PHYSICO-CHEMICAL STUDIES OF L-PROLINE AND L- LEUCINE IN AQUEOUS TETRABUTYLPHOSPHONIUM *P* -TOLUENE SULPHONATE SOLUTIONS AT DIFFERENT TEMPERATURES WITH THE MANIFESTATION OF SOLVATION CONSEQUENCES

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Apparent molar volumes (ϕ_V), viscosity *B*-coefficients and apparent molar isentropic compressibilty for L-leucine and L-proline in (0.001, 0.003, and 0.005) mol · kg^{-1} aqueous tetrabutyl phosphonium p-toluene sulphonate solutions have been determined at (298.15, 303.15, and 308.15) K from solution density, ρ, viscosity, η and at 298.15 K from solution's speed of sound u measurements as a function of the concentration of L-leucine and L-proline. The limiting apparent molar volume (ϕ_V^0) and experimental slopes (S_V^*) obtained from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The viscosity data were analyzed using the Jones-Dole equation, and the derived parameters *A* and *B* have also been interpreted in terms of solute-solute and solute-solvent interactions, respectively, in the mixed solutions. The limiting apparent molar isentropic compressibility ($\emptyset_K^o$) and experimental slopes, (S_K^*) values are also in perfect agreement with the above mentioned parameters. The refractive index(nD), molar refraction (R_M) has also been reported.

1. INTRODUCTION

The exploration of molecular interaction in solution is always an interest to chemists. The study of volumetric and viscometric properties allows investigation into the molecular interaction in solution phase, specificallyallows us to understand the nature and strength of the intermolecular forces operating among mixed components.[1-3]

The complexity in the nature of interactionarise in the solution consisting of multiple solutes or solvents and hinders the solution to behave ideally.This deviation from ideality are expressed in terms of thermodynamic parameters such as apparent molar properties in case of solid-liquid mixtures. These thermodynamic properties of solvent mixtures quantifies the difference between the actual property and the ideal property and thereforeare useful in the study of molecular interactions and arraangements. In particular, they reflect the interaction that take place between solutes, solute-solvent and solvent-solvent species. At the molecular level, the addition of a solute modifies not only the exisitng solvent structure (the existing interaction)but also rearranges the interaction of the solute molecules. The extent of solute-solvation reorganizationstricty depends upon the interactions taking place between solute-solute, solute-solvent, solvent-solvent species. Thus quantification of these interactions becomes important to understand a solution system. For example, the understanding of all the interaction of a drug in solution (blood plasma ,etc)becomes important to formulate its course of dissolution, transport and action in human body. In solution chemistry, elucidation of the nature of interaction are done through experimental studies involving density, viscosity, and refractive index measurements.

The present research work is intimately related to the studies of solute-solute, and solvent-solvent interactions of L-proline and L-leucine in aqueous tetrabutylphosphonium *p*-toluene sulphonate (TBPPTS) solutions at 298.15, 303.15 and 308.15K probed by density, viscosity and refractive index measurements.

Ionic liquids (ILs) are one of the most interesting and rapidly developing areas of modern physical chemistry, technologies and engineering, their molecular interaction with amino acids would be of utmost importance for pharmaceutical applications.[4-6]

2. Experimental Section

2.1. Source and purity of samples

Tetrabutylphosphonium p-toluene sulphonate (TBPPTS) was procured from Sigma Aldrich (assay >95%), L-proline and L-leucine were also purchased from Sigma Aldrich (assay > 99% and >98%). Triply distilled water with a specific conductance $<10^{-6}$ S cm^{-1} was used for the preparation of different aqueous solutions. The physical properties of 0.001, 0.003 and 0.005 molalities of aqueous TBPPTS solutions are listed in Table 1.

2.2. Apparatus and Procedure

The Density (ρ) was measured by means of vibrating-tube Anton Paar Density-Meter (DMA 4500M) with a precision of 0.00005 g.cm^{-3}. It was calibrated by double-distilled water and dry air.The temperature was automatically kept constant within ± 0.01 K.

The viscosity (η) was measured using a Brookfield DVIII Ultra Programmable Rheometer with fitted spindle size of 42.The viscosities were obtained using the following equation:

$$\eta = (100/RPM) \times TK \times torque \times SMC \quad (1)$$

where RPM, TK (0.09373) and SMC (0.327) are the speed, viscometer torque constant and spindle multiplier constant, respectively. The instrument was calibrated against the standard viscosity samples supplied with the instrument, water and aqueous CaCl$_2$ solutions.[7] Temperature of the solution was maintained to within ± 0.01∘C using Brookfield Digital TC-500 temperature thermostat bath. The viscosities were measured with an accuracy of ±0.1%. Each measurement reported herein is an average of triplicate reading with a precision of 0.3%.

Refractive index was measured with the help of a Digital Refractometer Mettler Toledo. The light source was LED with λ=589.3 nm. 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 units. The solutions studied here were prepared by mass and the conversion of molarity into molality was accomplishedusing experimental density values.[8]

The ultrasonic speed (u) was measured by multifrequency ultrasonic interferometer (Model M-81) from Mitral Enterprises, India. The interferometer working at 5Mhz is based on the

same principles as was used by Freyer et atl.[9] and Kiyoharo et al.[10] The obtained speeds were corrected for diffraction errors as given by Murthy and Subramanyam.[11] The uncertainty in the speed is $\pm$ 0.2ms^{-1}. The temperature was controlled within $\pm$ 0.012K using a Lauda thermostat during the measurement.

The experimental values of densities (ρ), viscosities (η), speed of sound (u) and refractive indices (n_D) of solutions are reported in Table 2 and the derived parameters are reported in Table 3 and Table 4.

3. RESULTS AND DISCUSSION

3.1. Density calculation

Apparent molar volumes (ϕ_V) were determined from the density of the solutions using the following equation[12]

$$.\phi_V = M / \rho - 1000(\rho - \rho_o)/m\rho\rho_o \ (2)$$

Where, M is the molar mass of the solute (L-Proline or L-Leucine), m is the molality of the solution ρ_0 and ρ are the densities of the mixture (of TBPPTS & water) and the solution respectively. The limiting apparent molar volume ϕ_V^0 was calculated by least-square treatment to the plots of ϕ_V _versus_ $\sqrt{m}$ using the Masson equation.[13]

$$\phi_V = \phi_V^0 + S_V^* \sqrt{m} \ (3)$$

where ϕ_V^0 is the limiting apparent molar volume at infinite dilution and S_V^* is the volumetric virial coefficient. A plot of ϕ_V against square root of molal concentration ($\sqrt{m}$) is linear with S_V^* as slopes. The values of ϕ_V^0 and S_V^* are reported in Table 4.

A perusal of Table 4 shows that ϕ_V^0 values for L-proline and L-leucine increases with the increase in amount of TBPPTS in solvent mixture and are higher in case of L-leucine than L-proline. This indicates the presence of strong solute-solvent interactions and that these interactions aremore in case of L-leucine than L-proline. Furthermore, linear increasewith the increase in temperature is also noted.

L-proline< L-leucine

The volumetric virial coefficient S_V^* characterizes the pair wise interaction of solvated species in solution.[14-17] The sign of S_V^* determines the interaction between the solute species. In the present study S_V^* values were found to be negative and decrease further with the increase of temperature and the amount of TBPPTS in solvent mixture. This trend in S_V^* values indicate weak solute-solute interactions in the mixtures. A quantitative comparison of the magnitude of values shows that ϕ_V^0 values are much greater in magnitude than those of S_V^* for all of the solutions. This suggests that solute-solvent interactions dominate over solute-solute interactions in all of the solutions and at all experimental temperatures. Furthermore, S_V^* values are negative at all temperatures, and the values decrease with the increase of all experimental temperatures which may be attributed to more violent thermal agitation at higher temperatures, resulting in diminishing the force of solute-solute interactions. Again, the S_V^* values decrease with the increasing amount of TBPPTS in the solvent mixture which may be attributed to the increase in the solvation of ions.

3.2. Viscosity calculation

The viscosity data has been analyzed using Jones-Doleequation.[18]

$$\left(\eta / \eta_0 - 1 \right) / \ m^{1/2} = \ A \ + \ Bm^{1/2} \ (4)$$

where η_0 and η are the viscosities of the solvent and solution respectively. *A* and *B* are the viscosity co-efficient estimated by a least-squares method and are reported in Table 4. The values of the *A* co-efficient were found to decrease with the increase in amount of TBPPTS in the solvent mixture and also with the experimental temperature. The results indicate the presence of very weak solute-solute interactions. These results are in excellent agreement with those obtained from S_V^* values discuss earlier.

The effects of solute-solvent interactions on the solution viscosity can be inferred from the *B*-coefficient.[19,20] The viscosity *B*-coefficient is a valuable tool to provide information concerning 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, and strengthened with the amount of TBPPTS in solvent mixture and with the experimental temperatures and is in excellent agreement with the results obtained from ϕ_V^0 values discussed earlier.

3.3. Refractive index calculation

The molar refraction, R can be evaluated from the Lorentz-Lorenz relation.[21]

$$R = \left\{(n_D^2 - 1)/(n_D^2 + 2)\right\}(M/\rho) \quad (5)$$

where R, n_D, M and ρ are the molar refraction, the refractive index, the molar mass and the density of solution respectively. The refractive index of a substance is defined as the ratio c_0/c, where c is the speed of light in the medium and c_0 the speed of light in vacuum. Stated more simply, 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.[22]

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 and with the increase of amount of TBPPTS in solvent mixture refractive index value also increases. Hence a perusal of Tables 2 and 3 it is inferred that the refractive index and the molar refraction values respectively are higher for L-leucine compare to L-proline, 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 good agreement with the results obtained from density and viscosity parameters discussed above. The trend in the package of the studied amino acid in aqueous TBPPTS is L-proline< L-leucine

3.4 Ultrasonicspeed calculation

Apparentmolarisentropiccompressibility

The adiabatic compressibility, defined by the thermodynamic relation:

$$\beta_S = -\frac{1}{V}(\partial V/\partial P)_S \quad (6)$$

where V is volume, P is pressure and S is entropy. The β_S is related to the solution density ρ, and the ultra sonic speed u, by the Newton–Laplace's equation:

$$\beta_S = \frac{1}{u^2 \rho} \quad (7)$$

Providing the relation between thermodynamics and acoustics.

Theapparentmolaradiabaticcompressibility$(\emptyset_K)$ of the solutions was determined from the following relation:

$$\emptyset_K = \frac{M\beta_s}{\rho} + 1000(\beta_s\rho_o - \beta_o\rho)/m\rho\rho_o \quad (8)$$

Where β_o and β_s are the adiabatic compressibilities of the binary solution and ternary solution, respectively, and *m* is the molarity of the ternary solution. The values of $\emptyset_K$ are reported in Table3. Limiting apparent molar adiabatic compressibility $(\emptyset_K^o)$ or apparent molar adiabatic compressibility at infinite dilution and experimental slopes,(S_K^*), were obtained by fitting $\emptyset_K$ against the square root of concentration using the least-square method[24]

$$\emptyset_K = \emptyset_K^o + S_K^* \cdot \sqrt{m} \quad (9)$$

The values of $\emptyset_K^o$ and S_K^* are presented in Table 4. The values are important parameters that provided information about the extent of solute-solvent and solute-solute interaction, respectively. The behavior is useful in characteristic of solvation and electrostriction (the contraction of the solvent around the solute) of salt in solutions. From Table 4 it is observed that the values of limiting apparent molar isentropic compressibility is positive and increases with the increase in amount of TBPPTS in solvent mixture and are higher in case of L-leucine than L-proline and hence indicates shows strong solute solvent interaction. The result is in good agreement with the ϕ_V^0 values discussed earlier.

TABLES

Table 1: Densities (ρ) and Viscosities(η) of aqueous tetrabutyl phosphonium *p*-toluene sulphonate solutions at 298.15K, 303.15K and 308.15K and refractive index at 298.15K.

T (K)	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPas)	n_D	u (ms^{-1})
		$m_1=0.001^a$		
298.15	0.9989	0.902	1.3320	1488.2
303.15	0.9974	0.819		
308.15	0.9959	0.742		
		$m_1=0.003^a$		
298.15	1.0004	0.914	1.3332	1498.3
303.15	0.9989	0.831		
308.15	0.9974	0.755		
		$m_1=0.005^a$		
298.15	1.0018	0.931	1.3345	1530.1
303.15	1.0004	0.855		
308.15	0.9989	0.772		

^{a}Molality of tetrabutyl phosphonium *p*-toluene sulphonate in water in mol·kg^{-1}

Table 2: Experimental values of densities (ρ) and viscosities (η)of L-Proline and L-Leucine in different molalities (m_1) of aqueous tetrabutyl phosphonium *p*-toluene sulphonate solutions at 298.15K, 303.15K and 308.15K and refractive Index (n_D)and speed of soumd (u)at 298.15K.

m (mol·kg^{-1})	ρ x 10^{-3} (kg· m^{-3})	η (mPa·s)	n_D	u (ms^{-1})	m (mol·kg^{-1})	ρx 10^{-3} (kg· m^{-3})	η (mPa·s)	m (mol·kg^{-1})	ρ x 10^{-3} (kg· m^{-3})	η (mPas)
					L-Proline					
		298.15K				303.15K			318.15K	
					m_1 = 0.001					
0.0100	0.99939	0.921	1.3326	1495.6	0.0100	0.99784	0.837	0.0100	0.99631	0.764
0.0251	1.00028	0.942	1.3332	1498.0	0.0251	0.99867	0.859	0.0251	0.99730	0.792
0.0401	1.00126	0.963	1.3337	1507.8	0.0401	0.99966	0.880	0.0401	0.99854	0.818
0.0552	1.00227	0.982	1.3342	1515.8	0.0552	1.00079	0.901	0.0552	0.99991	0.846
0.0703	1.00335	1.002	1.3347	1527.4	0.0703	1.00198	0.920	0.0702	1.00154	0.871
0.0855	1.00445	1.020	1.3353	1539.8	0.0854	1.00332	0.940	0.0853	1.00324	0.900
					m_1 = 0.003					
0.0100	1.00088	0.933	1.3351	1505.8	0.0100	0.99927	0.848	0.0100	0.99751	0.775
0.0250	1.00171	0.956	1.3357	1513.8	0.0251	1.00009	0.870	0.0251	0.99820	0.804
0.0401	1.00264	0.978	1.3362	1517.8	0.0401	1.00113	0.891	0.0402	0.99933	0.830
0.0551	1.00365	0.999	1.3367	1523.8	0.0552	1.00238	0.910	0.0553	1.00074	0.858
0.0702	1.00473	1.019	1.3372	1533.8	0.0703	1.00372	0.931	0.0704	1.00253	0.886
0.0853	1.00586	1.039	1.3378	1543.8	0.0854	1.00522	0.952	0.0854	1.00454	0.911
					m_1 = 0.005					
0.0100	1.00201	0.950	1.3365	1537.8	0.0100	1.00046	0.866	0.0100	0.99897	0.792
0.0250	1.00252	0.973	1.3369	1558.0	0.0250	1.00097	0.886	0.0251	0.99962	0.821
0.0401	1.00322	0.995	1.3374	1565.8	0.0401	1.00173	0.906	0.0402	1.00071	0.848
0.0551	1.00406	1.017	1.3379	1583.8	0.0552	1.00272	0.927	0.0552	1.00207	0.876
0.0702	1.00508	1.040	1.3385	1595.8	0.0703	1.00399	0.948	0.0703	1.00353	0.905
0.0853	1.00612	1.061	1.3390	1617.8	0.0854	1.00531	0.969	0.0854	1.00528	0.932
					L-Leucine					

298.15K						303.15K			318.15K	
					$m= 0.001$					
0.0100	0.99943	0.926	1.3335	1535.6	0.0100	0.99790	0.841	0.0101	0.99633	0.764
0.0251	1.00052	0.955	1.3339	1538.2	0.0251	0.99897	0.868	0.0252	0.99747	0.792
0.0402	1.00181	0.983	1.3345	1540.8	0.0402	1.00038	0.894	0.0403	0.99895	0.819
0.0552	1.00322	1.010	1.3350	1543.2	0.0553	1.00199	0.920	0.0554	1.00080	0.848
0.0703	1.00478	1.039	1.3356	1545.0	0.0704	1.00373	0.946	0.0705	1.00284	0.874
0.0854	1.00643	1.067	1.3362	1548.8	0.0855	1.00567	0.974	0.0855	1.00509	0.902
					$m= 0.003$					
0.0100	1.00087	0.937	1.3360	1548.2	0.0100	0.99932	0.854	0.0100	0.99753	0.778
0.0250	1.00183	0.967	1.3364	1550.0	0.0251	1.00031	0.884	0.0251	0.99853	0.811
0.0401	1.00301	0.995	1.3370	1552.0	0.0401	1.00169	0.913	0.0402	1.00008	0.845
0.0552	1.00437	1.022	1.3375	1554.4	0.0552	1.00331	0.943	0.0553	1.00203	0.876
0.0702	1.00582	1.051	1.3381	1556.6	0.0703	1.00505	0.970	0.0703	1.00442	0.911
0.0853	1.00751	1.080	1.3388	1558.6	0.0853	1.00710	1.002	0.0854	1.00693	0.941
					$m= 0.005$					
0.0100	1.00212	0.954	1.3373	1584.0	0.0100	1.00063	0.878	0.0100	0.99894	0.796
0.0250	1.00306	0.983	1.3383	1588.2	0.0250	1.00159	0.908	0.0251	0.99992	0.828
0.0400	1.00436	1.012	1.3393	1614.6	0.0401	1.00297	0.939	0.0402	1.00139	0.862
0.0551	1.00591	1.041	1.3403	1628.2	0.0551	1.00466	0.969	0.0552	1.00342	0.897
0.0701	1.00760	1.069	1.3413	1648.0	0.0702	1.00667	1.000	0.0702	1.00581	0.930
0.0851	1.00955	1.098	1.3423	1670.2	0.0852	1.00884	1.028	0.0852	1.00846	0.964

Table 3: Molality, apparent molar volume (ϕ_V),$(\eta/\eta_0-1)/m^{1/2}$ of L-Proline and L-Leucine in different molalities (m_1) of aqueoustetrabutyl phosphonium *p*-toluene sulphonate solutionsat 298.15K, 303.15K and 308.15K and molar refraction (R) and apparent molar adiabatic compressibility(ϕ_K)at 298.15K.

m (mol·kg^{-1})	ϕ_V x10^6 (m^3·mol^{-1})	$(\eta/\eta_0-1)/m^{1/2}$ (kg$^{1/2}$·mol$^{-1/2}$)	R (cm^3·mol^{-1})	ϕ_K x 10^{10} (m^3·mol^{-1}·Pa^{-1})	m (mol·kg^{-1})	ϕ_V x10^6 (m^3·mol^{-1})	$(\eta/\eta_0-1)/m^{1/2}$ (kg$^{1/2}$·mol$^{-1/2}$)	m (mol·kg^{-1})	ϕ_V x 10^6 (m^3·mol^{-1})	$(\eta/\eta_0-1)/m^{1/2}$ (kg$^{1/2}$·mol$^{-1/2}$)
					L-Proline					
	298.15					303.15			308.15	
				$m_1 = 0.001$						
0.0100	62.2713	0.210	23.6703	0.278	0.0100	75.3263	0.220	0.0100	75.4286	0.292
0.0251	58.3966	0.280	23.6867	0.260	0.0251	66.0212	0.308	0.0251	59.8191	0.426
0.0401	55.1929	0.338	23.6964	0.242	0.0401	59.6951	0.372	0.0401	49.3911	0.511
0.0552	53.1906	0.377	23.7073	0.231	0.0552	54.2637	0.426	0.0552	42.3505	0.596
0.0703	51.0453	0.418	23.7145	0.218	0.0703	50.2994	0.465	0.0702	34.6538	0.656
0.0855	49.4216	0.448	23.7213	0.208	0.0854	45.9623	0.505	0.0853	28.7147	0.728
				$m_1 = 0.003$						
0.0100	69.1010	0.208	23.7962	0.304	0.0100	80.2166	0.205	0.0100	103.3999	0.265
0.0250	63.5033	0.290	23.8138	0.277	0.0251	68.4039	0.297	0.0251	82.9465	0.410
0.0401	59.6050	0.350	23.8245	0.258	0.0401	60.0699	0.361	0.0402	66.8044	0.496
0.0551	56.3790	0.396	23.8352	0.242	0.0552	52.2774	0.405	0.0553	54.3628	0.581
0.0702	53.5361	0.433	23.8423	0.226	0.0703	46.6089	0.454	0.0704	41.8106	0.655
0.0853	51.1085	0.468	23.8507	0.213	0.0854	41.0567	0.498	0.0854	31.0935	0.707
				$m_1 = 0.005$						
0.0100	95.9554	0.204	23.8562	0.405	0.0100	106.0907	0.129	0.0100	106.2490	0.259
0.0250	86.9717	0.285	23.8756	0.357	0.0250	91.0963	0.229	0.0251	85.6259	0.401
0.0401	79.9844	0.343	23.8910	0.325	0.0401	81.1000	0.298	0.0402	69.4578	0.492
0.0551	74.2676	0.393	23.9030	0.295	0.0552	72.3759	0.359	0.0552	57.1941	0.574
0.0702	68.4340	0.442	23.9114	0.267	0.0703	63.3923	0.411	0.0703	48.7560	0.650
0.0853	64.4245	0.478	23.9199	0.245	0.0854	56.9913	0.456	0.0854	39.8805	0.710
					L-Leucine					

298.15						303.15			308.15	
				$m_1 = 0.001$						
0.0100	74.2809	0.266	27.0470	0.315	0.0100	85.4048	0.268	0.0101	89.5510	0.296
0.0251	64.8745	0.371	27.0507	0.273	0.0251	70.1711	0.378	0.0252	69.0744	0.425
0.0402	57.5194	0.448	27.0540	0.241	0.0402	57.8438	0.457	0.0403	55.4233	0.518
0.0552	51.9929	0.509	27.0563	0.217	0.0553	48.5960	0.525	0.0554	42.4657	0.608
0.0703	46.6905	0.573	27.0581	0.194	0.0704	41.4503	0.585	0.0705	32.3368	0.671
0.0854	42.2000	0.626	27.0598	0.174	0.0855	34.4684	0.647	0.0855	23.3029	0.738
				$m_1 = 0.003$						
0.0100	86.1338	0.252	27.1764	0.359	0.0100	91.2686	0.277	0.0100	117.4766	0.305
0.0250	74.7386	0.366	27.1833	0.310	0.0251	75.6517	0.403	0.0251	85.7939	0.469
0.0401	66.3921	0.443	27.1894	0.275	0.0401	62.0620	0.493	0.0402	64.0873	0.595
0.0552	59.3269	0.503	27.1934	0.244	0.0552	51.4073	0.574	0.0553	46.9288	0.682
0.0702	54.0045	0.566	27.1972	0.222	0.0703	43.6457	0.631	0.0703	30.8219	0.780
0.0853	47.7382	0.622	27.2003	0.195	0.0853	34.9725	0.705	0.0854	18.9843	0.843
				$m_1 = 0.005$						
0.0100	100.9862	0.247	27.2391	0.402	0.0100	105.1311	0.263	0.0100	125.3103	0.311
0.0250	81.4218	0.353	27.2867	0.322	0.0250	82.3395	0.392	0.0251	89.6704	0.459
0.0400	67.5471	0.435	27.3243	0.258	0.0401	66.2205	0.491	0.0402	68.4967	0.583
0.0551	56.7032	0.504	27.3550	0.213	0.0551	53.1503	0.568	0.0552	48.6791	0.690
0.0701	48.5103	0.560	27.3817	0.178	0.0702	41.1548	0.641	0.0702	32.2061	0.773
0.0851	40.1557	0.615	27.4012	0.143	0.0852	31.5113	0.694	0.0852	18.4848	0.853

Table 4: Limiting apparent molar volumes (ϕ_V^0), experimental slopes(S_V^*) and *A, B* coefficients of L-Proline and L-Leucine in different molalities (m_1) of aqueous tetrabutyl phosphonium *p*-toluene sulphonate solution at 298.15, 303.15 and 308.15K and limiting partial molar adiabatic compressibility (ϕ_K^0) and experimental slope (S_V^*) at 298.15K.

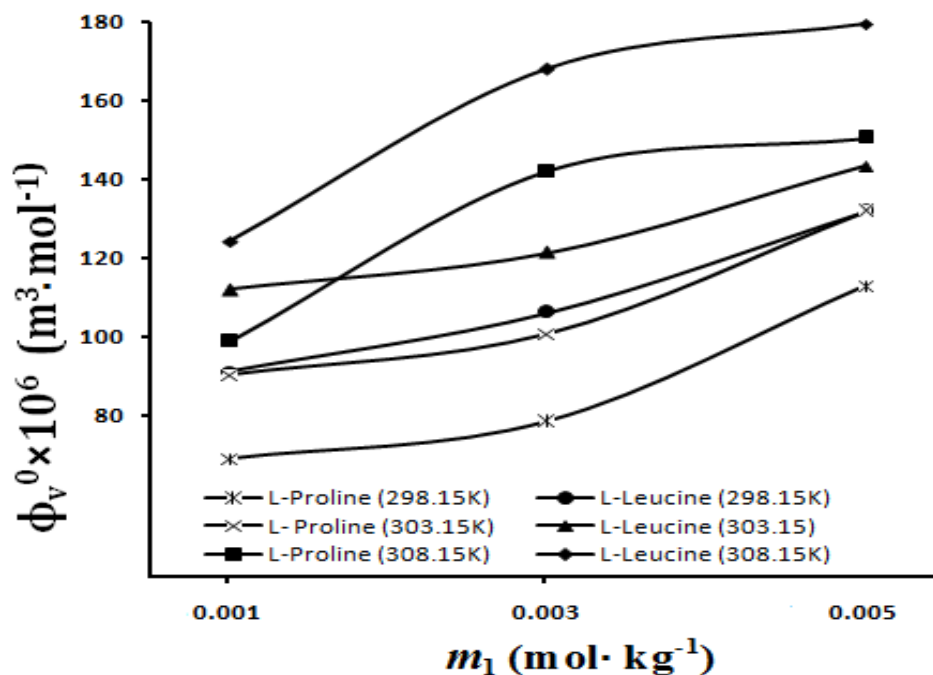| T(K)	ϕ_V^0 x 10^6 ($m^3 mol^{-1}$)	S_V^* x 10^6 ($m^3\ mol^{-3/2}\ kg^{1/2}$)	*A* (kg mol^{-1})	*B* ($kg^{1/2}\ mol^{-1/2}$)	ϕ_K^0 x 10^{10} ($m^3 \cdot mol^{-1} \cdot Pa^{-1}$)	S_V^* x 10^6 ($m^3\ mol^{-3/2}\ kg^{1/2} \cdot Pa^{-1}$)
			L-Proline			
			$m_1 = 0.001$			
298.15	68.94	-67.24	0.085	1.245	0.317	-0.371
303.15	90.27	-151.90	0.072	1.487		
308.15	98.78	-241.7	0.067	2.242		
			$m_1 = 0.003$			
298.15	78.39	-93.67	0.075	1.355	0.352	-0.472
303.15	100.70	-204.40	0.055	1.510		
308.15	141.90	-376.5	0.038	2.308		
			$m_1 = 0.005$			
298.15	112.90	-165.90	0.059	1.432	0.489	-0.835
303.15	131.80	-255.80	0.041	1.704		
308.15	150.4.	-406.24	0.026	2.341		
			L-Leucine			
			$m_1 = 0.001$			
298.15	91.16	-167.30	0.075	1.867	0.388	-0.732
303.15	111.90	-266.60	0.068	1.955		
308.15	124.10	-345.20	0.062	2.300		
			$m_1 = 0.003$			
298.15	106.00	-198.40	0.061	1.905	0.444	-0.847
303.15	121.20	-294.70	0.054	2.203		
308.15	168.00	-514.70	0.023	2.827		
			$m_1 = 0.005$			
298.15	131.70	-316.40	0.052	1.921	0.534	-1.351
303.15	143.30	-384.50	0.036	2.266		
308.15	179.40	-554.70	0.017	2.852		

FIGURES

Figure 1: The plots of limiting apparent molar volumes (ϕ_v^0) for L-Proline and L-Leucine in different molalities (m_1) of aqueous tetrabutyl phosphonium *p*-toluene sulphonate solutions at 298.15K, 303.15K and 308.15K.
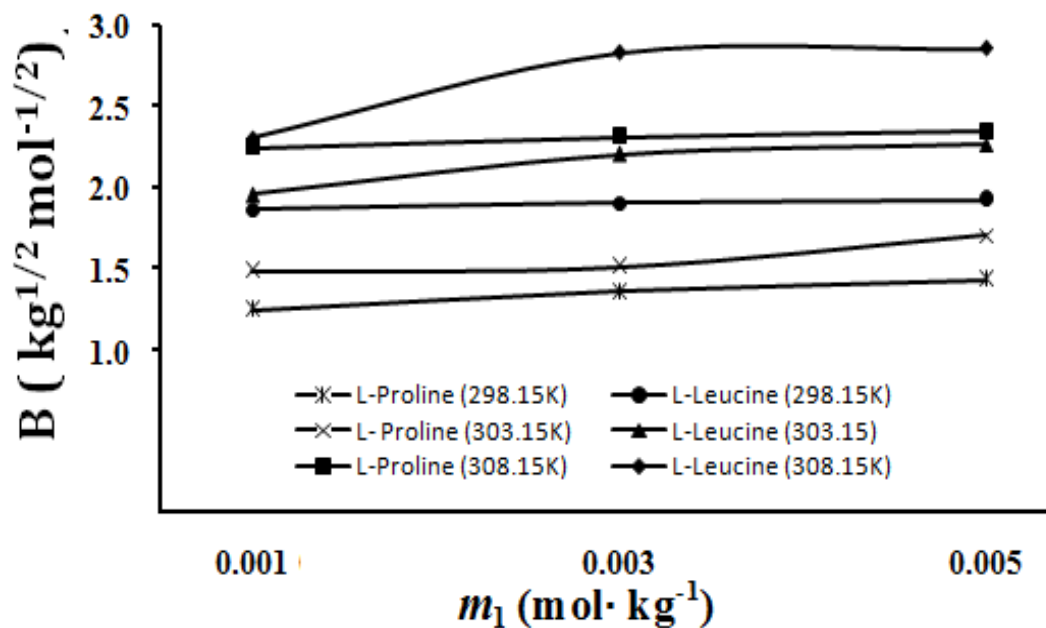

Figure 2: The plots of viscosity *B*-coefficient for L-Proline and L-Leucine in different molalities (m_1) of aqueous tetrabutyl phosphonium *p*-toluene sulphonate solutions at 298.15K, 303.15K and 308.15K.

4. CONCLUSION

The values of the limiting apparent molar volume (ϕ_V^0), viscosity *B*-coefficients and limiting apparent molar isentropic compressibility indicates the presence of strong solute-solvent interactions which increases with the increase in amount of TBPPTS in solvent mixture and with the increase in the experimental temperature. The refractive index and the molar refraction values suggest that L-Leucine molecules are more tightly packed in the solution leading to higher solute-solvent interaction than L-Glycine.

6. REFERENCES

1. R. R. Dogonadze, E. Kalman, A. A. Kornyshev, J. Ulstrup, The Chemical Physics of Solvation, Part B, Spectroscopy Solvation, Elsevier, Amsterdam, 1986.

2. A. Sinha, G. Ghosh, M. N. Roy, J. Phys. Chem. Liq., 2010; 48: 62-78.

3. A. Sinha, A. Bhattacharjee, M. N. Roy, J. Disp. Sc. Techn., 2009; 30: 1003-1007.

4. I.M. Marrucho, L.C. Branco, L.P.N. Rebelo. Annu. Rev. Chem. Biomol. Eng., 2014; 5: 527–46.

5. K. S. Egorova, E. G. Gordeev, V. P. Ananikov, Chem. Rev., 2017; 117: 7132–7189.

6. C. D. Meletis, J. E. Barker, Alternative and Complementary Therapies, 2005; 11: 24-28.

7. I.M. Abdulagatov, N.D. Azizov, Fluid Phase Equilibria, 2006; 240: 204-219.

8. M.N. Roy, B. Sinha, R. Dey, A. Sinha, Int. J. Thermophy., 2005; 26: 1549-1563.

9. E.B. Freyer, J.D. Hubbard, and D.H. Andrews, J. Am. Chem. Soc., 1929; 51: 795.

10. O.Kiyoharo, J.P.E. Grolier, and G.C.Benson, Can.J.Chem., 1974; 52: 2287.

11. N.M.Murthy and S.V.Subramanyam, Bull. Chem.Soc.Jpn., 1977; 50: 2589.

12. E.Ayranci, J. Chem. Eng. Data., 1997; 42: 934-937.

13. D.O. Masson, Philos. Mag., 1929; 8: 218-235.

14. R. K. Wadi, P. Ramasami, J. Chem. Soc., Faraday Trans., 1997; 93: 243–247.

15. T. S. Banipal, D. Kaur, P. K.Banipal, J. Chem. Eng. Data, 2004; 49: 1236-1246.

16. M. Natarajan, R. K. Wadi, H. C. GaurJ. Chem. Eng. Data, 1990; 35: 87–93.

17. K. Belibagli, E.Agranci, J. Solution Chem., 1990; 19: 867–882.

18. G. Jones, M. Dole, J. Am. Chem. Soc., 1929; 51: 2950-2964.

19. F. J. Millero, Chem. Rev., 1971; 71: 147-176.

20. F. J. Millero, A. Losurdo, C. Shin, J. Phys. Chem., 1978; 82: 784-792.

21. V. Minkin, O. Osipov, Y. Zhdanov, Dipole Moments in Organic Chemistry, Plenum Press: New York, London, (1970).

22. M. Born, E. Wolf, 7th Ed., Cambridge University Press: London, (1999).

23. M. Deetlefs, K. Seddon, M. Shara, Phys. Chem. Chem. Phys., 2006; 8: 642-649.

24. M.N. Roy, D.Ekka and R. Dewan, Acta Chim. Slov., 2011; 58: 792.