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Research Article

Extensive Study on Molecular Interactions of Three Essential Amino Acids Insight into H_2O+ [bmpyrr]PF_6 Media

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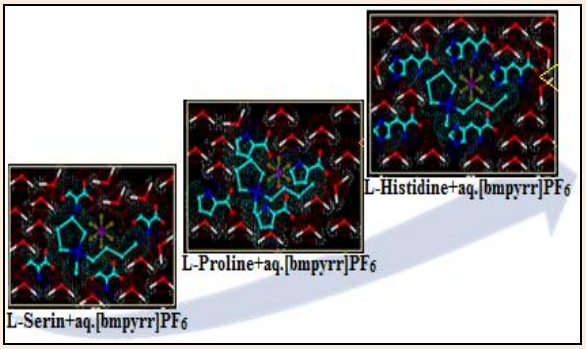
Abstract

van der Waals forces, H-bonding, electrostatic forces, and configurational theory on volumetric, transport properties, molar refraction of molecular interaction, association behaviour have been studied through the precise measurements of density, viscosity, refractive index of L-Serine, L-Proline, and L-Histidine, in w_1=0.001, 0.003, 0.005, mass fraction of aq .1-butyl-1-methylpyrrolidinium hexafluorophosphate binary mixtures at 298.15K. The density, viscosity, and refractive index data have been analysed using the Masson, Jones-Dole, and Lorentz-Lorenz equations respectively. The limiting molar volume, viscosity *B*-coefficient and limiting molar refraction, interpreted the ion-solvent or solute-solvent interactions have been calculated and discussed. The group contribution of zwitterionic, -CH_2 and other functional groups to limiting molar volume and viscosity *B*-coefficient, have been taken into account and discussed for the same.



Keywords: 1-butyl-1-methylpyrrolidinium hexafluo-rophosphate, essential amino acids, molecular interactions, group contributions

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Introduction

Ionic size, shape and charge of the ionic liquid, 1-butyl-1-methylpyrrolidinium hexafluorophosphate, affect the interaction in aqueous medium. The specificity of ion-solvent interaction behaviour, especially in an aqueous medium has been emphasized and its role in various biophysical processes has been recognized [1]. Ion–ion and ion–solvent interactions or the behaviour of amino acids can be informative depending on the volumetric and transport properties of solutions. [bmpyrr]PF_6–water binary mixtures are exhibited a wide range of viscosity and a high degree of hydrogen bonding effect. The addition of [bmpyrr]PF_6 could break or make the structure in solution, as viscosity being a property of the solution depending upon the intermolecular forces, the structural aspects.

The stabilisation/destabilisation of native conformations of biological macromolecules is commonly related to several non-covalent interactions including hydrogen bonding, electrostatic and hydrophobic interactions [2, 3]. These interactions are affected by the surrounding solutes and solvent molecules; for this reason, the behaviours of proteins are strongly influenced by the presence of solutes. However, due to the complex conformational and configurational three-dimensional structures of proteins, direct investigations of the solute–solvent effect on these biological macromolecules are very challenging [4]. Therefore, for better understanding we are taken three simple essential amino acids e.g., L-Serine, L-Proline, and L-Histidine with polar uncharged side chain, special case, electrically charged side chain respectively are model compound of protein and peptide molecules; utterly used in synthesis of protein molecules in living organism. If we add an ionic liquid in the solution medium, how these molecule are acting or functioning through the solute-solvent or ion-solvent interactions, let's we examine the interactions quantitatively and qualitatively by measuring the derived parameters, viz., apparent molar volume, viscosity B-coefficient, group contribution supplemented, molar refraction from experimental data of density, viscosity, and refractive index respectively.

To the best of our knowledge, the studies in the present ternary solution systems have not been reported earlier. Therefore, in the present study, we have endeavoured to make certain the nature of solute–solvent or ion-solvent interactions of L-Serine, L-Proline, and L-Histidine, in w_1 = 0.001, 0.003, 0.005 mass fraction of aq. [bmpyrr]PF_6 binary mixtures at 298.15 K, to explain the various interaction occurring in the studied ternary solution systems.

Experimental

Source and purity of Materials

The titled compounds i.e., amino acids and [bmpyrr]PF_6 of puriss grade were procured from Sigma-Aldrich, Germany and used as purchased. The mass fraction purity of L-Serine, L-Proline, L-Histidine and [bmpyrr]PF_6 were ≥0.99, ≥0.98, ≥0.99, and ≥0.975 respectively.

Apparatus and Procedure

Solubility of the ionic liquid [bmpyrr]PF_6 in water (deionized, triply distilled water with a specific conductance of 1×10^{-6} S·cm^{-1}) and titled amino acids in aqueous [bmpyrr]PF_6, have been checked precisely, prior to start of the experimental work, and seen that the selected amino acids unreservedly soluble in all proportion of aq. [bmpyrr]PF_6. The mother solutions of amino acids were prepared by mass (Mettler Toledo AG-285 with uncertainty 0.0003g), and then the working solutions (six set) were prepared by mass dilution. The conversions of molarity into molality have been done [5] using density values of respective solutions and adequate precautions were taken to reduce evaporation losses during mixing and throughout the experiment.

The densities (ρ) of the solvents were measured by means of vibrating u-tube Anton Paar digital density meter (DMA 4500M) with a precision of ±0.00005g cm^{-3} maintained at ±0.01K of the desired temperature. It was calibrated by passing deionized, triply distilled water and dry air [6].

The viscosities (η) were measured using a Brookfield DV-III Ultra Programmable Rheometer with fitted spindle size-42. The detail description has already been described earlier [7].

Refractive index was measured with the help of a Digital Refractometer Mettler Toledo. The light source was LED, λ=589.3nm. The refractometer was calibrated twice using distilled water and calibration was checked after every few measurements [4]. The uncertainty of refractive index measurement was ±0.0002 units.

Result and Discussion

Table 1 Experimental values of density (ρ), viscosity (η), refractive index (n_D), and pH of deferent mass fraction (w_1) of aq. [bmpyrr]PF_6 mixtures at 298.15 K*

Aq. [bmpyrr]PF_6	ρ×10^{-3} /kg·m^{-3}	η /mP·s	n_D	pH
w_1 = 0.001	0.99709	0.900	1.3322	5.98
w_1 = 0.003	0.99726	0.904	1.3325	5.81
w_1 = 0.005	0.99742	0.910	1.3329	6.26

* Standard uncertainties u are: $u(\rho)$ =2×10^{-6} kg·m^{-3}, $u(\eta)$ =0.003 mP·s, $u(n_D)$ =0.0002, u(pH) =0.01, and $u(T)$ =0.01K

The physical properties of binary mixtures in different mass fractions (w_1=0.001, 0.003, 0.005) of aq. [bmpyrr]PF_6 solutions at 298.15K have been reported in **Table 1**. The experimental measured values of density, viscosity, refractive index of chosen three amino acids (i.e., L-Serine, L-Proline, and L-Histidine) as a function of concentration (molarity), in different mass fractions of aq. [bmpyrr]PF_6 mixture, have been listed in **Table 2**.

Table 2 Experimental values of density (ρ), viscosity (η), refractive index (n_D), and pH of selected amino acids in deferent mass fraction (w_1) of aq. [bmpyrr]PF_6 mixtures at 298.15 K*

molality /mol·kg^{-1}	ρ×10^{-3} /kg·m^{-3}	η /mP·s	n_D	pH	molality /mol·kg^{-1}	ρ×10^{-3} /kg·m^{-3}	η /mP·s	n_D	pH
Glycine					L-Serine				
w_1 = 0.001					w_1 = 0.001				
0.0100	0.99744	0.901	-	-	0.0100	0.99753	0.902	1.3323	6.00
0.0251	0.99800	0.902	-	-	0.0251	0.99820	0.905	1.3326	5.90
0.0402	0.99858	0.904	-	-	0.0402	0.99888	0.908	1.3330	6.01
0.0553	0.99918	0.906	-	-	0.0553	0.99957	0.911	1.3333	5.96
0.0704	0.99979	0.908	-	-	0.0705	1.00026	0.915	1.3337	5.88
0.0855	1.00041	0.910	-	-	0.0857	1.00095	0.918	1.3341	5.94
w_1 = 0.003					w_1 = 0.003				
0.0100	0.99761	0.906	-	-	0.0100	0.99769	0.906	1.3327	6.05
0.0251	0.99816	0.908	-	-	0.0251	0.99835	0.910	1.3330	6.04
0.0402	0.99873	0.910	-	-	0.0402	0.99902	0.913	1.3333	5.96
0.0553	0.99931	0.912	-	-	0.0553	0.99971	0.917	1.3336	5.99
0.0704	0.99990	0.914	-	-	0.0705	1.00039	0.920	1.3339	5.94
0.0855	1.00050	0.916	-	-	0.0857	1.00109	0.924	1.3342	5.96
w_1 = 0.005					w_1 = 0.005				
0.0100	0.99776	0.913	-	-	0.0100	0.99784	0.913	1.3332	6.27
0.0251	0.99829	0.915	-	-	0.0251	0.99848	0.916	1.3335	6.14
0.0402	0.99885	0.918	-	-	0.0402	0.99913	0.920	1.3338	6.22
0.0553	0.99942	0.920	-	-	0.0553	0.99978	0.924	1.3341	6.25
0.0704	1.00000	0.923	-	-	0.0705	1.00044	0.928	1.3344	6.21
0.0855	1.00059	0.925	-	-	0.0857	1.00111	0.932	1.3347	6.08
L-Proline					L-Histidine				
w_1 = 0.001					w_1 = 0.001				
0.0100	0.99742	0.903	1.3324	6.98	0.0100	0.99766	0.906	1.3325	7.48
0.0251	0.99792	0.907	1.3327	6.94	0.0251	0.99852	0.913	1.3331	7.58
0.0402	0.99842	0.911	1.3330	6.54	0.0403	0.99938	0.919	1.3339	7.62
0.0554	0.99893	0.915	1.3332	6.43	0.0555	1.00025	0.925	1.3346	7.62
0.0706	0.99944	0.919	1.3335	6.47	0.0707	1.00111	0.932	1.3353	7.60
0.0858	0.99995	0.923	1.3338	6.49	0.0860	1.00199	0.939	1.3359	7.60
w_1 = 0.003					w_1 = 0.003				
0.0100	0.99758	0.907	1.3328	6.41	0.0100	0.99782	0.911	1.3329	7.52
0.0251	0.99808	0.911	1.3331	6.28	0.0251	0.99867	0.918	1.3335	7.54
0.0402	0.99858	0.915	1.3334	6.42	0.0403	0.99953	0.925	1.3342	7.55
0.0554	0.99909	0.919	1.3337	6.22	0.0555	1.00039	0.932	1.3348	7.56
0.0706	0.99960	0.924	1.3340	6.16	0.0707	1.00126	0.939	1.3354	7.58
0.0858	1.00011	0.928	1.3343	6.43	0.0860	1.00213	0.946	1.3361	7.59
w_1 = 0.005					w_1 = 0.005				
0.0100	0.99774	0.914	1.3333	5.95	0.0100	0.99797	0.917	1.3335	7.55
0.0251	0.99823	0.918	1.3337	6.02	0.0251	0.99881	0.925	1.3341	7.52
0.0402	0.99873	0.922	1.334	5.88	0.0403	0.99966	0.932	1.3347	7.57
0.0554	0.99923	0.926	1.3343	5.91	0.0554	1.00052	0.939	1.3353	7.52
0.0706	0.99974	0.931	1.3346	5.94	0.0707	1.00138	0.946	1.3358	7.59
0.0858	1.00219	0.936	1.3349	6.15	0.0859	1.00225	0.953	1.3363	7.54

* Standard uncertainties u are: $u(\rho)$ =2×10^{-6} kg·m^{-3}, $u(\eta)$ =0.003 mP·s, $u(n_D)$ =0.0002, u(pH) =0.01, and $u(T)$ =0.01K

Apparent molar volume

Volumetric properties, like, apparent molar volume, ϕ_V, and limiting apparent molar volume, ϕ_V^0, regard a perceptive tools for understanding of interactions taking place in solution systems. The apparent molar volume can be considered to be the sum of the geometric volume of the central solute molecule and changes in the solvent volume due to its

interaction with the solute around the peripheral or co-sphere. For the consequence, the apparent molar volumes ϕ_V have been determined from the solutions densities using the suitable equation [3] and the values are given in Table 3.

Table 3 Apparent molar volume (ϕ_V), $(\eta_r\text{-}1)/\sqrt{m}$, and molar refraction ($R_M$) of selected amino acids in different mass fraction (w_1) of aq. [bmpyrr]PF_6 mixtures at 298.15K*

Aq. solvent mixture	$\phi_V \times 10^{-6}$ /m^3 mol^{-1}	$(\eta_r\text{-}1)/\sqrt{m}$ /$kg^{1/2}mol^{-1/2}$	R_M /m^3 mol^{-1}	Aq. solvent mixture	$\phi_V \times 10^{-6}$ / m^3 mol^{-1}	$(\eta_r\text{-}1)/\sqrt{m}$ /$kg^{1/2}mol^{-1/2}$	R_M /m^3 mol^{-1}
Glycine				L-Serine			
w_1 = 0.001				w_1 = 0.001			
0.0100	40.19	0.011	-	0.0100	61.07	0.022	21.629
0.0251	38.78	0.017	-	0.0251	60.71	0.035	21.632
0.0402	37.93	0.022	-	0.0402	60.44	0.046	21.641
0.0553	37.18	0.027	-	0.0553	60.25	0.054	21.644
0.0704	36.61	0.032	-	0.0705	60.02	0.063	21.652
0.0855	36.12	0.038	-	0.0857	59.85	0.068	21.661
w_1 = 0.003				w_1 = 0.003			
0.0100	40.18	0.020	-	0.0100	62.26	0.027	21.649
0.0251	39.18	0.027	-	0.0251	61.66	0.042	21.652
0.0402	38.43	0.033	-	0.0402	61.21	0.051	21.655
0.0553	37.90	0.038	-	0.0553	60.80	0.061	21.658
0.0704	37.46	0.043	-	0.0705	60.51	0.068	21.661
0.0855	37.05	0.047	-	0.0857	60.20	0.076	21.664
w_1 = 0.005				w_1 = 0.005			
0.0100	41.18	0.031	-	0.0100	63.35	0.033	21.675
0.0251	40.37	0.036	-	0.0251	62.89	0.044	21.679
0.0402	39.42	0.043	-	0.0402	62.55	0.056	21.683
0.0553	38.81	0.048	-	0.0553	62.27	0.065	21.686
0.0704	38.31	0.053	-	0.0705	62.06	0.075	21.689
0.0855	37.87	0.058	-	0.0857	61.84	0.083	21.693
L-Proline				L-Histidine			
w_1 = 0.001				w_1 = 0.001			
0.0100	82.37	0.033	23.704	0.0100	98.69	0.071	31.955
0.0251	82.17	0.049	23.712	0.0251	98.45	0.091	31.980
0.0402	82.02	0.061	23.719	0.0403	98.26	0.107	32.022
0.0554	81.91	0.071	23.720	0.0555	98.12	0.120	32.055
0.0706	81.81	0.079	23.727	0.0707	98.00	0.134	32.088
0.0858	81.72	0.087	23.735	0.0860	97.87	0.148	32.112
w_1 = 0.003				w_1 = 0.003			
0.0100	82.96	0.036	23.726	0.0100	99.47	0.082	31.985
0.0251	82.60	0.050	23.734	0.0251	99.07	0.100	32.010
0.0402	82.33	0.062	23.741	0.0403	98.77	0.117	32.043
0.0554	82.14	0.071	23.749	0.0555	98.54	0.130	32.068
0.0706	81.95	0.083	23.756	0.0707	98.33	0.146	32.092
0.0858	81.82	0.091	23.763	0.0860	98.16	0.158	32.125
w_1 = 0.005				w_1 = 0.005			
0.0100	83.35	0.041	23.755	0.0100	100.36	0.081	32.032
0.0251	82.94	0.055	23.769	0.0251	99.86	0.104	32.058
0.0402	82.64	0.067	23.776	0.0403	99.46	0.120	32.083
0.0554	82.43	0.077	23.784	0.0554	99.15	0.135	32.107
0.0706	82.20	0.087	23.791	0.0707	98.88	0.149	32.123
0.0858	82.05	0.098	23.798	0.0859	98.63	0.161	32.138

* Standard uncertainties u are: $u(T)$ =0.01K

The values of ϕ_V are positive and large for all the systems, suggesting strong solute-solvent interactions. The apparent molar volumes ϕ_V were found to decreases with increasing concentration (molarity, m) of amino acid in different mass fraction of aq. [bmpyrr]PF_6. ϕ_V, varied linearly with m and could be least-squares fitted to the Masson equation

[8] from where limiting molar volume ϕ_V^0 (infinite dilution partial molar volume) have been estimated and the values have been represented in Table 4.

Table 4 Limiting apparent molar volume (ϕ_V^0), experimental slope (S_V^*), viscosity *A*- and *B*-coefficient, and limiting molar refraction (R_M^O) of selected amino acids in different mass fraction (w_1) of aq. [bmpyrr]PF_6 mixtures at 298.15 K*

Aq. [bmpyrr]PF_6	$\phi_V^0 \times 10^{-6}$ /m^3 mol^{-1}	S_V^* /$m^3 \cdot mol^{-3/2} \cdot kg^{1/2}$	*B* /$kg^{1/2} \cdot mol^{-1/2}$	*A* /$kg \cdot mol^{-1}$	R_M^O /m^3 mol^{-1}
Glycine					
w_1 = 0.001	42.21	-21.14	0.138	-0.004	-
w_1 = 0.003	42.61	-22.61	0.141	0.004	-
w_1 = 0.005	43.02	-17.68	0.144	0.014	-
L-Serine					
w_1 = 0.001	61.70	-6.29	0.243	-0.003	21.60
w_1 = 0.003	63.35	-10.73	0.254	0.001	21.64
w_1 = 0.005	64.14	-7.86	0.261	0.005	21.66
L-Proline					
w_1 = 0.001	82.70	-3.36	0.280	0.005	23.68
w_1 = 0.003	83.54	-5.92	0.285	0.006	23.70
w_1 = 0.005	84.02	-6.78	0.291	0.009	23.73
L-Histidine					
w_1 = 0.001	99.11	-4.20	0.393	0.029	31.85
w_1 = 0.003	100.15	-6.83	0.398	0.039	31.90
w_1 = 0.005	101.27	-8.98	0.414	0.040	31.97

* Standard uncertainties *u* are: $u(T)$ =0.01K

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{m} \quad (1)$$

The trend of variation of $\phi_V^0$of selected amino acids follows the order

L-Serine < L-Proline < L-Histidine

The increase in ϕ_V^0 for amino acids with increasing mass fraction (Figure 1) suggests that in these cases, both the ion-hydrophilic and ion-hydrophobic group interactions play a major role. Due to these interactions, the electrostatic interaction to water molecules caused by the charge centers of the amino acid will be reduced and a number of pyrrolidinium or hexafluorophosphate ions are attached, which results in an increase in apparent molar volume. This trend can also be explained with the equation of Shahidi et. al. [9].

$$\phi_V^0 = V_{vW} + V_v - V_s \quad (2)$$

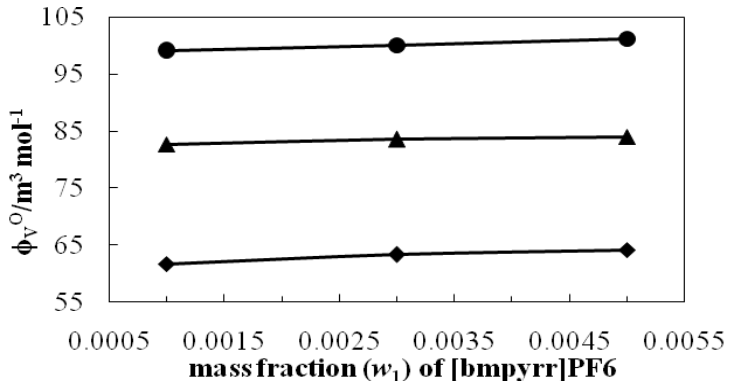
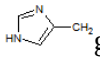


Figure 1 Plot of limiting molar volume (ϕ_V^0) vs mass fraction for L-Serine (♦), L-Proline (▲), L-Histidine (●) in aq. [bmpyrr]PF_6 respectively

In which the partial molar volume of the amino acid may be considered to be made up of the van der Waals volume (V_{vW}), the volume associated with voids (V_v) or empty space, and the volume due to shrinkage (V_s,) that arises due to the electrostriction of the solvent caused by the hydrophilic groups present in the amino acid. The presence of [bmpyrr]PF_6 in water decreases the extent of electrostriction caused by the amino acid, which results in a decrease in shrinkage volume. Assuming that V_{vW} and V_v are not significantly affected, an increase in ϕ_V^0, are results.

It noted (Table 4 and Fig. 1) that ϕ_V^0 of L-Proline is more than that of L-Serine owing to greater electrostriction. This is because the methylene groups provide an increasing structure enforcing tendency and as a result, the water in the overlapping cospheres is more structured than in the bulk. When this water relaxes to the bulk, there is a decrease in volume. But, in amino acids, the interactions increase with the addition of CH_2 groups, and consequently there is a net increase in volume. The results can be rationalizing on the basis that the partial molar volume is observed to increase with the increasing molar mass and size of the amino acid. The $\phi_V^0$for glycine, L-alanine, L-valine has been studied earlier [3]. When one H of glycine is replaced by a -CH_2OH (L-Serine), -$CH_2CH_2CH_2$- (L-Proline),  (L-Histidine) groups, there is a massive change in ϕ_V^0, this should increase by virtue of its increased side chain group effect as well as size. L-Serine has a hydrophilic polar uncharged alcoholic –CH_2OH group which interacts with the hexafluorophosphate ion with H-bond, as a result its ϕ_V^0 increases with concentration. L-Proline is the special case of amino acid, contain cyclic group including zwitterionic NH_2 group, which is found to be higher ϕ_V^0 value than L-Serine. Thus, the structure-enhancing behavior of L-Proline has been observed. If -H of glycine are replaced by  group (L-Histidine), the increase in the partial molar volume should be more, relative to L-Serine and L-Proline owning to greater effect of electrically charged side chain group, as it observed. The maximum values of ϕ_V^0 for L-Histidine in the series of studied amino acids can be attributed to its great effect of more electronegative nitrogen atom, which is responsible for making the H-bond with pyrrolidinium or hexafluorophosphate ions and as well as largest size and mass.

Viscosity

The viscosity of the aq. [bmpyrr]PF_6 binary mixtures increases with an increase in employed concentration (w_1=0.001, 0.003, and 0.005) (Table 1), which can be attributed to the structure-making influence of [bmpyrr]PF_6 with water molecules, in its vicinity. The viscosity of the ternary solution (amino acid+aq. [bmpyrr]PF_6) increases with the increasing molality (Table 2). The viscosity *B*-coefficient is depend [10] on the size and shape of the solute molecules indicates the solute-solvent interactions. The *B*-coefficients of all the amino acids studied were positive (Table 4) and increased with the mass fraction of [bmpyrr]PF_6 (Fig. 2) which may be considered to arise due to increasing amino acid-[bmpyrr]PF_6 interaction as well as increase in solvation.

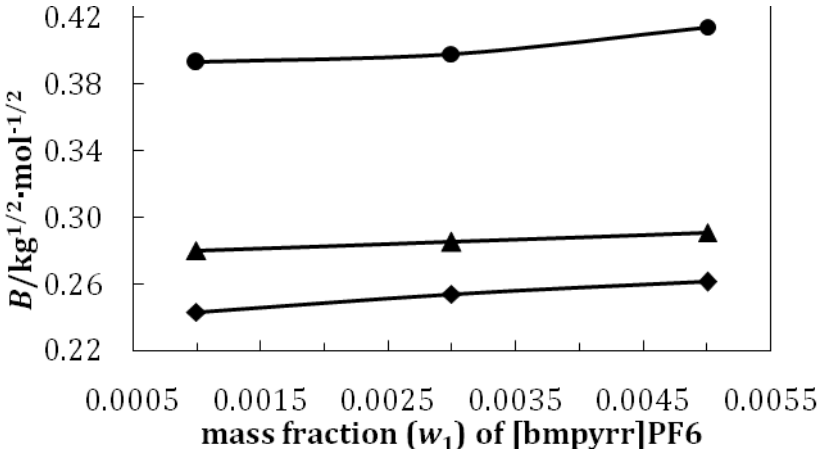
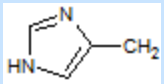
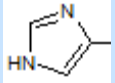


Figure 2 Plot of viscosity *B*-coefficient vs mass fraction for L-Serine (♦), L-Proline (▲), L-Histidine (●) in aq. [bmpyrr]PF_6 respectively

Contributions of the zwitterion, CH_2 groups and other alkyl of the amino acids to ϕ_V^0 and viscosity B-coefficient

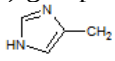
The entire group present in the amino acids affect to a great extent in interaction with pyrrolidinium or hexafluorophosphate ions, occurring in the solution systems. The group contributions of zwitterion, -CH, -CH_2, and other side chain group to limiting molar volume and viscosity *B*-coefficient, have been estimated in the same way as described by Ekka et. al. [3] and reported in Table 5. The contribution of (NH_3^+, COO^-) to ϕ_V^0 is larger than that of the

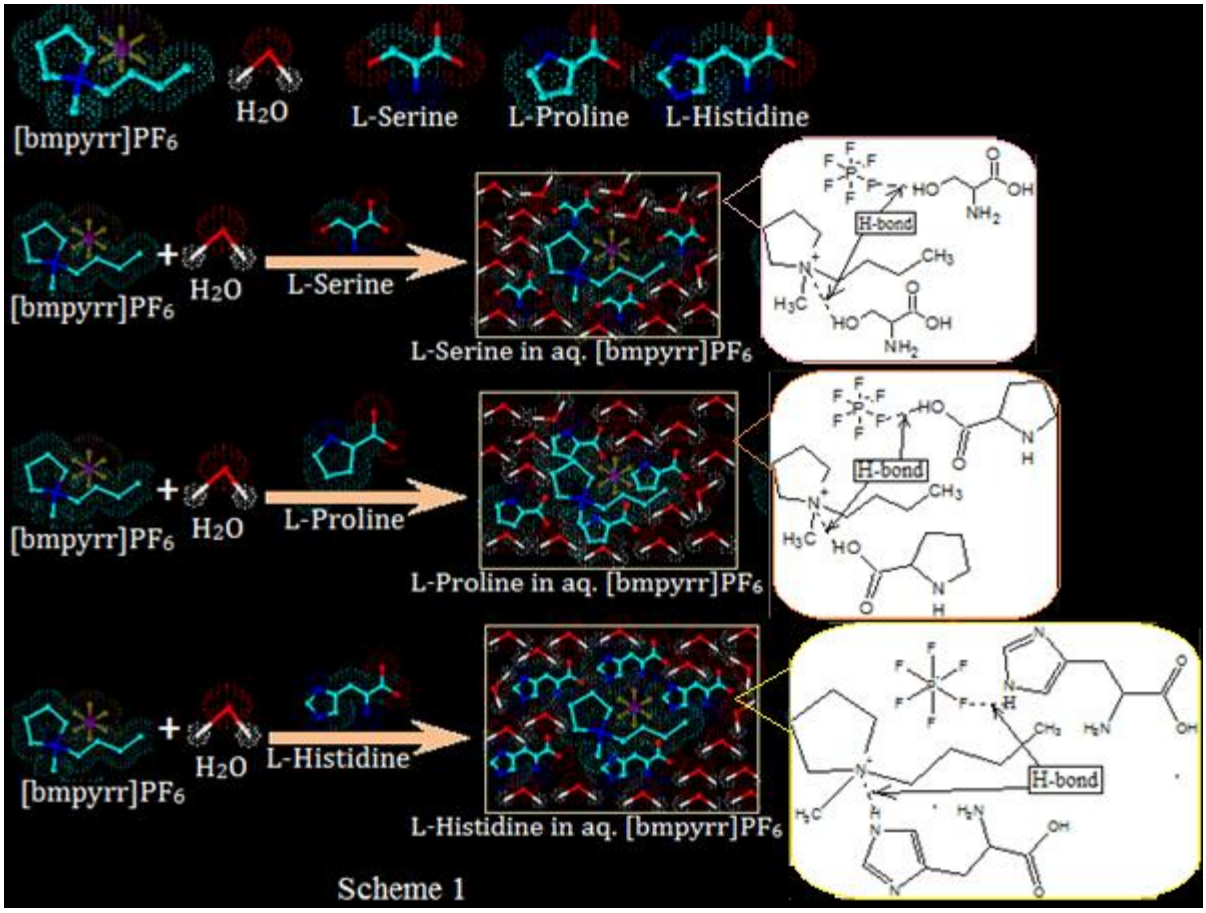
Table 5 Contributions of zwitter ionic group (NH_3^+, COO^-), CH_2 group, end group and the other alkyl chains to the limiting apparent molar volume, ϕ_V^0 and viscosity *B*-coefficient for amino acids in different mass fraction of aq. [bmpyrr]PF_6 respectively at 298.15K*

Groups	ϕ_V^0 /m^3 mol^{-1}			*B*/$kg^{1/2}\cdot mol^{-1/2}$		
	w_1=0.001	w_1=0.003	w_1=0.005	w_1=0.001	w_1=0.003	w_1=0.005
L-Serine						
NH_3^+, COO^-	25.89	25.31	25.24	0.048	0.045	0.043
-CH-	8.20	8.67	8.86	0.045	0.048	0.050
-CH_2-	16.39	17.34	17.71	0.090	0.096	0.100
-CH_2OH	27.62	29.37	30.05	0.150	0.161	0.168
L-Proline						
NH_3^+, COO^-	21.72	21.83	22.05	0.083	0.084	0.084
-CH-	10.28	10.41	10.45	0.028	0.029	0.030
-CH_2-	20.56	20.82	20.90	0.055	0.057	0.060
-$[CH_2]_3$-	50.70	51.30	51.52	0.170	0.173	0.177
L-Histidine						
NH_3^+, COO^-	35.18	35.42	35.54	0.119	0.120	0.118
-CH-	3.55	3.62	3.71	0.008	0.009	0.011
-CH_2-	7.10	7.23	7.41	0.016	0.017	0.021
	60.38	61.12	62.03	0.266	0.270	0.286
	53.28	53.89	54.62	0.250	0.253	0.265

* Standard uncertainties *u* are: *u*(*T*) =0.01K

CH_2- group and decreases with the increase in the mass fraction (w_1) of aq. [bmpyrr]PF_6, that designated the interactions of polar head groups (NH_3^+, COO^-) of amino acids are stronger; and the strength decreases with increase in mass fraction of aq. [bmpyrr]PF_6. The contribution of -CH_2 group increases with increase in mass fraction of aq. [bmpyrr]PF_6, suggesting that the -CH_2 group pretend the +I effect. For a particular mass fraction (w_1=0.001), contribution of (NH_3^+, COO^-) groups for L-Serine is less significant than side chain –CH_2OH, which advocated that the uncharged polar –CH_2OH group are greater contributed through the H-bonding (Scheme 1). Again, the -CH_2 group contribution has been found to the same trend suggesting that the -CH_2 group pretend the +I effect, as a result interaction are more fascinating. In case of L-Proline, the (NH_3^+, COO^-) group acting a major role in the interactions.

For L-Histidine, contribution of both zwitterions (NH_3^+, COO^-) and  groups are found to be greater and increases with increase in mass fraction of [bmpyrr]PF_6; that proposed both the groups strongly affect with the hydrophilic as well as hydrophobic solvation. This is due to the greater fascinating of H-bonding of two nitrogen atoms in imidazole side chain with solvent molecules. Scheme 1



Scheme 1 The schematic representation of plausible interaction as well as solvation of ions of [bmpyrr]PF_6 with three investigated amino acids

Hydration and solvation numbers

The hydration numbers (n_H) have also been estimated in the same way as described by Ekka et. al. [3] Solvation numbers S_n have been calculated from the relation $S_n=B/\phi_V^0$ [11]. S_n is indicating of the formation of a primary solvation sphere around a solute and if the range 0 to 2.5 for S_n indicates unsolvated solutes in the solution [11]. A decrease in hydration number (n_H) on addition of [bmpyrr]PF_6 (Table 6) is due to the decrease in the electrostriction of water. The scrutiny of S_n values given in Table 2 indicated that the amino acids are solvated and its salvation increases at higher concentration of [bmpyrr]PF_6 in the studied solutions. Such trends in S_n values are due to the fact that [bmpyrr]PF_6 itself interacts with amino acids and thus increases solvation (Scheme 1).

Table 6 Hydration number (n_H), and solvation number (S_n) of chosen amino acids in deferent mass fraction of aq. [bmpyrr]PF_6 respectively at 298.15K*

Aq. sol. mix	n_H			S_n		
w_1	0.001	0.003	0.005	0.001	0.003	0.005
L-Serine	3.53	3.03	2.79	3.94	4.01	4.07
L-Proline	2.93	2.68	2.53	3.39	3.41	3.46
L-Histidine	6.74	6.43	6.09	3.97	3.97	4.09

* Standard uncertainties u are: $u(T)$ =0.01K

Moreover, it is interesting note have been observed (Figure 3) that *B*-coefficients are linearly variation with limiting partial molar volumes ϕ_V^0 for the amino acids in aq. [bmpyrr]PF_6 solution. This correlation is not unexpected, as both the viscosity *B*-coefficient and the partial molar volume reflect the solute–solvent interactions in the solutions. The positive slope shows the linear variation of *B*-coefficient with limiting apparent molar volumes ϕ_V^0. A similar correlation has also been found for α-amino acids in different solvents [12].

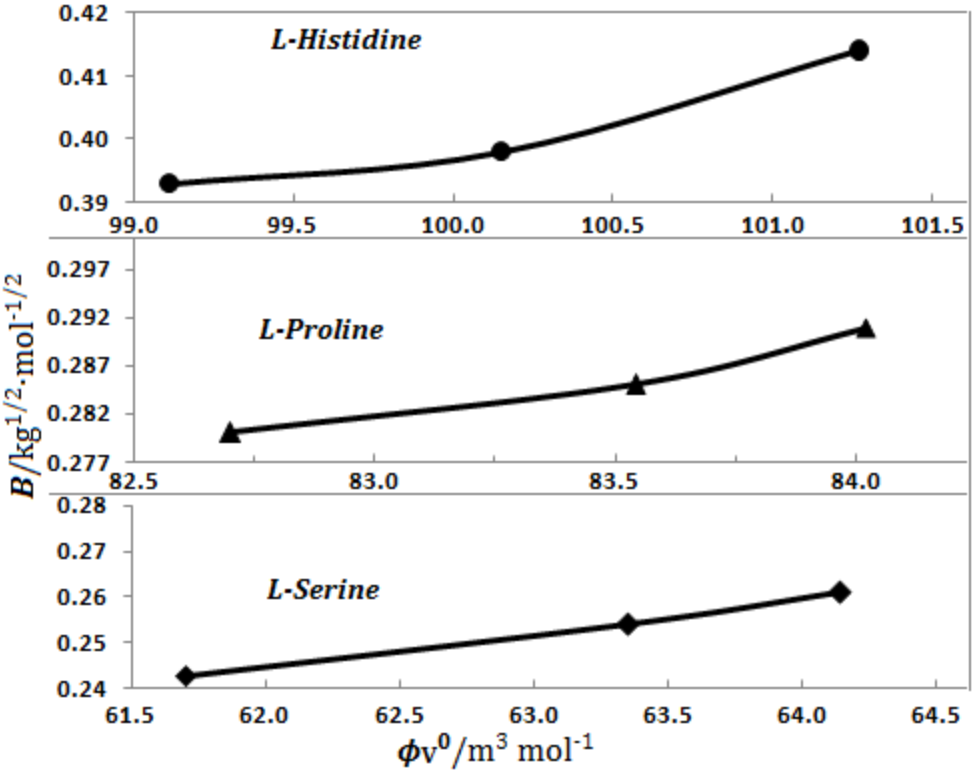


Figure 3 Plot of viscosity *B*-coefficient vs limiting molar volume (ϕ_V^0) for L-Serine (♦), L-Proline (▲), L-Histidine (●) in aq. [bmpyrr]PF_6 respectively

Refractive index

The refractive index and molar refraction is also a convenient method for investigating the molecular interaction existing in solution. The molar refraction (R_M) can be evaluated from the Lorentz-Lorenz relation [13]. The refractive index of a substance is defined as the ratio c_o/c, where c and c_o is the speed of light in the medium and in vacuum. Stated more simply that the refractive index of a compound describes its ability to refract light as it moves from one medium to another and thus, the higher the refractive index of a compound, the more the light is refracted [14]. As stated by Deetlefs et al.[15] the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser. Hence, a perusal of Table 2 and Table 3 we found that the refractive index and the molar refraction are higher for the studied amino acids in all the mass fraction of [bmpyrr]PF_6, indicating to the fact that the molecules are more tightly packed in the solution.

The Limiting molar refraction (R^0_M) estimated from the following [4] and presented in Table 4.

$$R_M = R_M^0 + R_S \sqrt{m} \qquad (4)$$

Accordingly, we found that the higher values of refractive index, and R^0_M (Fig. 4), which representing the fact that the amino acids are more tightly packed and greater ion-solvent interaction with [bmpyrr]PF_6 molecules or more solvated in solution. This is also in good agreement with the results obtained from apparent molar volume and viscosity *B*-coefficients discussed above.

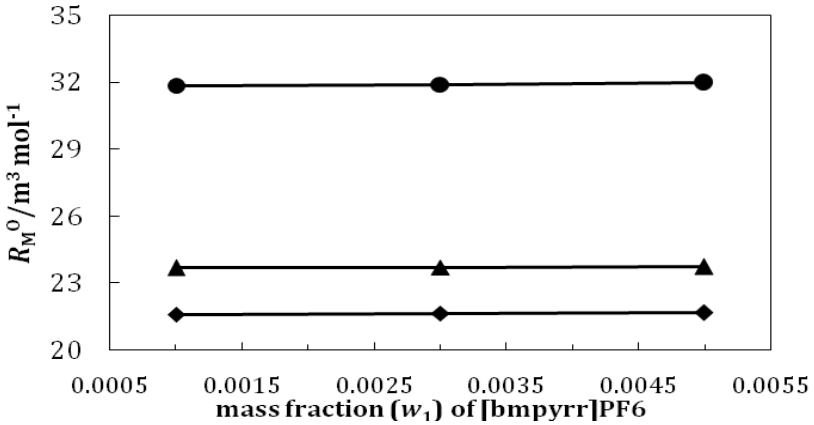


Figure 4 Plot of limiting molar refraction vs mass fraction for L-Serine (⧫), L-Proline (▲), L-Histidine (●) in aq. [bmpyrr]PF_6 respectively

Conclusion

The present study quantifies experimentally the ion-solvent interactions, solvation behaviour and solution structure of the three amino acids as a function of concentration in aq. [bmpyrr]PF_6. It is no doubt that the ion-solvent interaction is dominant over the interaction of ion or solute itself. The work also provided the qualitative and quantitative statement that the ion-solvent interaction or ion-solvation behaviour are higher for L-Histidine than L-Proline, which is in turn greater than L-Serine; and these ion-solvation is strengthen with increasing mass fraction of [bmpyrr]PF_6 in aqueous media. The parameters resolute by the chemical analysis of different equations improved with experimental data sustain the same culmination discussed and explained in this study demanding the uniqueness of the work.

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