molar volume (Φ_v^0) , the temperature range 298.15K to 308.15K and the results obtained were found to follow the following polynomial equation:**[18]**

$$\Phi_v^0 = a_0 + a_1T + a_2T^2 \quad (3)$$

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 8** shows the empirical coefficient values (a_0, a_1 and a_2) of L-Asparagine and L-Glutamine in different concentration of the ILs BTBAC 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 9(a)** and **Table9 (b)** for L-Asparagine and L-Glutamine in BTBAC solution respectively at pressure 1.013bar.

$$\Phi_E^0 = (\delta\Phi_v^0/\delta T)_P = a_1 + 2a_2T \quad (4)$$

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 signify 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.[**19**]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:**[20]**

$$(\delta\Phi_E^0/\delta T)_P = (\delta^2\Phi_v^0/\delta T^2)_P = 2a_2 \quad (5)$$

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 **Table9(a)**and **Table 9(b)** respectively for L-Asparagine and L-Glutamine in BTBAC solution at different temperatures confirms the mode of solute–solvent interaction is structure-breaking and the structure-breaking effect is strongest in 0.001m aqueous BTEAC solution with highest packing or caging effect.

3.2 Viscosity

In aqueous electrolytic solutions the extent of ionic hydration and structural interactions**[21-23]** within the ionic hydration co-spheres **[24]**can be explored easily by

studying viscosity coefficient with varying concentration and temperature of the aqueous solution. The results in **Table 3** and **Table 4** 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(BTBAC), 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:[**25]**

$$\eta_r = \eta / \eta^0 = 1 + A\sqrt{c} + Bc \qquad (6)$$

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 BTBAC.

Rearrangement of the above Equation (7) gives following:

$$(\eta_r - 1) / \sqrt{c} = A + B\sqrt{c} \qquad (7)$$

Here, viscosity A-coefficient is a constant, also known as Falken hagen coefficient,**[26]** 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 7(a)** and **Table7 (b)** for L-Glutamine and L-Asparagine solutions in BTBAC at (298.15, 303.15 and 308.15)K and pressure at 1.013bar, respectively. **Figure 1** shows the variation of B values of L-Glutamine and L-Asparagine in aqueous solution of BTBAC respectively, against 0.001m IL, 0.003m IL and 0.005m IL solutions at different temperatures .

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.[**27]**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 8(a)** and **Table8 (b),** 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-coeffiecient 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.**[24]**

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-Glutamine and L-Asparagine in aqueous BTBAC 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 measureof 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.[**28-30]** Viscosity B-coefficients of L-Arginie and L-Glutamine solutions along with dB/dT values in different concentrations of the IL, BTBAC at (298.15, 303.15 and 308.15) K and pressure at 1.013bar are given in **Table 10(a)** and **Table 10(b)**, 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-Glutamine and L-Asparagine both behave as structure-breaker in the aqueous ionic liquid solutions BTBAC.

According to Eyring and co-workers [31], that the $\Delta\mu_1^{0\neq}$, *the free energy of activation per mole of the solvent of viscous flow can be get from the given following equation*

$$\eta_O = \frac{hN}{V_1^0} exp\ (\frac{\Delta\mu_1^{0\#}}{RT}) \qquad (8)$$

Where h denotes as Planck constant, N_A indicates Avogadro's number and V_1^0 signify as the solvent's partial molar volume. The above equation reframe to get in the following form

$$\Delta\mu_1^{0\neq} = RT \ln (\eta_0 V_1^0 / hN_A) \quad (9)$$

Applying two Equations. (7) As well as (9) [32, 33] then the following equation can be attained

$$B = (V_1^0 - V_2^0) / 1000 + V_1^0 (\Delta\mu_1^{0\#} - \Delta\mu_2^{0\neq}) / 1000\, RT \quad (10)$$

Where V_2^0 express as a limiting partial molar volume (Φ_v^0) of the solute present in the solution mixture, at infinite dilution ,$\Delta\mu_2^{0\neq}$ denotes ionic activation energy per mole of solute. Using the above equation (10) the following equation can be get

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

According to transition state theory, solvent molecules also passes to the transition state by the viscous flow. The $\Delta\mu_2^{0\neq}$*is the contribution of free energy transfer of ionic liquid from ground state to transition state. It was found from the* **Table11** that the $\Delta\mu_2^{0\neq}$ values are all positive and much higher than that of $\Delta\mu_1^{0\neq}$ representing in the ground state, which indicates that the interaction between the two amino acid and the aqueous BTBAC mixture is stronger in the ground state than that in the transition state. The solute and solvent molecules are held together strongly in the ground state than that of in the transition state thereafter in the transition state distortion and breaking of intermolecular bond take place frequently (34). Moreover *the value of* $\Delta\mu_1^{0\neq}$ increase with increasing the molality of the ionic liquid in the presence of amino acid which signify that with increasing the molality of ionic liquid in the ground state become more structured. To determination of entropy for activation, $\Delta S_2^{0\neq}$ [34] in the experimental mixture of solutions, the following equation has been used

$$d(\Delta\mu_2^{0\#}) /dt = - \Delta S_2^{0\neq} \quad (12)$$

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

Enthalpy of activation ($\Delta H_2^{0\neq}$) has been calculated from the following relation (34)

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\,\Delta S_2^{0\neq} \quad (13)$$

The value of $\Delta H_2^{0\neq}$, $\Delta S_2^{0\neq}$ *which show in the table the value of* $\Delta\mu_2^{0\neq}$ *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 Eakins et al. [32], for positive viscosity B-coefficient $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0}$ 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 [32,33]. For positive values of $\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ suggest that the formation of transition state is associated with bond breaking and rising accordingly. However, any specific mechanism in this context is quite difficult to develop though the disordered state of the slip-plane may be proposed [34]. Finally, according to Feakins et al. model, as $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$ the both the amino acid (l-Asparagine &l-glutamine) performs as structure breakers that again supports the *dB/dT* characteristics in an aqueous BTBAC mixture.

The ratio of (B/Φ_v^0) which has a high value [35] indicates that the primary solvation shell is formed.

According to a **Table 12,** *B*-coefficients for both the amino acids increase with temperature (positive *dB/dT*) and also the high value of the ratio (B/Φ_v^0) signifying the construction of a primary solvation shell as structure-disruptor.

The ratio of (B/Φ_v^0) which has a high value [35] indicates that the primary solvation shell is formed. according to a **Table 12**, ratio (B/Φ_v^0) for both the amino acids(L-Asparagine and L-Glutamine) increase with increasing temperature and also the high value of the ratio (B/Φ_v^0) suggesting the construction of a primary solvation shell as structure-disruptor.

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 acids (L-Glutamine and L-Asparagine) solutions in ionic liquid(IL) are provided in **Table 13(a) , Table 13(b) .**

The molar refraction R_M can be evaluated from the Lorentz–Lorenz relation:[**36]**

$$R_M = \{(n_D^2 - 1) / (n_D^2 + 2)\}(M/\rho) \qquad (14)$$

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.[**37]** 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.[**38]** 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 13(a) , Table 13(b)** decrease but the molar refraction (R_M) **Table 3** and **Table 4** 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-Glutamine in BTBAC have higher values than that of L-Asparagine in BTBAC 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 7** (a)and **Table 7(b)** can be calculated using the following equation:

$$R_M = R_M^0 + R_S\sqrt{m} \qquad (15)$$

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^0as shown in **Figure 2** and **Figure 3** with rise in mass fraction of co-solvent and temperature also signifies that solute–solvent interaction predominant over solute-solute interactions

3.4 Conductivity Study

The conductivity study of the L-Asparagine and L-Glutamine a for the interaction (solute – cosolute) in the aqueous solution of IL has been done at three different temperatures. Transport phenomena, molecular and ionic interaction in the ternary system gives some valuable information [39]. The specific conductivities (k) of aqueous IL solution has been monitored with increasing the concentration of L-Asp andL-Glu acid at three different temperatures and Tabulated in Table 14. Consequently, it has been observed that molal conductivity(Λ) values increases with increase in temperatures and gradual addition of L-Asp and L-Glu acid to the IL solution causes a continuous decrease in molal conductivity of the solution. The mobility of the ionic species in solution playing

the important role, in spite of growing number of ionic species with added L-ascorbic acid solution, as a result the molal conductivity decreases [39,40]. It may be due to the growing of solute-solvent interaction governed by the dipole-dipole, ion-dipole and hydrophobic – hydrophobic interaction in solution mixtures between the solute and solvent molecules.

3.5 Surface Tension

Surface tension (γ) measurement gives notable indication about solute-solvent interaction in the ternary systems. Solute amino acids molecules have surface active property as described in earlier literature [41]. Studied solvent systems contain IL with positively charged hydrophilic head group and a hydrophobic tail group acts as prominent surface-active agents. Thus, this study has attracted immense interest in the strengthening of Surface phenomena. value of surface tension of L-Asparagine and L-Glutamine is tabulated in Table 15.

The surface tension values vary linearly with an increase concentration of amino acids. The linear raising surface tension data demonstrates that with increase in concentrations amino acid molecules interact with the IL and moves from surface to the bulk of the solutions. This definitely due to the solute-solvent interaction which subsequently lower the surface activity of the amino acids and IL in this solution system.

3.6 NMR Study

The 1H NMR spectroscopy [42] is used to elucidate the changes in the electronic location of various protons of amino acids in the presence of IL. The chemical shift of all detectable protons of IL and amino acids in D2O are shown in Fig. 4 (Pic. 1,2,3). The chemical shift of various protons of L-Aspargine+IL and L-Glutamine+IL in D2O are also shown in Fig. 5 (Pic. 4 and Pic. 5). The nature of moieties present in the vicinity of protons affects their chemical change (δ) values. The change in chemical shifts (δ)values of amino acid in presence of IL are shown in Fig. 5. The deshielding and shielding effects of the surrounding groups are known to cause downfield (higher frequency) or upfield (lower frequency) shifts in δ values. The downfield chemical shifts of aromatic protons and upfield shifts of most of the aliphatic protons of amino acids are observed in presence of both amino acids. The various types of protons of both the amino acids show upfield shifts in 1H NMR in presence of BTBAC. An upfield shift is revealing an increase in electron density around the amino acids due to hydrophobic-hydrophobic interaction between amino acids and BTBAC[43,44–46]. The pi-electron cloud of the quinoline group of BTBAC interacts with the protons of amino acids, increasing the electron density around the protons of amino acids (shielding effect). However the upfield shift is maximum in the case

of l-glutamine+BTBAC is maximum compared to l-aspargine+BTBAC indicates greater interaction in L-glutamine+ BTBAC system.

3.7 Computational Study

Gaussian 09 Quantum Chemical calculation: Theoretical basis of the interaction

Theoretically, this is very interest field. There is no obey the exact sequence of the structure of molecules. The basic idea is to evaluate the empirical formula that repeats the physical forces and chemical contacts. Using the method of UB3LYP for numerical calculation, diffused basis function has been used to evaluate the weak molecular interaction associate with atoms in molecule. For this purpose, we apply the 6-31G (d) as a basis set for an accurate explanation of weak molecular interactions which represented by the transition states of the structure.

The Quantum chemical calculation reveals that the O$\cdots N \cdots O$, C$= O \cdots H - O, H \cdots O - H$, weak H-bond interactions in L-Glu/L-Asp cluster surrounded by the solvent sphere in aqueous IL (47) . There is formation of weak H-bond interaction, cohesive force of interaction.(47,48). Under proper conditions the hydrogen atom is attracted strong force between two atoms rather than one atom. The aforementioned statement was good thought out in our present work. We have depicted the L-Glu$\cdots ILs$ and $L - Asp \cdots ILs$ Complex of cluster through quantum chemical contrivance. So hereby, we compared the calculated values with experimental values in order to verify the correct sequence of interactions associated with atoms in molecule theoretically.

Several approximate properties of different systems of aqueous L-Glu-IL and L-Asp-IL Cluster are summarized in the table 16. The extent of stabilization energy (E) that can be obtained from the values of optimization energy of pure as well as mixed of molecular assembly. optimization energy signifies the solute-solvent interaction. The higher the value of solute – solvent interaction, lower is the optimization energy. It was observed that the stabilization is more prominent in case of (BTBAC+L-GLU+H2O) System among all the systems which also signify that the geometry gets optimum in case of (BTBAC+L-GLU+H2O) system. The weak non covalent bond between IL with L-Glu and IL with L-ASP can be explained from the idea of solution thermodynamic.

4. Conclusion

In the overview of this study, that there is a strong interaction between L-glutamine and BTBAC and it becomes stronger with rise in temperature and increase in mass fraction of BTBAC. All of these above physicochemical and spectroscopic along

with computational works confirms the amino acids and IL (BTBAC) have engaged each other, solute-cosolute interaction is much greater than the solute-solute and solvent-solvent interactions in the ternary system.

Acknowledgement

The authors are thankful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (no. 540/6/DRS/2007, SAP-1), India for financial support and instrumental facilities in order to continue this research work.

One of the authors, Prof. M. N. Roy, is thankful to University Grant Commission, New Delhi, Government of India for being awarded onetime grant under Basic Scientific Research via the grant-in-Aid no. F.4-10/2010 (BSR) regarding his active service for augmenting of research facilities to facilitate further research work.

Table 1. Experimental values of density (ρ), viscosity (η) and molar refraction (R_M) of different molality (m) of aqueous IL (BTBAC) solution at 298.15K, 303.15K and 308.15K

Conc. of Aq. IL (BTBAC) m /mol.kg^{-1}	ρ×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
0.001	0.99709	0.99574	0.99410	0.913	0.876	0.839	26.8978	26.8908	26.8764
0.003	0.99715	0.99580	0.99415	0.921	0.880	0.846	26.9125	26.9055	26.8985
0.005	0.99719	0.99589	0.99419	0.930	0.893	0.853	26.9272	26.9202	26.9058

Table 2. Experimental values of refractive index (n_D) and specific conductance (κ) of different molality (m) of aqueous IL (BTBAC) solution at 298.15 K, 303.15 K and 308.15 K

Conc. of Aq. IL (BTAC) 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	1.3320	1.3319	1.3317	0.105	0.171	0.235
0.003	1.3322	1.3321	1.3320	0.203	0.243	0.288
0.005	1.3324	1.3323	1.3321	0.255	0.327	0.349

Table 3. Density (ρ), viscosity (η) and molar refraction (R_M) of L-Asparagine in aqueous (BTBAC) ionic liquid solutions at 298.15K, 303.15K and 308.15K

Conc. of L-Asparagine soln.in molality, m(mol.kg^{-1})	ρ×10^{-3} (kg.m^{-3})			η(mPa.s)			R_M		
	298.15K	303.15K	308.15K	293.15K	303.15K	308.15K	293.15K	303.15K	308.15K
0.001m IL									
0.010	0.99761	0.99624	0.99459	0.919	0.882	0.845	27.1822	27.2121	27.2424
0.025	0.99843	0.99702	0.99535	0.925	0.888	0.851	27.1747	27.1983	27.2364
0.040	0.99926	0.99782	0.99615	0.931	0.894	0.857	27.1670	27.1913	27.2295
0.055	1.00008	0.99862	0.99697	0.936	0.899	0.863	27.1595	27.1844	27.2219
0.070	1.00089	0.99945	0.99782	0.941	0.905	0.869	27.1523	27.1766	27.2136
0.085	1.00177	1.00029	0.99868	0.946	0.910	0.875	27.1507	27.1760	27.2124
0.003m IL									
0.010	0.99767	0.99629	0.99462	0.926	0.885	0.851	27.1954	27.2256	27.2564
0.025	0.99848	0.99705	0.99538	0.932	0.892	0.858	27.1882	27.2123	27.2431
0.040	0.99931	0.99785	0.99615	0.938	0.898	0.864	27.1804	27.2053	27.2369
0.055	1.00018	0.99869	0.99695	0.943	0.904	0.870	27.1716	27.1973	27.2299
0.070	1.00105	0.99952	0.99784	0.948	0.909	0.877	27.1628	27.1895	27.2279
0.085	1.00196	1.00038	0.99872	0.954	0.915	0.883	27.1603	27.1884	27.2187
0.005m IL									
0.010	0.99773	0.99638	0.99464	0.935	0.897	0.856	27.2086	27.2380	27.2633
0.025	0.99855	0.99711	0.99544	0.941	0.903	0.862	27.1937	27.2253	27.2489
0.040	0.99942	0.99792	0.99627	0.947	0.909	0.868	27.1848	27.2183	27.2411
0.055	1.00032	0.99874	0.99712	0.952	0.915	0.874	27.1752	27.2108	27.2327
0.070	1.00126	0.99962	0.99797	0.958	0.921	0.880	27.1645	27.2016	27.2243
0.085	1.00223	1.00059	0.99892	0.964	0.927	0.887	27.1604	27.1975	27.2207

Table 4. Density (ρ), viscosity (η) and molar refraction (R_M) of L-Glutamine in aqueous (BTBAC) ionic liquid solutions at 298.15K, 303.15K and 308.15K

Conc. of L-Glutamine soln.in molality (mol.kg^{-1})	ρ×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									
0.010	0.99764	0.99628	0.99462	0.921	0.884	0.849	30.0657	30.0903	30.1240
0.025	0.99849	0.99709	0.99542	0.930	0.893	0.858	30.0483	30.0741	30.1081
0.040	0.99938	0.99795	0.99627	0.939	0.902	0.867	30.0.80	30.0646	30.0988
0.055	1.00027	0.99882	0.99710	0.948	0.912	0.877	30.0276	30.0548	30.0902
0.070	1.00117	0.99973	0.99747	0.956	0.921	0.887	30.0252	30.0439	30.0804
0.085	1.00210	1.00064	0.99890	0.965	0.929	0.897	30.0137	30.0411	30.0770
0.003m IL									
0.010	0.99771	0.99632	0.99466	0.929	0.888	0.853	30.0718	30.0973	30.1311
0.025	0.99853	0.99712	0.99544	0.938	0.896	0.863	30.0636	30.0814	30.1157
0.040	0.99942	0.99800	0.99630	0.947	0.906	0.872	30.0532	30.0713	30.1062
0.055	1.00031	0.99886	0.99716	0.957	0.917	0.882	30.0428	30.0610	30.0966
0.070	1.00125	0.99975	0.99810	0.967	0.926	0.894	30.0310	30.0515	30.0929
0.085	1.00219	1.00067	0.99900	0.977	0.936	0.904	30.0273	30.0402	30.0822
0.005m IL									
0.010	0.99776	0.99640	0.99469	0.939	0.899	0.859	30.0868	30.1196	30.1519
0.025	0.99859	0.99718	0.99550	0.949	0.909	0.869	30.0700	30.1043	30.1386
0.040	0.99950	0.99805	0.99640	0.960	0.919	0.880	30.0590	30.0944	30.1278
0.055	1.00042	0.99895	0.99730	0.970	0.929	0.891	30.0477	30.0837	30.1171
0.070	1.00136	0.99989	0.99832	0.980	0.939	0.901	30.0359	30.0718	30.1027
0.085	1.00233	1.00083	0.99932	0.990	0.950	0.912	30.0313	30.0600	30.0972

Table 5. Apparent molar volume, (Φv) and $(\eta/\eta^0 - 1)/\sqrt{m}$ of L-Asparagine solution in 0.001m, 0.003m and 0.005m aqueous BTBAC solution at different temperatures (293.15K, 303.15K, 313.15K)

Conc. of L-Asparagine soln. in molality, m ($mol.kg^{-1}$)	Φv x 10^6 ($m^3.mol^{-1}$)	$(\eta/\eta^0-1)/\sqrt{m}$ ($kg^{1/2}.mol^{-1/2}$)	Φv x 10^6 ($m^3.mol^{-1}$)	$(\eta/\eta^0-1)/\sqrt{m}$ ($kg^{1/2}.mol^{-1/2}$)	Φv x 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**	
0.010	80.3507	0.066	82.4660	0.068	83.6242	0.071
0.025	79.0427	0.083	81.3108	0.086	82.6060	0.090
0.040	78.1942	0.098	80.3972	0.102	81.3261	0.107
0.055	77.6333	0.107	79.6422	0.111	80.4199	0.121
0.070	77.0868	0.115	78.9367	0.125	79.4539	0.134
0.085	76.4591	0.123	78.3389	0.132	78.7080	0.146
0.003m IL	**298.15K**		**303.15K**		**308.15K**	
0.010	80.3664	0.054	83.4287	0.057	85.7070	0.059
0.025	79.3540	0.075	82.3121	0.086	83.7198	0.089
0.040	78.3173	0.092	81.1301	0.102	82.5750	0.106
0.055	77.2556	0.101	80.0741	0.116	81.6867	0.120
0.070	76.6260	0.110	78.8129	0.124	79.8701	0.138
0.085	75.7461	0.122	77.9808	0.136	78.8096	0.149
0.005m IL	**298.15K**		**303.15K**		**308.15K**	
0.010	81.4171	0.054	84.9350	0.045	87.3824	0.035
0.025	79.0989	0.075	83.3595	0.070	83.7313	0.066
0.040	77.3132	0.091	81.7413	0.089	81.2187	0.088
0.055	75.9830	0.101	80.1890	0.105	79.7130	0.104
0.070	74.9495	0.113	78.6443	0.118	78.5982	0.119
0.085	73.5310	0.125	77.1799	0.130	76.9479	0.136

Table 6. Apparent molar volume, (Φv) and $(\eta/\eta^0 - 1)/\sqrt{m}$ of L-Glutamine solution in 0.001m, 0.003m and 0.005m in aqueous (BTBAC) solution at different temperatures (298.15K, 303.15K, 308.15K)

Conc. of L-Glutamine soln.in molality ($mol.kg^{-1}$)	Φv x 10^6 ($m^3.mol^{-1}$)	$(\eta/\eta^0-1)/\sqrt{m}$ ($kg^{1/2}.mol^{-1/2}$)	Φv x 10^6 ($m^3.mol^{-1}$)	$(\eta/\eta^0-1)/\sqrt{m}$ ($kg^{1/2}.mol^{-1/2}$)	Φv x 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**	
0.010	91.4027	0.087	93.5098	0.091	95.5544	0.095
0.025	90.1126	0.117	92.1772	0.122	93.4547	0.127
0.040	89.1234	0.142	91.1660	0.148	92.2328	0.154
0.055	88.1717	0.163	90.0066	0.174	51.5363	0.182
0.070	87.5817	0.177	88.9201	0.193	90.7103	0.205
0.085	86.8444	0.194	88.1899	0.206	89.4326	0.227
0.003m IL	**298.15K**		**303.15K**		**308.15K**	
0.010	92.1687	0.087	95.6445	0.091	97.1596	0.082
0.025	90.9159	0.116	93.3863	0.115	94.6480	0.127
0.040	89.6275	0.141	91.4421	0.147	92.5627	0.153
0.055	88.5420	0.166	90.3720	0.178	91.3301	0.180
0.070	87.2921	0.188	89.4958	0.197	89.5495	0.213

0.085	86.4870	0.207	88.5449	0.217	88.8343	0.234
0.005m IL	**298.15K**		**303.15K**		**308.15K**	
0.010	93.4499	0.086	96.4599	0.67	97.5276	0.070
0.025	91.3160	0.112	94.5938	0.113	93.8561	0.118
0.040	89.3859	0.155	92.4161	0.145	90.7921	0.157
0.055	87.8234	0.178	90.3689	0.171	89.1130	0.189
0.070	86.7143	0.198	88.7711	0.194	86.9413	0.211
0.085	85.6552	0.216	87.7097	0.218	85.4925	0.236

Table 7(a). Limiting apparent molar volumes (Φv^0), Limiting molar refraction (R_M^0), experimental slopes (S_V^*), viscosity A, B-coefficients of L-Asparagine solution in IL at different temperatures

Temp. (K)	**Φv^0 x 10^6 (m^3. mol^{-1})**	**R_M^0**	**Sv* x 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	82.266	27.201	-19.864	0.3006	0.0360
303.15	84.704	27.230	-21.702	0.3353	0.0341
308.15	86.486	27.261	-26.111	0.3917	0.0297
0.003m IL					
298.15	83.005	27.217	-24.226	0.3459	0.0204
303.15	86.676	27.245	-29.026	0.3996	0.0198
308.15	89.406	27.274	-35.091	0.4618	0.0136
0.005m IL					
298.15	85.445	27.235	-40.163	0.3639	0.0170
303.15	89.546	27.260	-40.881	0.4450	-0.0004
308.15	92.373	27.285	-52.938	0.5133	-0.0160

Table 7(b). Limiting apparent molar volumes (Φv^0), Limiting molar refraction (R_M^0), experimental slopes (S_V^*), viscosity A, B-coefficients of L-Glutamine solution in IL at different temperatures

Temperature(K)	**Φv^0 x 10^6 (m^3. mol^{-1})**	**R_M^0**	**Sv* x 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	93.841	30.091	-23.854	0.5548	0.0309
303.15	96.586	30.117	-28.424	0.6141	0.0276
308.15	98.482	30.148	-30.362	0.6888	0.0208
0.003m IL					
298.15	95.554	30.100	-30.603	0.6312	0.0190
303.15	99.263	30.128	-37.330	0.6787	0.0155
308.15	101.68	30.158	-44.776	0.7816	0.0013
0.005m IL					
298.15	97.733	30.117	-41.624	0.6839	0.0163
303.15	101.73	30.152	-48.014	0.7720	-0.0102
308.15	103.85	30.187	-63.495	0.8655	-0.0174

Table 8. The empirical coefficient values (a_0, a_1 and a_2) of L-Asparagine solution & L-Glutamine solution in different concentration of the IL (0.001, 0.003m, 0.005m) at 298.15K, 303.15K and 308.15K

Conc. of aq. IL soln. 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-Asparagine solution			L-Glutamine solution		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
0.001	-1249	8.3767	-0.0131	-1660.6	10.759	-0.0170
0.003	-1836.9	12.051	-0.0188	-2461.1	16.279	-0.0258
0.005	-2462.1	16.141	-0.0255	-3533.6	23.372	-0.0375

Table 9(a). Values of limiting molar expansibilities (Φ_E^0) for L-Asparagine solution in IL(BTBAC) at different temperatures

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	0.56517	0.43417	0.30317	-0.0262
0.003	0.84056	0.65266	0.46456	-0.0376
0.005	0.93535	0.68035	0.42535	-0.0510

Table 9(b). Values of limiting molar expansibilities (Φ_E^0) for L-Glutamine solution in IL(BTBAC) at different temperatures

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	0.6219	0.4519	0.2819	-0.0340
0.003	0.89446	0.63646	0.37846	-0.0516
0.005	1.01075	0.63575	0.26075	-0.0750

Table 10(a). Viscosity B-coefficients of L-Asparagine solution along with dB/dT values in different concentrations of IL at (298.15, 303.15 and 308.15) K

Temperature (K)	0.001m IL		0.003m IL		0.005m IL		dB/dT
	B		B		B		
298.15	0.30006		0.3459		0.3639		0.0091
303.15	0.3353		0.3996		0.4450		0.0116
308.15	0.3917		0.4618		0.5131		0.0149

Table 10(b). Viscosity B-coefficients of L-Glutamine solution along with dB/dT values in different concentrations of IL at (298.15, 303.15 and 308.15) K

Temperature (K)	0.001m IL		0.003m IL		0.005m IL		
	B		B		B		dB/dT
298.15	0.5548		0.6312		0.6839		0.0134
303.15	0.6141		0.6787		0.7720		0.0150
308.15	0.6888		0.7816		0.8655		0.0182

Table 11. Values of $(\bar{V}_1^0 - \bar{V}_2^0)$, $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $T\Delta S_2^{0\neq}$, $\Delta H_2^{0\neq}$ for L-Asparagine and L-glutamine in different molality (0.001,0.003,0.005) of aqueous solution of IL(BTBAC) mixture at different temperatures and atmospheric pressure 0.1MPa

parameters	0.001			0.003			0.005		
	T=298.15K	303.15K	308.15K	T=298.15K	303.15K	308.15 K	298.15K	303.15K	308.15K
L-Asparagine									
$(\bar{V}_1^0 - \bar{V}_2^0)$ /m³.mol⁻¹	-64.26	-66.70	-68.48	-64.99	-68.67	-71.40	-67.43	-71.53	-74.36
$\Delta\mu_1^{0\neq}$/KJ.mol⁻¹	9.21	9.32	9.30	9.23	9.33	9.33	9.26	9.38	9.35
$\Delta\mu_2^{0\neq}$/KJ.mol⁻¹	59.46	65.98	74.79	65.80	75.31	85.19	68.92	82.44	93.26
$T\Delta S_2^{0\neq}$/KJ.mol⁻¹	297.76	302.75	307.74	578.14	587.83	597.53	725.33	737.50	749.67
$\Delta H_2^{0\neq}$/KJ.mol⁻¹	357.21	368.73	382.53	643.98	663.14	682.72	749.26	819.94	842.92
L-Glutamine									
$(\bar{V}_1^0 - \bar{V}_2^0)$ /m³.mol⁻¹	-75.83	-78.58	-80.48	-77.54	-81.26	-83.67	-79.72	-83.71	-91.71
$\Delta\mu_1^{0\neq}$/KJ.mol⁻¹	9.21	9.32	9.30	9.21	9.32	9.30	9.21	9.32	9.31
$\Delta\mu_2^{0\neq}$/KJ.mol⁻¹	96.05	106.94	118.79	106.78	116.40	132.41	114.31	129.86	144.62
$T\Delta S_2^{0\neq}$/KJ.mol⁻¹	677.69	689.05	700.49	871.08	893.52	922.36	903.93	919.09	934.24
$\Delta H_2^{0\neq}$/KJ.mol⁻¹	773.74	795.99	819.28	764.30	777.12	789.94	1018.24	1048.95	1078.88

#Combined standard uncertainty in molality according to stated purity u(m) = ±0.0001 mol kg^{-1} . *Standard uncertainty in temperature u(T) = ± 0.01 K. *Standard uncertainty in pressure u(P)=± 0.01 MPa

Table 12. Values of (B/Φ_v^0) for L-Asparagine and L-Glutamine in different molality of aqueous TBMS (IL) solutions at different temperature and atmospheric pressure 0.1MPa

Temperature(K)	B / Φ_v^0			B / Φ_v^0		
	0.001mol.Kg^{-1}	0.003mol.Kg^{-1}	0.005mol.Kg^{-1}	0.001mol.Kg^{-1}	0.003mol.Kg^{-1}	0.005mol.Kg^{-1}
	L-ASPARAGINE+ Aq. TBMS			L-GLUTAMINE +Aq. TBMS		
298.15	3.654	4.167	4.258	5.912	6.605	6.997
303.15	3.958	4.612	4.969	6.358	6.837	7.588
308.15	4.529	5.165	5.556	6.994	7.686	8.334

#Standard uncertainty in molality u (m) = ±0.0001mol kg^{-1}. *Standard uncertainty in temperature u (T) = ± 0.01 K. *Standard uncertainty in pressure u (P)= ± 0.01MPa

Table-13(a). Refractive index (n_D) and specific conductance (κ) of L-Asparagine in aqueous IL (BTBAC) solution at 293.15K, 303.15K and 313.15K

Conc. of L-Asparagine soln. in molality, m (mol.kg^{-1})	n_D 293.15K	303.15K	313.15K	κ (mS/cm) 293.15K	303.15K	313.15K
0.001m IL						
0.010	1.3322	1.3321	1.3319	0.482	0.503	0.520
0.025	1.3324	1.3322	1.3321	0.574	0.590	0.615
0.040	1.3326	1.3324	1.3323	0.653	0.683	0.709
0.055	1.3328	1.3326	1.3325	0.749	0.776	0.796
0.070	1.3330	1.3328	1.3327	0.826	0.859	0.888
0.085	1.3333	1.3331	1.3330	0.920	0.943	0.983
0.003m IL						
0.010	1.3324	1.3323	1.3321	0.545	0.572	0.607
0.025	1.3326	1.3324	1.3322	0.634	0.663	0.714
0.040	1.3328	1.3326	1.3324	0.720	0.765	0.809
0.055	1.3330	1.3328	1.3326	0.812	0.854	0.913
0.070	1.3332	1.3330	1.3329	0.903	0.935	0.999
0.085	1.3335	1.3333	1.3331	0.997	1.052	1.080
0.005m IL						
0.010	1.3326	1.3325	1.3322	0.660	0.748	0.813
0.025	1.3327	1.3326	1.3323	0.771	0.832	0.889
0.040	1.3329	1.3328	1.3325	0.870	0.917	0.967
0.055	1.3331	1.3330	1.3327	0.965	1.020	1.040
0.070	1.3333	1.3332	1.3329	1.053	1.080	1.123
0.085	1.3336	1.3335	1.3332	1.114	1.163	1.210

Table13(b). Refractive index (n_D) and specific conductance (κ) of L-Glutamine in aqueous IL (BTBAC) solution at 298.15K, 303.15K and 308.15K

Conc. of L-Glutamine soln. in molality, m (mol.kg^{-1})	n_D 298.15K	303.15K	308.15K	κ (mS/cm) 298.15K	303.15K	308.15K
0.001m IL						
0.010	1.3322	1.3320	1.3318	0.352	0.382	0.410
0.025	1.3323	1.3321	1.3319	0.453	0.486	0.523
0.040	1.3325	1.3323	1.3321	0.557	0.582	0.614
0.055	1.3327	1.3325	1.3323	0.640	0.692	0.710
0.070	1.3330	1.3327	1.3325	0.756	0.790	0.819
0.085	1.3332	1.3330	1.3328	0.847	0.896	0.903
0.003m IL						
0.010	1.3323	1.3321	1.3319	0.441	0.463	0.496
0.025	1.3325	1.3322	1.3320	0.543	0.570	0.597
0.040	1.3327	1.3324	1.3322	0.683	0.702	0.724
0.055	1.3329	1.3326	1.3324	0.784	0.819	0.821
0.070	1.3331	1.3328	1.3326	0.902	0.923	0.943
0.085	1.3334	1.3330	1.3329	0.975	1.030	1.050
0.005m IL						
0.010	1.3325	1.3324	1.3322	0.542	0.582	0.612
0.025	1.3326	1.3325	1.3323	0.641	0.670	0.690
0.040	1.3328	1.3327	1.3325	0.768	0.774	0.796
0.055	1.3330	1.3329	1.3327	0.871	0.876	0.906
0.070	1.3332	1.3331	1.3329	0.980	0.989	1.01
0.085	1.3335	1.3333	1.3332	1.06	1.080	1.09

Table 14. Molar conductance (Λ) of L-Asparagine and L-Glutamine solution in (0.001m, 0.003m, 0.005m) IL at 298.15K, 303.15K and 308.15K

Concentration of amino acid solutions in molality, m(mole/kg)	Molar Conductance of L-asparagine solution Λ ($S.cm^2.mol^{-1}$)			Molar conductance of L--glutamine solution Λ ($S.cm^2.mol^{-1}$)		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
0 .001m IL						
0.010	48.20	50.30	52.00	35.20	38.20	41.00
0.025	22.96	23.60	24.60	18.12	19.44	20.92
0.040	16.325	17.075	17.725	13.925	14.55	15.35
0.055	13.6181	14.109	14.4725	11.6360	12.5818	12.909
0.070	11.800	12.2714	12.6857	10.80	11.2857	11.700
0.085	10.8235	11.094	11.5647	9.9647	10.5411	10.6235
0.003m IL						
0.010	54.50	57.20	60.7	44.10	46.30	49.60
0.025	25.36	26.52	28.56	21.72	22.80	23.88
0.040	18.00	19.125	20.225	17.075	17.55	18.10
0.055	14.7636	15.527	16.600	14.2545	14.8909	14.9272
0.070	12.900	13.3571	14.2714	12.8885	13.1857	13.4714
0.085	11.7294	12.3764	12.7058	11.470	12.117	12.352
0.005m IL						
0.010	66.00	74.80	81.30	54.20	58.20	61.20
0.025	30.84	33.28	35.56	25.64	26.80	27.600
0.040	21.75	22.925	24.175	19.20	19.35	19.900
0.055	17.5454	18.5454	18.9090	15.8363	15.9272	16.4727
0.070	15.0428	15.4285	16.04285	14.00	14.1228	14.4285
0.085	13.1058	13.6823	14.23529	12.47	12.705	12.8235

Table15. Surface Tension values of L-Asparagine and L-glutamine solutions in BTBAC at different concentration (0.001m, 0.003m, 0.005m) at room temperature

Concentration of amino acid solutions in molality(mole/kg)	**Surface Tension of L- Asparagine solutions** (mN/m)	**Surface Tension of L-Glutamine solutions** (mN/m)
0.001mIL	60.5	60.5
0.010	62.3	64.2
0.025	63.2	65.5
0.040	63.9	66.6
0.055	64.8	67.5
0.070	65.7	68.6
0.085	66.8	69.8
0.003mIL	57.6	57.6
0.010	63.9	65.9
0.025	64.8	66.8
0.040	65.7	67.7
0.055	66.9	68.7
0.070	68.1	69.4
0.085	69.3	70.3
0.005mIL	54.7	54.7
0.010	64.7	66.5
0.025	65.8	67.2
0.040	66.9	68.3
0.055	67.7	69.1
0.070	68.8	70.2
0.085	69.9	71.1

Table16. Optimization energies of pure BTBAC, L-Glu, L-Asp and (BTBAC + L-Glu), (BTBAC + L-Asp), systems using UB3LYP methodology and 6-31G (d) as a basis set

System (Debye)	Calculation Method	Basis Set	Optimization energy (a.u.)	Dipole moment
L-Glu	UB3LYP	6-31G(d)	-531.58350924	3.0454
L-Asp	UB3LYP	6-31G(d)	-492.79440798	4.1309
BTBAC	UB3LYP	6-31G(d)	-799.0179491	0.9693
(BTBAC + L-Glu)	UB3LYP	6-31G(d)	-1321.24634420	9.0790
(BTBAC + L-ASP)	UB3LYP	6-31G(d)	-1290.71439476	14.5571

Figures

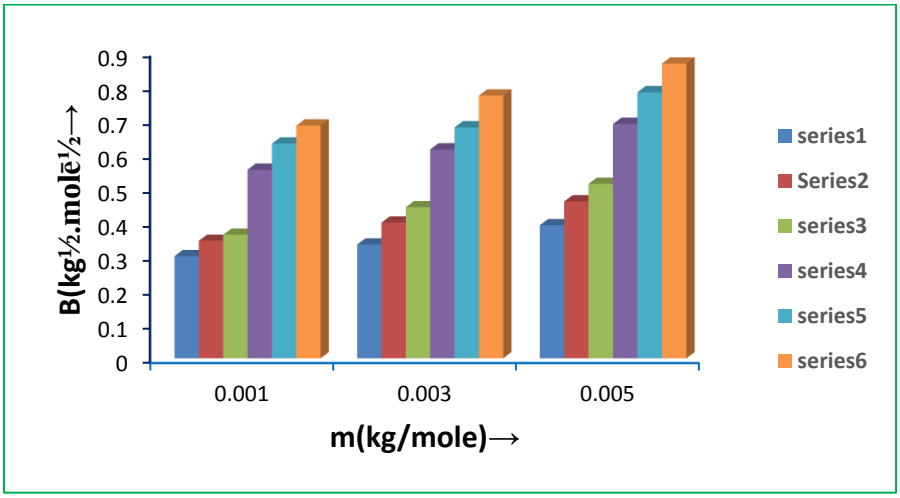

Figure1.Variation of B values of L-Glutamine and L-Asparagine in aqueous solution of BTBAC respectively, against 0.001m IL, 0.003m IL and 0.005m IL solutions at different temperatures

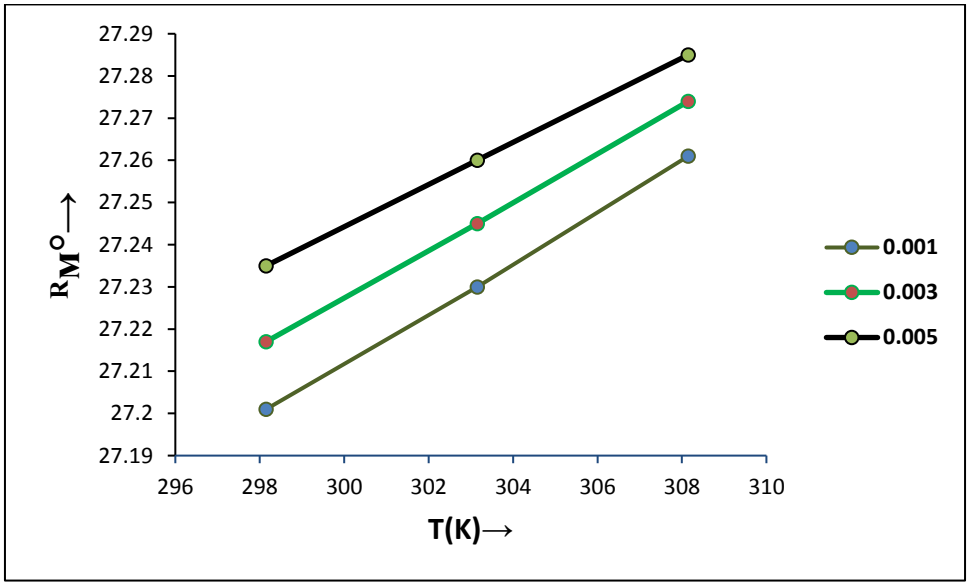

Figure2.variation of $^{R}M°$ values of L-asparagine solution Against(298.15k,303.15k,308.15k) in aqueous IL at 0.001m,0.003m,0.005m

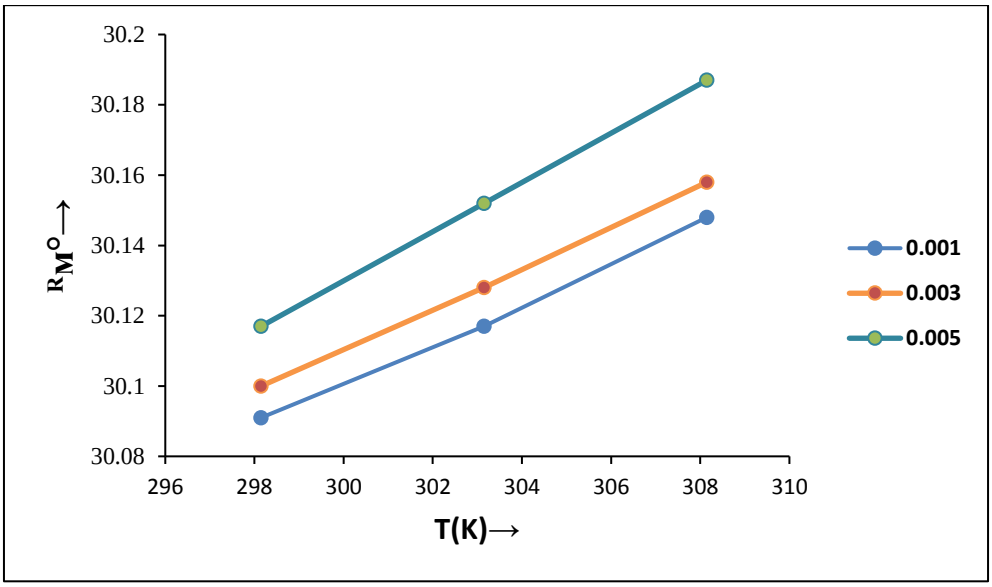

Figure3. variation of$^{R}M^{\circ}$of L-glutamine solution Against (298.15k,303.15k,308.15k) in aqueous IL at 0.001m,0.003m,0.005m

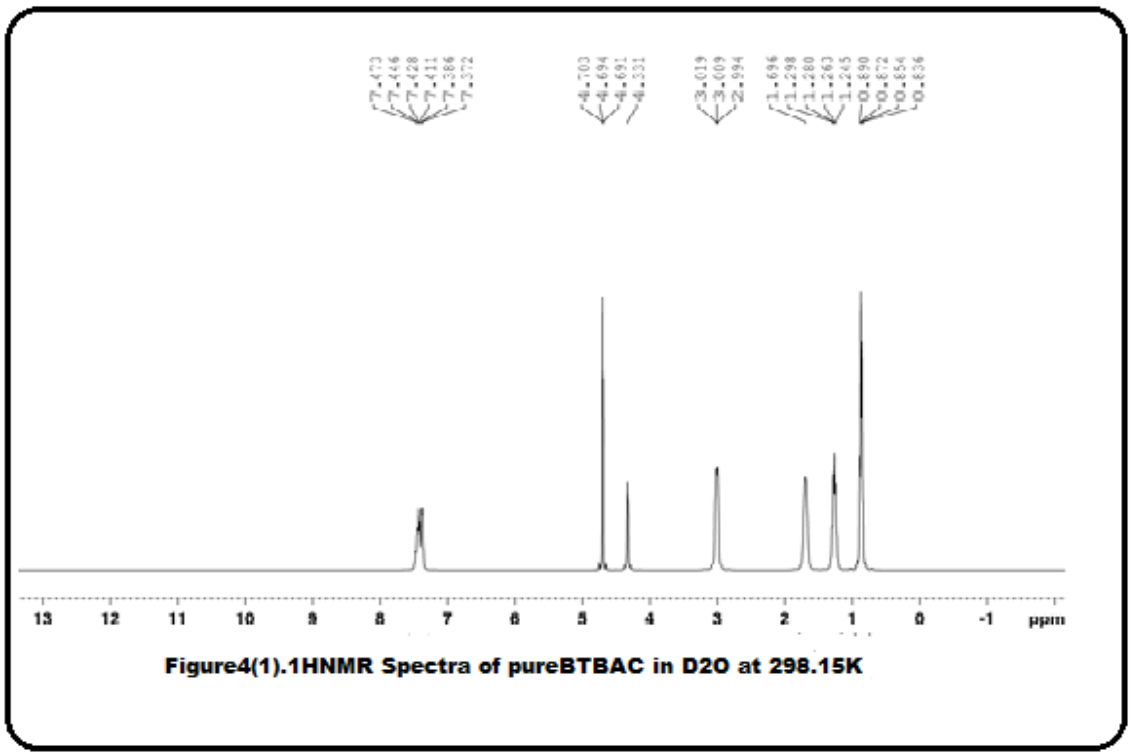

Figure4(1).1HNMR Spectra of pureBTBAC in D2O at 298.15K

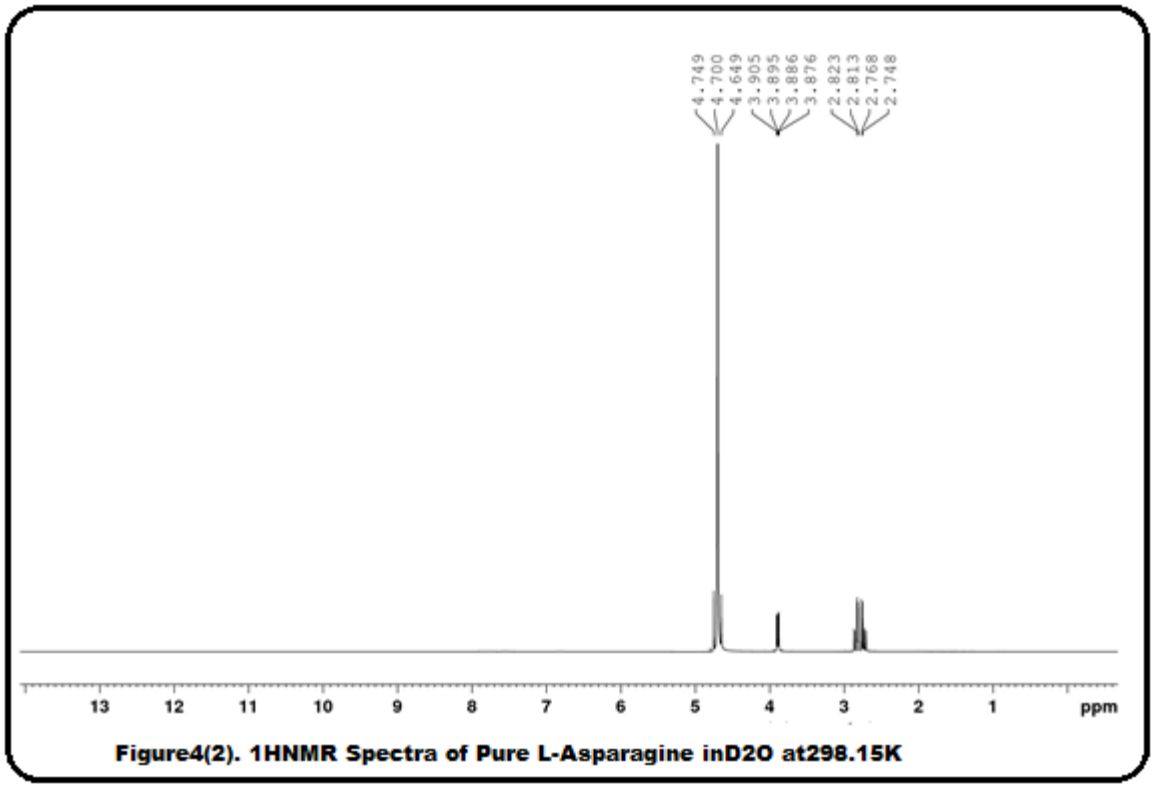

Figure4(2). 1HNMR Spectra of Pure L-Asparagine inD2O at298.15K

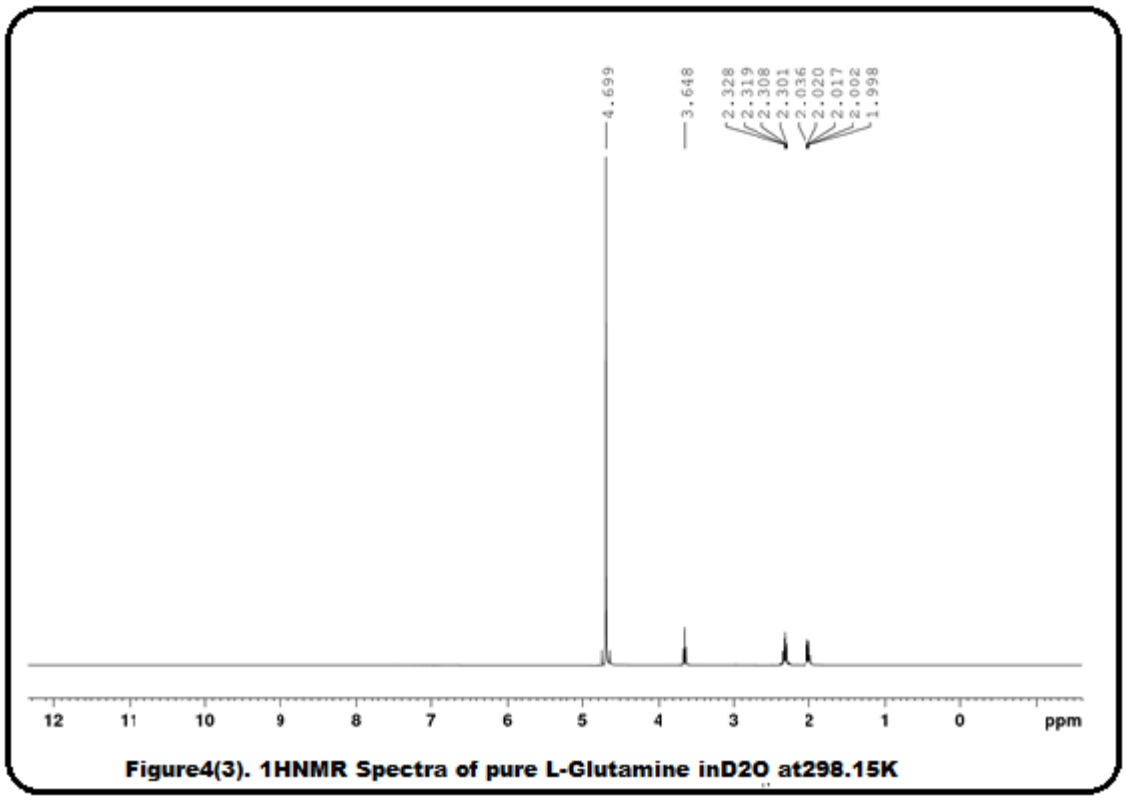

Figure4(3). 1HNMR Spectra of pure L-Glutamine inD2O at298.15K

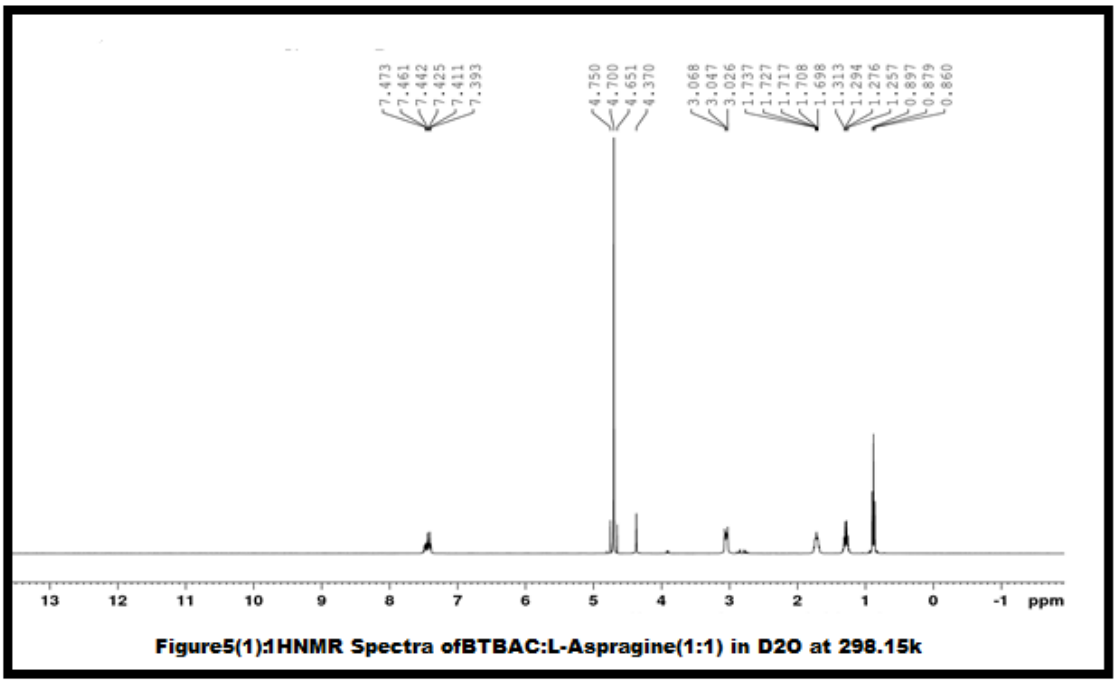

Figure5(1)1HNMR Spectra ofBTBAC:L-Aspragine(1:1) in D2O at 298.15k

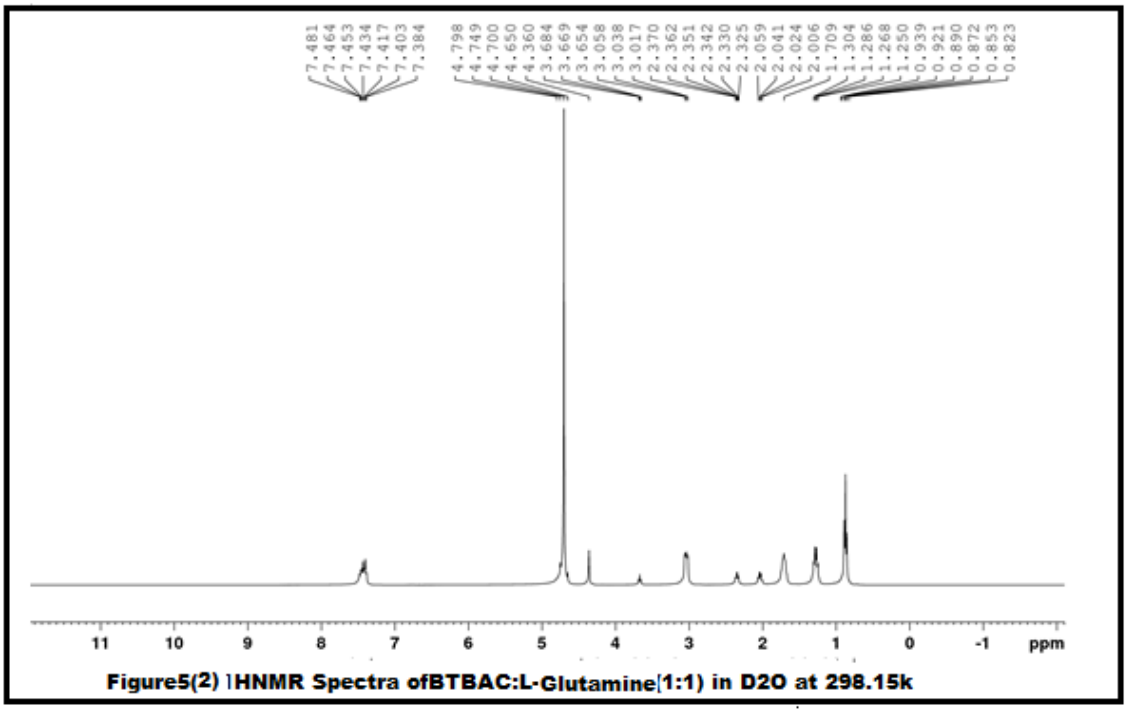

Figure5(2) 1HNMR Spectra ofBTBAC:L-Glutamine(1:1) in D2O at 298.15k

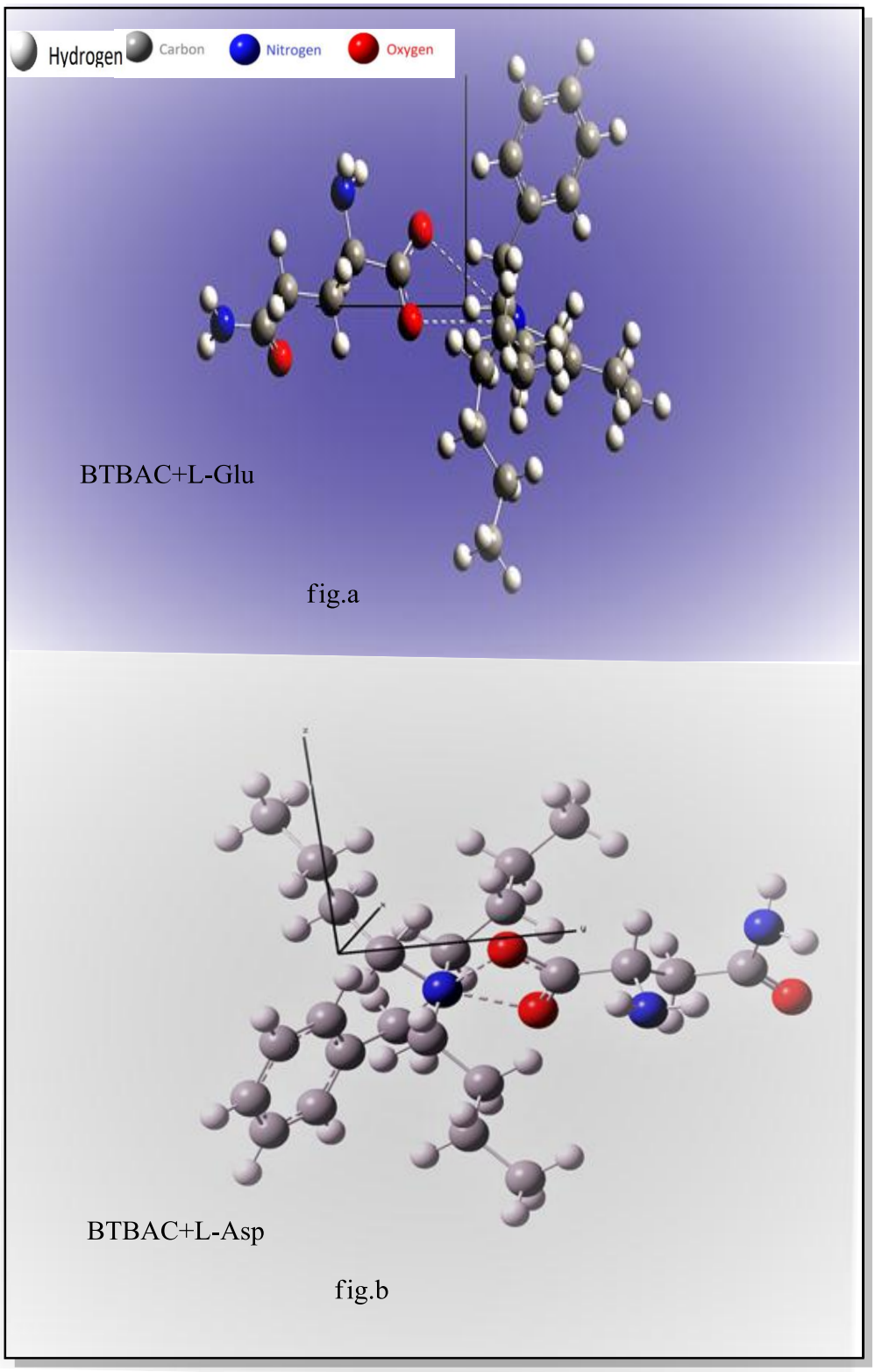

Fig. (a, b): Optimised geometry of(a) BTBAC + L-Glu and(b) BTBAC+L-Asp systems.

Scheme-1