CHAPTER V

EXPLORING SOLUTE- SOLVENT INTERACTIONS OF α-AMINO ACIDS IN AQUEOUS [EPYBF$_4$] ARRANGEMENTS BY VOLUMETRIC, VISCOMETRIC, REFRACTOMETRIC AND ACOUSTIC APPROACH

5.1. INTRODUCTION

Amino acids are the basic component of proteins and are considered to be one of the most important model compounds of protein molecules, which participate in all the physiological processes of living cells. They are quite helpful in understanding the water–protein–ionic liquid interactions in solutions. Amino acids, particularly important in biochemistry are critical to life and have many functions in metabolism. One particularly important function is to serve as the building blocks of proteins. Due to their central role in biochemistry, amino acids are important in nutrition and are commonly used in food technology and industry.In the present study, we have attempted to find out the nature of solute-solvent interactions of amino acids (glycine, L-alanine, and L-valine) in 0.001, 0.003, and 0.005 mass fractions of aqueous ionic liquid binary mixtures at 298.15K as literature survey reveals that no work has been carried out in the present ternary systems.

Ionic liquids (ILs) are very attractive because of their unique properties, such as high thermal stability, large liquid range, ability of dissolving a variety of chemicals, negligible vapour pressure, miscibility with common molecular liquids, large electrochemical window and their potential as “designer solvents” and “green” replacements i.e. alternative solvents to volatile organic solvents [1-3]used in reactions involving inorganic compounds as well as bio-catalysts. They are also used as heat transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells).[4-6] Solvent properties such as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the solute-solvent interactions and the solvent-solvent interactions. The volumetric, viscometric and interferrometric behavior of solutes is very useful in elucidating the various interactions occurring in solutions. In studies on the effect of concentration (molality), the apparent molar volumes of

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solutes have been extensively used to obtain information on solute-solute, solute-solvent, and solvent-solvent interactions.[7-11]In view of the above and in continuation of our study, we have undertaken a systematic study on the density, viscosity, refractive index and ultrasonic speed of some amino acids in aqueous 1-ethylpyridinium tetrafluoroborate [$EPyBF_4$]solutions at 298.15 K and we report the limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*) and viscosity *B*-coefficients, molar refraction R_M and limiting apparent molar adiabatic compressibility (ϕ_K^0) in solution.

5.2.Experimental Section

5.2.1 *Source and purity of samples*

[$EPyBF_4$]of puriss grade was procured from Sigma-Aldrich, Germany and was used as purchased. The mass fraction purity of [$EPyBF_4$] was ≥ 0.99.The amino acids Glycine (S.D. Fine Chemicals, >99%), L-Alanine (S.D. Fine Chemicals, >98.5%), and L-Valine (LobaChemie, India, >99%) were used without further purification.

5.2. 2. Apparatus and Procedure

The density (ρ) was measured by means of vibrating-tube Anton Paar density-meter (DMA 4500M) with an accuracy of 0.00005 g·cm^{-3}. It was calibrated by double-distilled water and dry air. [12]

The viscosity was measured using a Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 having an accuracy of 1.0% and fitted to a Brookfield Digital Bath TC-500.

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. The uncertainty of refractive index measurement was 0.0002.

The ultrasonic velocities, *u* (ms^{-1}) were measured using an ultrasonic interferometer (Model M 83) from Mittal enterprises. The interferometer working at 2 MHz is based on the same principle as was used by Freyer et al. [13] and Kiyoharo et al.[14-15]The obtained velocities were corrected for diffraction errors as given by Subrahmayan et al.[16]The maximum uncertainty in the velocity is 0.5ms^{-1}.

5.3. Results and Discussions

5.3.1. Density Calculation

The physical properties of different mass fraction of the aqueous ionic liquid mixture are listed in Table 1.The measured experimental values of densities, viscosities, refractive index and ultrasonic speeds of the three amino acids in different mass fractions (w_1 = 0.001, 0.003, 0.005) of aqueous ionic liquid [$EPyBF_4$] solution at 298.15 K as a function of concentration (molality) are listed in Table 2. Volumetric properties, such as ϕ_V and ϕ_V^0 are regarded as sensitive tools for the understanding of interactions in solutions.For this purpose, the apparent molar volumes ϕ_V given in Table 3 were determined from the solution densities using the following equation

$$\phi_V = M/\rho - (\rho - \rho_o)/m\rho_o\rho \qquad (1)$$

Where M is the molar mass of the solute, m is the molality of the solution, $\rho$and ρ_0 are the densities of the solution and aqueous ionic liquid mixture, respectively. The limiting apparent molar volumes ϕ_V^0 were calculated using a least-squares treatment to the plots of ϕ_V versus $c^{1/2}$ using the following Masson equation [17]

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{c} \qquad (2)$$

where ϕ_V^0 is the limiting apparent molar volume at infinite dilution and S_V^* is the experimental slope. The plots of ϕ_V against the square root of the molar concentration $c^{1/2}$ were found to be linear with negative slopes. The values of ϕ_V^0 and S_V^* are reported in Table 4. The variation of ϕ_V^0 for these three amino acids with the mass fraction of the ionic liquid is shown in Figure 1.

Table 4 shows that ϕ_V^0 values for the studied amino acids are positive and increase with an increase in concentrations, indicating the presence of strong solute-solvent interactions and these interactions are further reinforced as the mass fraction of aqueous IL in the mixture increases. From this study we can say that the trend in the solute-solvent interaction is

Glycine < L-Alanine < L-Valine

This observation can be interpreted in such a way that with the increase in the number of carbon atoms in the studied amino acids, the solute-solvent interaction also increases. Similar results were found for amino acid in methanoic acid (Formic acid).[18]

The S_V^* values of the amino acid solutions given in Table 4 decrease with the increase in the number of carbon atoms of the studied amino acids and also with the increase in the mass fraction of [EPyBF$_4$] in the solvent mixture rendering minimum solute-solute interaction in the higher equivalents.

5.3.2. **Viscosity Calculation**

The viscosity data has been analyzed using Jones–Dole equation. [19]

$$\left(\eta/\eta_0 - 1\right)/\sqrt{c} = A + B\sqrt{c} \qquad (3)$$

where η_0 and η are the viscosities of the solvent and solution respectively. The coefficients A and B were estimated by a least squares method and are reported in Table 4. The values of the A coefficient are found to decrease from glycine to valine and with the increase in mass fraction of aqueous ionic liquid mixture. The results indicate the presence of very weak solute–solute interactions. These results are in excellent agreement with those obtained from S_V^* values discussed earlier.

The genuine effects of solute-solvent interactions on the solution viscosity can be concluded from the B-coefficient [20-21].The viscosity B-coefficient is a valuable tool to provide information regarding the solvation of the solutes and their effects on the structure of the solvent. From Table 4 and Figure 2 it is evident that the values of the B-coefficient are positive, thereby suggesting the presence of strong solute-solvent interactions. The higher B-coefficient values for higher viscosity are due to the solvated solute molecules associated with the solvent molecules, and this type of interactions is strengthened with a rise of mass fraction (w_1) of aqueous ionic liquid solution. These findings are in agreement with the results obtained from ϕ_V^0 values discussed earlier.

5.3.3. **Refractive index Calculation**

The molar refraction, R_M can be evaluated from Lorentz-Lorenz relation [22]

$$R_M = \{(n_D^2-1)/ (n_D^2+2)\} (M/\rho) \quad (4)$$

where R_M, n_D, M and ρ are the molar refraction, refractive index, molar mass and density of solution, respectively. As stated by Deetlefs et al.[23] the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser. Tables2 and 3 show that the refractive indices (n_D) and the molar refractions (R_M) increase with the increase of mass fraction of aqueous ionic liquid mixture.

Tables 2 and3 show that the refractive index and the molar refraction values, respectively are higher for L-Valine compared to the other two amino acids indicating the fact that the molecules are more tightly packed in the mixture. The interaction in the solution is basically solute–solvent interaction and a small amount of solute–solute interaction. This is also in good agreement with the results obtained from density and viscosity parameters discussed above. The trend in the package of the studied amino acids in aqueous mixture of ionic liquid is

Glycine < L-Alanine < L-Valine

5.3.4. **Ultrasonic Speed Calculation**

The adiabatic compressibility (β) was evaluated from the following equation:

$$\beta = 1/u^2\rho \quad (5)$$

Where ρ is the density of the solution and u is the speed of sound in the solution.

The apparent molar adiabatic compressibility ϕ_K of the solution was determined from the relation

$$\phi_K = M\beta/\rho + \left(\beta\rho_o - \beta_o\rho\right) / m\rho\rho_o \quad (6)$$

Where β_0 and β are the adiabatic compressibility of the solvent and solution, respectively and m is the molality of the solution. Limiting molar adiabatic

compressibilities (ϕ_K^0) and experimental slopes (S_K^*) were obtained by fitting ϕ_K against the square root of molality ($\sqrt{m}$) using the least squares method.

$$\phi_K = \phi_K^0 + S_K^* \cdot \sqrt{m} \qquad (7)$$

The values of $\sqrt{m}$ and ϕ_K are reported in Table 3 and the values of ϕ_K^0 and S_K^* are presented in Table 4.The values of ϕ_K^0 and S_K^* are important parameters providing information about the extent of solute-solvent and solute-solute interaction, respectively. The behavior is useful for characterizing solvation and electrostriction (the contraction of the solvent around the solute) of salts in solutions.

From Table 4 and Fig. 3, it is observed that the values of limiting apparent molar compressibility ϕ_K^0 are positive and increase with the increase in concentration (w_1) of ionic liquid solution for all the studied solutions, indicating a stronger solute-solvent interaction. This is consistent with the conclusions drawn from the ϕ_V^0 values discussed earlier. It is also observed that the values of ϕ_K^0 for the studied amino acids follow the order:

Glycine < L-Alanine < L-Valine

Since the contribution of methylene group to the apparent compressibility is positive, it implies that the ions having the larger hydrophobic group may have more positive values for the molarcompressibility. Hence, L-Valine, which has the largest hydrophobic group, has the highest ϕ_K^0 values.

5.4. Conclusion

Extensive study of thermophysical and thermodynamic properties of simple amino acids in aqueous 1-ethylpyridinium tetrafluoroborate [$EPyBF_4$] solution at 298.15 K was done. It is evident that of the investigated amino acids L-Valine shows stronger association with the solvent molecules than L-Alanine, which, in turn, shows stronger association than Glycine.The derived properties obtained from the studies of thermophysical properties suggest that the solute–solvent interaction is dominant over the solute–solute interaction in solutions. Above all, this study demands a novelty of some amino acids prevailing in the aqueous solutions of 1-ethylpyridinium tetrafluoroborate [$EPyBF_4$].

TABLES:

Table 1. The values of Density (ρ), Viscosity (η), Refractive index (n_D), and Speed of sound (u) in different mass fraction of 1-ethylpyridinium tetrafluoroborate solution at 298.15K[a]

Mass-fraction of 1-ethylpyridinium tetrafluoroborate	ρx 10^{-3} (kg m^{-3})	η (mPa s)	n_D	U (ms^{-1})
w_1 = 0.001	0.99715	0.91	1.3336	1499.8
w_1 = 0.003	0.99826	0.92	1.3343	1505.2
w_1 = 0.005	0.99933	0.93	1.3351	1515.4

[a]uncertinity of the density ***u(****ρ)=0.00005*x10^{-3} *kg.m^{-3};* viscosity ***u(****η)= 0.01mPa s;* refractive index ***u(****n_D)= 0.0002;* speed of sound ***u(****u)= 0.5 ms^{-1};* temperature ***u(****T)= 0.01K; 95%* level of confidence.

Table 2. Experimental values of Densities (ρ), Viscosities (η), Refractive Index (n_D) and Ultrasonic Speed (u)of L-Glycine, L-Alanine and L-Valine in different mass fraction of 1-ethylpyridinium tetrafluoroborate at 298.15K[a]

molality (mol kg^{-1})	ρ x 10^{-3} (kgm^{-3})	η (mPas)	n_D	u (ms^{-1})	molality (mol kg^{-1}	ρ x 10^{-3} (kgm^{-3})	η (mPa s)	n_D	u (ms^{-1})
w_1 = 0.001					w_1 = 0.003				
L-Glycine					L-Glycine				
0.1002	0.99743	0.92	1.3338	1505.1	0.1001	0.99846	0.92	1.3345	1510.2
0.1584	0.99789	0.93	1.3342	1517.4	0.1584	0.99883	0.93	1.3347	1524.3
0.2005	0.99834	0.93	1.3345	1534.6	0.2004	0.99942	0.93	1.335	1543.7
0.2351	0.99884	0.94	1.3348	1556.8	0.2350	0.99996	0.93	1.3353	1568.3
0.2654	0.99937	0.94	1.3351	1582.6	0.2652	1.00047	0.94	1.3355	1599.3
0.2925	0.99993	0.95	1.3354	1613.9	0.2924	1.00089	0.94	1.3357	1635.0

L-Alanine					L-Alanine				
0.1002	0.99738	0.92	1.3341	1504.2	0.1001	0.99844	0.93	1.3348	1507.4
0.1584	0.99781	0.93	1.3344	1515.4	0.1584	0.99884	0.94	1.3352	1520.5
0.2005	0.99824	0.94	1.3347	1531.5	0.2004	0.99931	0.94	1.3356	1539.4
0.2351	0.99867	0.95	1.335	1552.2	0.2350	0.99972	0.95	1.3359	1563.5
0.2654	0.9991	0.96	1.3353	1578.2	0.2652	1.00021	0.96	1.3362	1592.9
0.2925	0.99953	0.97	1.3356	1609.0	0.2924	1.00071	0.97	1.3365	1628.8
L-Valine					L-Valine				
0.1002	0.99735	0.92	1.3344	1503.3	0.1001	0.99841	0.93	1.3351	1506.5
0.1584	0.99774	0.93	1.3347	1513.4	0.1584	0.99878	0.94	1.3355	1518.7
0.2005	0.99814	0.93	1.335	1528.9	0.2004	0.99916	0.95	1.3359	1536.8
0.2351	0.99856	0.94	1.3353	1548.7	0.2350	0.99966	0.97	1.3363	1560.6
0.2654	0.99896	0.94	1.3356	1573.6	0.2652	1.00005	0.98	1.3366	1589.7
0.2925	0.99938	0.95	1.3359	1603.5	0.2924	1.00047	0.99	1.3369	1624.7
w_1 = 0.005									
L-Glycine									
0.1001	0.99951	0.93	1.3353	1515.6					
0.1583	0.99996	0.94	1.3357	1531.3					
0.2002	1.00051	0.94	1.3361	1553.7					
0.2349	1.00089	0.95	1.3364	1582.3					
0.2651	1.00139	0.95	1.3367	1616.3					
0.2922	1.00189	0.96	1.337	1658.4					
L-Alanine									
0.1001	0.99951	0.93	1.3355	1512.8					
0.1583	0.99996	0.94	1.3359	1527.5					
0.2002	1.00051	0.95	1.3363	1548.4					
0.2349	1.00089	0.96	1.3366	1576.0					
0.2651	1.00139	0.97	1.3369	1609.4					
0.2922	1.00189	0.98	1.3372	1650.7					
L-Valine									
0.1001	0.99943	0.93	1.3357	1511.8					

0.1583	0.99978	0.94	1.3361	1525.0					
0.2002	1.00028	0.96	1.3365	1544.8					
0.2349	1.00069	0.97	1.3369	1570.9					
0.2651	1.00112	0.99	1.3372	1602.8					
0.2922	1.00168	1.00	1.3375	1641.6					

[a]uncertinity of the molality $u(m)=0.0002 molkg^{-1}$; density $u(\rho)=0.00005$x10^{-3} $kg.m^{-3}$; viscosity $u(\eta)=0.01$ mPa s; refractive index $u(n_D)= 0.0002$; speed of sound $u(u)= 0.5$ ms^{-1}; temperature $u(T)= 0.01K$; 95% level of confidence.

Table 3. Molality, apparent molar volume (ϕ_V), $(\eta/\eta_0-1)/m^{1/2}$, molar refraction (R_M), adiabatic compressibility (β) and apparent molal adiabatic compressibility (ϕ_K) of L-Glycine,L- Alanine, and L-Valine in 1-ethylpyridinium tetrafluoroborateat 298.15 K

molality (mol kg^{-1})	ϕ_V x 10^6 (m^3mol^{-1})	$(\eta/\eta_0-1)/m^{1/2}$ ($kg^{1/2}$ $mol^{-1/2}$)	R_M (cm^3 mol^{-1})	β x 10^{10} (Pa^{-1})	ϕ_K x 10^{10} (m^3 mol^{-1} Pa^{-1})
w_1 = 0.001					
L-Glycine					
0.1002	46.10	0.076	15.5151	4.4257	-2.4563
0.1584	44.78	0.089	15.5248	4.3522	-3.8040
0.2005	43.79	0.098	15.5304	4.2533	-4.7768
0.2351	42.98	0.106	15.5353	4.1308	-5.6517
0.2654	42.22	0.115	15.5397	3.9951	-6.3420
0.2925	41.48	0.123	15.5436	3.8395	-7.0241
L-Alanine					
0.1002	66.2789	0.098	18.4277	4.4312	-1.8191
0.1584	62.8692	0.131	18.4342	4.3641	-3.2530
0.2005	62.0167	0.152	18.4409	4.2710	-4.2610
0.2352	61.6293	0.171	18.4466	4.1560	-5.1164
0.2655	61.4079	0.193	18.4518	4.0185	-5.9282
0.2927	61.2646	0.205	18.4565	3.8644	-6.6478

L-Valine					
0.1002	97.4277	0.1086	24.2515	4.4367	-1.1359
0.1585	93.8174	0.1579	24.2600	4.3759	-2.6406
0.2006	92.6641	0.1953	24.2688	4.2859	-3.7496
0.2354	91.7752	0.2265	24.2763	4.1759	-4.6307
0.2658	91.5538	0.2579	24.2832	4.0426	-5.4482
0.2931	91.1746	0.2859	24.2892	3.8916	-6.1934
w_1 = 0.003					
L-Glycine					
0.1001	55.1660	0.032	15.5286	4.3913	-2.5940
0.1583	52.3611	0.048	15.5312	4.3089	-4.2056
0.2004	46.1503	0.059	15.5347	4.1988	-5.3233
0.2350	44.2379	0.069	15.5389	4.0659	-6.2413
0.2653	43.5744	0.078	15.5394	3.9078	-7.1238
0.2924	44.2057	0.085	15.5413	3.7374	-7.8350
L-Alanine					
0.1001	71.2139	0.076	18.4440	4.4077	-2.0565
0.1584	66.0048	0.109	18.4566	4.3304	-3.7534
0.2004	62.9495	0.135	18.4679	4.2227	-4.9430
0.2352	62.6536	0.157	18.4753	4.0919	-5.9006
0.2654	61.3396	0.175	18.4812	3.9403	-6.7485
0.2926	60.3715	0.192	18.4869	3.7666	-7.5572
L-Valine					
0.1001	102.3281	0.087	24.2737	4.4131	-1.3779
0.1585	96.5179	0.143	24.2909	4.3409	-3.1962
0.2006	94.8150	0.184	24.3079	4.2377	-4.4277
0.2354	91.8553	0.221	24.3220	4.1073	-5.4885
0.2657	91.7382	0.249	24.3322	3.9568	-6.3767
0.2930	91.3089	0.270	24.3416	3.7866	-7.1844
w_1 = 0.005					
L-Glycine					

0.1001	57.1083	0.054	15.5459	4.3555	-2.8370
0.1583	49.9034	0.075	15.5557	4.2647	-4.6513
0.2003	45.6006	0.086	15.5640	4.1404	-5.9550
0.2350	46.7377	0.096	15.5706	3.9905	-6.9978
0.2652	45.6720	0.106	15.5755	3.8225	-7.8602
0.2923	44.9825	0.114	15.5803	3.6291	-8.7166
L-Alanine					
0.1001	78.1424	0.075	18.4605	4.3720	-2.2626
0.1583	67.1350	0.116	18.4723	4.2863	-4.1757
0.2004	64.6333	0.140	18.4843	4.1696	-5.4298
0.2351	62.2226	0.160	18.4900	4.0228	-6.5508
0.2654	60.8451	0.183	18.4957	3.8557	-7.4819
0.2926	59.8360	0.199	18.5012	3.6633	-8.3808
L-Valine					
0.1001	107.2218	0.086	24.2883	4.3778	-1.5508
0.1584	99.2165	0.136	24.3060	4.3008	-3.4542
0.2005	93.4626	0.183	24.3200	4.1892	-4.8126
0.2353	92.4847	0.220	24.3363	4.0495	-5.9328
0.2657	91.6400	0.251	24.3454	3.8882	-6.8818
0.2930	89.5629	0.283	24.3515	3.7045	-7.7651

Table 4. Limiting apparent molar volumes (ϕ_V^0), experimental slopes(S_V^*), *A*, *B* coefficients, limitingapparent molar compressibility (ϕ_K^0), and experimental slope (S_K^*) of L-Glycine, L-Alanine, and L-Valine in aqueous 1-ethylpyridinium tetrafluoroborateat 298.15 K

Salt	ϕ_V^0 x 10^6 ($m^3 mol^{-1}$)	S_V^* x 10^6 (m^3 $mol^{-3/2}$ $kg^{1/2}$)	*A* ($kg\ mol^{-1}$)	*B* ($kg^{1/2}\ mol^{-1/2}$)	ϕ_K^0 x 10^{10} (m^3 mol^{-1} Pa^{-1})	S_K^* x 10^4 (m^3 $mol^{-3/2}$ Pa^{-1} $kg^{1/2}$)
w_1 = 0.001						
L-Glycine	48.11	−22.85	0.0511	0.24	0.05	−23.75
L-Alanine	69.11	−39.14	0.0415	0.55	0.71	−24.98
L-Valine	101.25	−40.21	0.0239	0.91	1.49	−26.15
w_1 = 0.003						
L-Glycine	61.55	−26.03	0.0221	0.27	0.12	−27.25
L-Alanine	77.25	−35.91	0.0135	0.60	0.77	−28.43
L-Valine	108.87	−55.71	0.0031	0.96	1.59	−30.05
w_1 = 0.005						
L-Glycine	65.88	−30.62	0.0101	0.30	0.18	−30.49
L-Alanine	89.25	−49.19	0.0092	0.63	0.87	−31.60
L-Valine	117.02	−69.23	0.0022	1.03	1.65	−32.20

FIGURES:

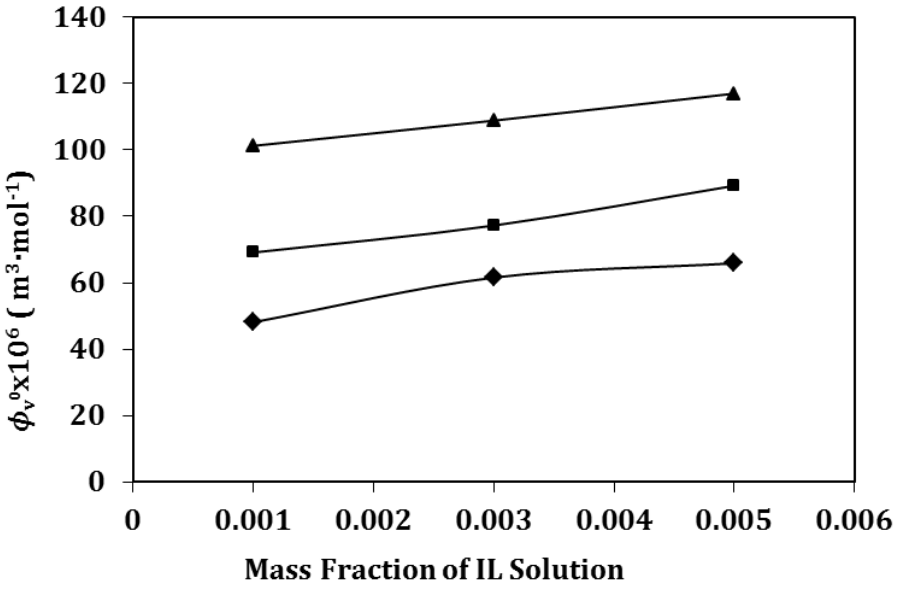

Fig 1. Plot of limiting apparent molar volume (ϕ_V^0) for glycine (♦), alanine (■) and valine (▲)against mass fraction of aqueous ionic liquid solution.

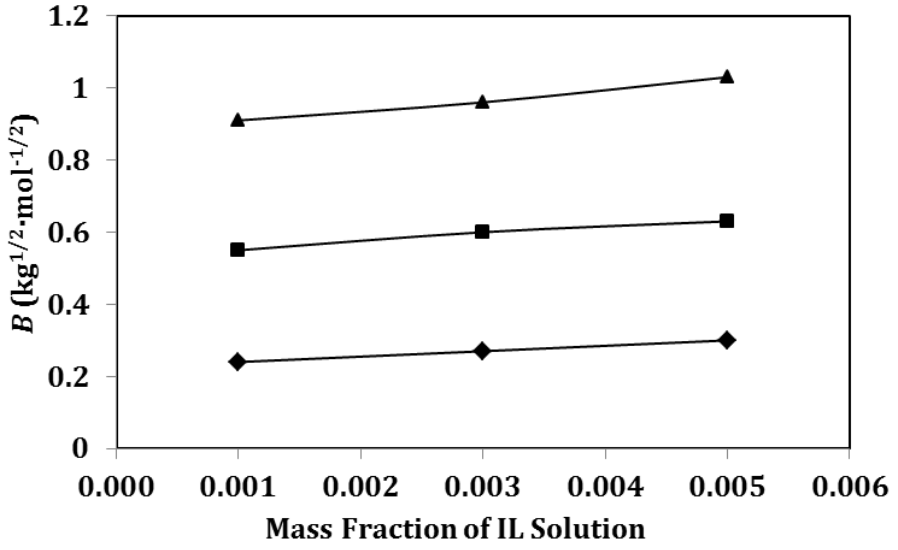

Fig 2. Plot of Viscosity *B*-coefficient for glycine (♦), alanine (■) and valine (▲) against mass fraction of aqueous ionic liquid solution.

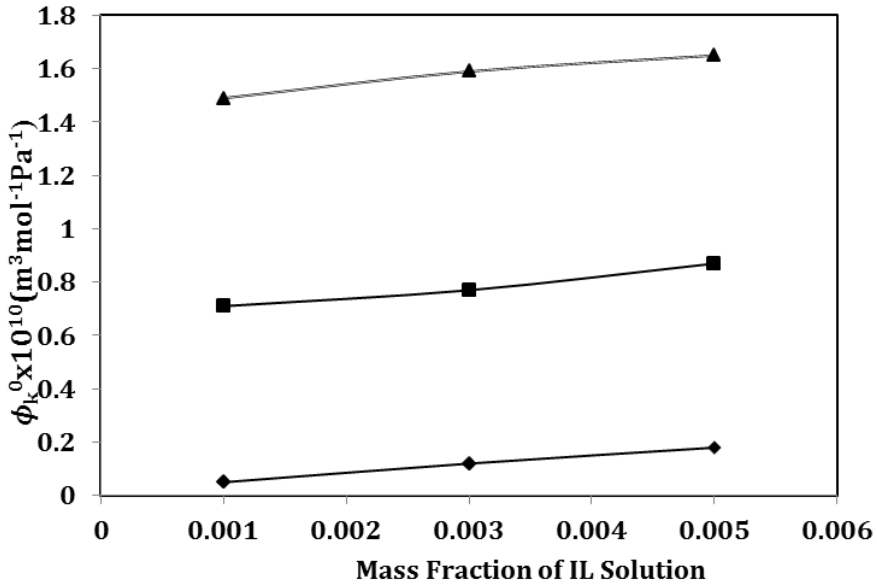

Fig 3. Plot of limiting molar compressibility (ϕ_K^0) for glycine (♦), alanine (■) and valine (▲) against mass fraction of aqueous ionic liquid solution