Physicochemical Investigation of Diverse Interactions of Some Biologically Potent Molecules Prevalent in Aqueous Ionic Liquid Solutions at Different Temperatures

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ABSTRACT

Densities, viscosities, conductivity, and refractive indices of L-ascorbic acid in aqueous solutions of an ionic liquid, 1-butylpyridinium bromide, have been measured at five different temperatures ranging from 293.15K to 313.15K. Some important parameters have been derived from the above physicochemical experiments, namely, limiting apparent molar volume (φ_V^0) and viscosity B-coefficients using extended Masson equation and Jones-Dole equation, respectively. Lorentz-Lorenz equation has used to evaluate molar refractive index (R_M) and limiting molar index (R_M^0). Specific conductivity measurement applied to ascertain ionic nature of the system.

Key words: Solute-co-solute interactions, Apparent molar volume, Viscosity B-coefficient, Molar refraction, Conductivity study

1. INTRODUCTION

Ionic liquids (ILs) are organic solvents that are liquids at or near room temperature in their pure state. They have been widely 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 ability to dissolve a variety of chemicals, and most importantly, negligible vapor pressure [1,2]. ILs 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 biosciences far studied [3,4].

Vitamin C, which is also known as L-ascorbic acid (AA), is highly polar and readily soluble in water. Vitamin C can help to prevent and treat scurvy and the common cold. It is essential for the synthesis of collagen, neurotransmitters, and creatinine [5]. Due to the great importance of Vitamin C in human beings, the volumetric and viscometric investigation of the solutes has gained increased significance in several areas of analytical chemistry such as pharmaceutical and food applications. As the body fluid is always circulating, it is interesting to study the transport properties of vitamins in aqueous solutions at different temperatures. Water is a very simple molecule but very complicated to understand especially when it is mixed with other solutes. Hence, it was believed to study the effect of dissolution of L-AA on the structure of aqueous ILs medium at different temperatures.

Measurements of density, viscosity and refractive index, and conductivity of aqueous IL solution of L-ascorbic 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$_2$O + IL + L-AA) systems. The nature and degree of molecular interactions indifferent

solutions depend upon the nature of the medium, extent of solvation taking place in solution, and also the structure and size of the solute molecule [6-10].

Therefore, in the present study, we have endeavored to make ascertain nature of the interaction of solute itself (L-AA) and with co-solute 1-butylpyridinium bromide (IL) in w_I=0.001, 0.003, and 0.005 mass fraction of aqueous medium at different temperatures (298.15–313.15) K with 5 intervals to explain various noncovalent interactions prevailing in the ternary systems under investigation.

2. EXPERIMENTAL SECTION

2.1. Source and Purity of Materials

1-butylpyridinium bromide and L-AA were purchased from Sigma-Aldrich. The mass fractions purity of both was ≥0.99. The reagents were always placed in the desiccators over P$_2$O$_5$ to keep them in dry atmosphere. These chemicals were used as received without further purification. The provenance and purity of the chemical used have been depicted in Table 1.

2.2. Apparatus and Procedure

Solubility of the 1-butylpyridinium bromide and L-AA in water (deionized and doubly distilled water) has been checked surely, before start of the experimental work and perceived that L-AA is soluble in all

proportion of aqueous IL solution. The mother solutions of L-AA were prepared by mass (Mettler Toledo AG-285 with uncertainty 0.0003 g) and then the working solutions (six sets) were prepared by mass dilution. The conversion of molarity into molality [11] has been done using experimental density values of respective solutions.

The densities (ρ) of the experimental solutions were measured using (DMA 4500M) vibrating u-tube Anton Paar digital density meter with a precision of ± 0.00005 g.cm^{-3} maintained at ± 0.01 K of the desired temperature. The calibration was carried out by passing deionized, triply distilled water and dry air [12].

A Brookfield DV-III Ultra Programmable Rheometer with fitted spindle size-42 is used to measure the viscosity (η). The detailed description has already been described earlier [12].

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

Measurements of conductivity were carried out in a Systronics-308 conductivity meter (accuracy $\pm 0.01\%$) using a dip-type dipping conductivity cell, CD-10, having a cell constant of approximately (0.1 ± 0.001) cm^{-1}. Measurements of experimental solutions were completed in a water bath maintained within T = (298.15 ± 0.01) K [14].

3. RESULTS AND DISCUSSION

The physical parameters of binary mixtures in different mass fractions (w_1=0.001, 0.003,0.005) of aqueous ILs solutions at five different temperatures (293.15K, 298.15K, 303.15K, 308.15K, and 313.15K) and at 1.013 bar have been reported in Table 2. The experimental measured values of density and viscosity of L-AA as a function of concentration (molality) in different mass fractions of aqueous ILs mixture at above-mentioned temperatures have been listed in Table 3.

3.1. Apparent Molar Volume

Volumetric properties, such as apparent molar volume (φ_V) and limiting apparent molar volume (φ_V^0), contemplate significant tools for the understanding of interactions taking place in solution systems. The apparent molar volume can be regarded 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. Therefore, the apparent molar volumes (φ_V) have been determined from the solution densities using the suitable equation [13] and the values are given in Table 4.

$$\varphi_V = M/\rho - 1000\ (\rho - \rho_0)/m\rho\rho_0 \qquad (1)$$

Where M is the molar mass of the L-AA, m is the molality of the solution, ρ and ρ_0 are the density of the solution and aqueous ILs mixture, respectively.

The values of φ_V are positive and large for all the systems, signifying strong solute-co-solute interactions. The apparent molar volumes (φ_V) are found to decrease with increasing concentration (molality, m) of AA in the same mass fraction of aqueous ILs at same temperature. It is also found that apparent molar volumes (φ_V) increase with both increasing temperature as well as mass fraction of aqueous IL solution and varied with $\sqrt{m}$ and could be least-squares fitted to the extended Masson equation [15] from where limiting molar volume, φ_V^0 (infinite dilution partial molar volume) have been estimated, and the values have been represented in Table 5.

$$\varphi_V = \varphi_V^0 + S_V^* \sqrt{m} \qquad (2)$$

Table 1: Source and purity of the chemicals

Chemical name	Source	Mass fraction purity	Purification method
1-butylpyridinium bromide	Sigma-Aldrich	≥ 0.99	Used as procured
L-ascorbic acid	Sigma-Aldrich	≥ 0.99	Used as procured

Table 2: Experimental values of density (ρ), viscosity (η), and refractive index (n_D) at various temperature and at pressure 1.013 bar of different mass fraction (w_1) of aq. IL mixtures*

Aq. IL mixture (w_1)	Temperature/ K	$\rho \times 10^{-3}/$ kg·m^{-3}	$\eta/$ mP·s	n_D
0.001	293.15	0.399890	1.130	1.3322
	298.15	0.99789	1.022	1.3323
	303.15	0.99650	0.924	1.3322
	308.15	0.99496	0.855	1.3321
	313.15	0.99321	0.803	1.3320
0.003	293.15	0.99814	1.132	1.3324
	298.15	0.99710	1.024	1.3324
	303.15	0.99658	0.933	1.3323
	308.15	0.99525	0.864	1.3322
	313.015	0.99340	0.807	1.3321
0.005	293.15	0.99320	1.141	1.3325
	298.15	0.99828	1.029	1.3325
	303.15	0.99650	0.937	1.3324
	308.15	0.99534	0.869	1.3323
	313.15	0.99243	0.813	1.3322

*Standard uncertainties u are: u (ρ) =0.002 kg·m^{-3}, u (η) =0.02 mP·s, u (n_D) =0.0002, and u (T) =0.01K, (0.68 level of confidence)

φ_V^0 is the apparent molar volume at infinite dilution and S_V^* is the experimental slope. At infinite dilution, solute molecule is surrounded only by the solvent molecules and remains an infinite distance from each other. Consequently, that φ_V^0 is unaffected by itself interaction of AA molecules and it is a measure only of the solute-co-solute (AA-IL) interaction.

Scrutiny of Table 5 shows that φ_V^0 are large and positive for all L-AA at all the studied temperatures, suggesting the presence of strong solute-co-solute interaction (Scheme 1). Comparing φ_V^0 with S_V^* values show that the magnitude of φ_V^0 is $>S_V^*$, suggesting that solute-co-solute interactions predominate over itself interaction of solute molecules in all solutions at all studied temperatures. Since the Sv*values signify the solute-solute interactions so the small values of Sv* indicates very less interactions associate with the L-ascorbic acid molecules in aqueous solutions. It has been observed from the table 5 that all the values of SV* are negative at all studied temperature and are very small which indicates very poor force of interactions involve in L-ascorbic acid molecules.

The variation of φ_V^0 with temperature is fitted to a polynomial of the following

$$\varphi_V^0 = a_0 + a_1\ T + a_2\ T^2 \qquad (3)$$

Where T is the temperature in K and a_0, a_1, and a_2 are the empirical coefficients depending on the solute, mass fraction of co-solute IL.

Table 3: Experimental values of density (ρ) and viscosity (η), L-ascorbic acid in different mass fractions of aqueous IL acid mixture (w_1) at five different temperatures and at pressure 1.013 bar*

$^a m$/mol·kg^{-1}	$\rho \times 10^{-3}$/kg·m^{-3}	η mP·s	$^a m$/mol·kg^{-1}	$\rho \times 10^{-3}$/kg·m^{-3}	η mP·s	$^a m$/mol·kg^{-1}	$\rho \times 10^{-3}$/kg·m^{-3}	η/mP·s
	w_1=0.001			w_1=0.003			w_1=0.005	
T=	293.15 K			293.15 K			293.15 K	
0.010	0.99905	1.136	0.010	0.99916	1.138	0.010	0.99943	1.145
0.025	1.00005	1.141	0.025	1.00016	1.141	0.025	1.00022	1.151
0.040	1.00103	1.148	0.040	1.00118	1.148	0.040	1.00125	1.157
0.055	1.00209	1.152	0.055	1.00223	1.152	0.055	1.00231	1.162
0.070	1.00317	1.158	0.070	1.00330	1.158	0.070	1.00333	1.166
0.085	1.00415	1.164	0.085	1.00432	1.166	0.085	1.00435	1.173
T =	298.15 K			298.15 K			298.15 K	
0.010	0.99798	1.028	0.010	0.99824	1.029	0.010	0.99837	1.033
0.025	0.99887	1.033	0.025	0.99899	1.034	0.025	0.99915	1.038
0.040	0.99988	1.038	0.040	0.99997	1.041	0.040	1.00005	1.045
0.055	1.0009	1.045	0.055	1.00102	1.046	0.055	1.00111	1.052
0.070	1.00197	1.050	0.070	1.00208	1.052	0.070	1.00223	1.056
0.085	1.00298	1.057	0.085	1.00316	1.058	0.085	1.00342	1.062
T=	303.15 K			303.15 K			303.15 K	
0.010	0.99659	0.930	0.010	0.99666	0.938	0.010	0.99676	0.941
0.025	0.99746	0.936	0.025	0.9975	0.943	0.025	0.99757	0.946
0.040	0.99847	0.941	0.040	0.99857	0.948	0.040	0.9986	0.952
0.055	0.99948	0.948	0.055	0.99959	0.953	0.055	0.99968	0.958
0.070	1.00053	0.954	0.070	1.00075	0.962	0.070	1.00073	0.964
0.085	1.00152	0.962	0.085	1.00084	0.968	0.085	1.00089	0.971
T=	303.15 K			308.15 K			308.15 K	
0.010	0.99503	0.861	0.010	0.99529	0.869	0.010	0.99538	0.871
0.025	0.99584	0.866	0.025	0.99599	0.874	0.025	0.996	0.877
0.040	0.99683	0.871	0.040	0.99696	0.880	0.040	0.99703	0.882
0.055	0.99789	0.875	0.055	0.99797	0.886	0.055	0.99808	0.888
0.070	0.99892	0.885	0.070	0.99908	0.894	0.070	0.99928	0.896
0.085	0.99991	0.892	0.085	1.00013	0.901	0.085	1.00038	0.903
T=	313.15K			313.15K			313.15K	
0.010	0.99326	0.809	0.010	0.99344	0.812	0.010	0.99346	0.817
0.025	0.99404	0.814	0.025	0.99408	0.817	0.025	0.99411	0.823
0.040	0.99502	0.820	0.040	0.99515	0.822	0.040	0.99519	0.829
0.055	0.99605	0.826	0.055	0.99613	0.828	0.055	0.99624	0.836
0.070	0.99708	0.833	0.070	0.99722	0.836	0.070	0.99735	0.844
0.085	0.99807	0.842	0.085	0.99832	0.844	0.085	0.99847	0.850

*Standard uncertainties u are: u (ρ)=0.00002 kg·m^{-3}, u (η)=0.02 mP·s, and u (T) =0.01K (0.68 level of confidence). ^{a}Molality has been expressed per kg (IL+water) solvent mixture

Values of coefficients of the above equation for the in aqueous IL mixtures are reported in Table 6.

The limiting apparent molar expansibilities, φ_E^0, can be evaluated by the following equation,

$$\varphi_E^0 = (\delta \varphi_V^0 / \delta T)_P = a_1 + 2a_2 T \qquad (4)$$

The limiting apparent molar expansibilities, φ_E^0, change in magnitude with the change of temperature. The values of φ_E^0 for different

solutions of studied L-AA at (T=293.15K–313.15K) are reported in Table 7.

All the values of $^*\varphi_E^0$ shown in the Table 7 are positive for L-ascorbic acid in aqueous solutions of ionic liquid at different mass fraction and at different studied temperatures. This fact helps to explain the absence of caging or packing effect for the IL in solution [16].

The long-range structure-making and breaking capacity of the solute in the mixed system can be determined by examining the sign of $(\delta \varphi_E^0/$

Table 4: Apparent molar volume (Ψ_V) and $(\eta_r-1)/\sqrt{m}$ of L-Ascorbic acid in different mass fraction (w_I) of aqueous IL mixtures at five different temperatures*

[a]molality/ mol·kg^{-1}	$\Psi_V\times10^6$/ m^{3}mol^{-1}	$(\eta r-1)/\sqrt{m}$/ kg$^{1/2}$mol$^{-1/2}$	[a]molality/ mol·kg^{-1}	$\Psi_I\times10^6$/ m^{3}mol^{-1}	$(\eta r-1)/\sqrt{m}$/ kg$^{1/2}$mol$^{-1/2}$	[a]molality/ mol·kg^{-1}	$\Psi_V\times10^6$/ m^{3}mol^{-1}	$(\eta r-1)/\sqrt{m}$/ kg$^{1/2}$mol$^{-1/2}$
w_1=0.001			w_1=0.003			w_1=0.005		
T=293.15 K			T=293.15 K			T=293.15 K		
0.010	161.3074	0.10	0.010	164.2890	0.10	0.010	165.2465	0.10
0.025	130.2733	0.15	0.025	131.4611	0.15	0.025	140.2315	0.15
0.040	123.0157	0.20	0.040	122.7562	0.20	0.040	127.9780	0.20
0.055	118.2601	0.23	0.055	118.2516	0.23	0.055	121.8612	0.23
0.070	115.2568	0.26	0.070	115.3915	0.26	0.070	118.9343	0.26
0.085	114.4912	0.29	0.085	114.1324	0.29	0.085	117.0449	0.29
T=298.15 K			T=298.15 K			T=298.15 K		
0.010	165.4707	0.10	0.010	166.4314	0.10	0.010	167.4118	0.10
0.025	136.3732	0.15	0.025	142.3587	0.15	0.025	142.2825	0.15
0.040	126.0911	0.20	0.040	130.5747	0.20	0.040	130.2784	0.20
0.055	121.2318	0.23	0.055	123.9409	0.23	0.055	123.0563	0.23
0.070	117.7392	0.26	0.070	120.0063	0.26	0.070	117.9590	0.26
0.085	116.1897	0.29	0.085	117.2309	0.29	0.085	113.8659	0.29
T=303.15 K			T=303.15 K			T=303.15 K		
0.010	167.6947	0.10	0.010	168.6877	0.10	0.010	171.6834	0.10
0.025	138.1137	0.15	0.025	139.7137	0.15	0.025	140.1794	0.15
0.040	127.1993	0.20	0.040	126.6911	0.20	0.040	127.1490	0.20
0.055	122.2345	0.23	0.055	121.6820	0.23	0.055	120.3674	0.23
0.070	118.8225	0.26	0.070	116.8140	0.26	0.070	116.7937	0.26
0.085	117.3267	0.29	0.085	114.0258	0.29	0.085	112.1710	0.29
T=308.15 K			T=308.15 K			T=308.15 K		
0.010	169.9583	0.10	0.010	172.9363	0.10	0.010	172.9211	0.10
0.025	141.4943	0.15	0.025	147.1081	0.15	0.025	150.3231	0.15
0.040	129.8377	0.20	0.040	133.8415	0.20	0.040	134.3368	0.20
0.055	123.2543	0.23	0.055	127.0749	0.23	0.055	126.7021	0.23
0.070	119.9223	0.26	0.070	121.7701	0.26	0.070	120.1852	0.26
0.085	118.2437	0.29	0.085	119.0530	0.29	0.085	117.1584	0.29
T=313.15K			T=313.15K			T=313.15K		
0.010	172.2706	0.10	0.010	173.2509	0.10	0.010	174.2580	0.10
0.025	143.7050	0.15	0.025	149.7550	0.15	0.025	149.7513	0.15
0.040	131.4999	0.20	0.040	132.9996	0.20	0.040	132.7442	0.20
0.055	125.0295	0.23	0.055	127.0351	0.23	0.055	125.5640	0.23
0.070	121.3304	0.26	0.070	122.0384	0.26	0.070	120.5955	0.26
0.085	119.4161	0.29	0.085	118.6930	0.29	0.085	117.2690	0.29

*Standard uncertainties u are: u (T) =0.01K, the accuracy of φ_V is 1.01×10^{-6} m^3 mol^{-1} and $(\eta_r-1)/\sqrt{m}$ is 0.002 kg$^{1/2}$mol$^{-1/2}$ (0.68 level of confidence). [a]Molality has been expressed per kg of (IL+water) solvent mixture

$\delta T)_P$ developed by Hepler [17].

$$(\delta\varphi_E{}^0/\delta T)_P = (\delta^2\varphi_V{}^0/\delta T^2)_P = 2a_2 \tag{5}$$

The positive sign or small negative of $(\delta\varphi_E{}^0/\delta T)_P$ signifies the molecule is a structure-maker; otherwise, it is a structure-breaker [18]. The perusal of Table 6 shows that $(\delta\varphi_E{}^0/\delta T)_P$ values of AA are all positive under investigation. It shows the more symmetric rearrangement of the interacting molecules (AAandIL) with the formation of H-bonding, van der Waal forces, dipole-dipole interactions, etc. This symmetric arrangement is signifying the molecules of AA and IL is interacting with structure–making tendency in all of the studied solution systems. Table 6 also showing the positively magnitude of $(\delta\varphi_E{}^0/\delta T)_P$ values in of L-AA is depicting this structure–making tendency.

3.2. Viscosity

The experimental viscosity data for studied systems are listed in Table 3. The relative viscosity (η_r) has been calculated using the extended Jones-Dole equation [19] for non-electrolytes.

$$(\eta/\eta_0 - 1)/\sqrt{m} = (\eta_r - 1)/\sqrt{m} = A + B \cdot \sqrt{m} \qquad (6)$$

Where $\eta_r = \eta/\eta_0$ is the relative viscosity, η and η_0 are the viscosities of ternary solutions (AA + IL) and solvent (aqueous IL), respectively, and m is the molality of L-AA in ternary solutions. Where A is known as Falkenhagen coefficient [20] as it is determined by the ionic attraction theory of Falkenhagen-Vernon and B is empirical constants known as viscosity B- coefficients, which are specifying to the interaction of solute itself and/or with co-solute molecules, respectively. The values of A-and B-coefficients are estimated by the least-square polynomial method by plotting $(\eta_r-1)/\sqrt{m}$ against $\sqrt{m}$ with second order and reported in Table 4. It is observed from Table 4, the values of the A-coefficient are found to decrease with an increase in temperature. This fact indicates the presence of very weak solute-solute interaction and also in excellent agreement with those obtained from S_V^* values.

Table 5: Limiting apparent molar volume (φ_V^0), experimental slope (S_V^*), viscosity A-, and B-coefficient of L-ascorbic acid in different mass fraction (w_1) of aqueous IL mixtures at five different temperatures*

Mass fraction (w_1)	T/K	$\Psi_V^0 \times 10^6/$ m^3 mol^{-1}	$S_V^* \times 10^6/$ m^{3}mol$^{-3/2}$ kg$^{1/2}$	B/kg mol^{-1}	A/kg$^{1/2}$ mol$^{-1/2}$
0.001	293.15	174.80	-228.31	0.52	0.03
	298.15	181.69	-244.93	0.58	0.05
	303.15	184.34	-251.01	0.64	0.02
	308.15	188.46	-261.69	0.73	0.04
	313.15	191.45	-267.62	0.78	0.01
0.003	293.15	178.73	-244.21	0.63	0.01
	298.15	185.87	-251.03	0.69	0.03
	303.15	188.56	-274.23	0.76	0.05
	308.15	192.86	-276.06	0.81	0.02
	313.15	195.14	-283.01	0.88	0.03
0.005	293.15	183.3	-245.13	0.71	0.03
	298.15	189.22	-271.58	0.77	0.01
	303.15	193.16	-295.63	0.83	0.04
	308.15	198.09	-292.71	0.93	0.01
	313.15	198.68	-296.67	0.99	0.05

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

Table 6: Values of various coefficients and standard deviation of equation-3 for L-ascorbic acid in different aqueous IL solutions*

Aqueous IL Mixture (w_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}	$(\delta\varphi_E^0/\delta T)$ $P \times 10^6/$m^3 mol^{-1} K^{-2}
0.001	-1720	11.76	-0.018	-0.03
0.003	-2181.40	14.84	-0.023	-0.02
0.005	-2585.5	17.54	-0.027	-0.05
Average standard deviation	2.1	0.001	0.0002	0.0001

The valuable information about the solvation of the solvated solutes and their effects on the structure of the co-solute IL in the local vicinity of the solute (L-AA) molecules in solutions have been obtained from viscosity B-coefficient [21]. It is found from Table 4; the values of B-coefficient are positive and much higher than A-coefficient which signifies solute-co-solute interaction is dominant over solute-solute and co-solute-co-solute interaction. It is also observed that the positive magnitude of viscosity B-coefficient increases with increasing temperature and also increases with an increase in mass fraction of aqueous IL which suggests that solute-co-solute interaction is strengthened with a rise in temperature as well as the mass fraction of aqueous IL mixture. These results are in good agreement with those obtained from limiting apparent molar volume φ_V^0 values.
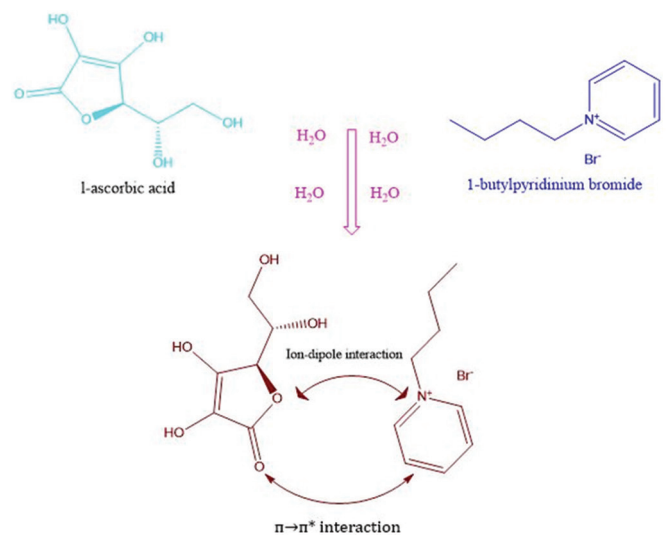
Scheme 1: Plausible solute-co -solute interaction

Table 7: Limiting apparent molar expansibilities (φ_E^0) for L-ascorbic acid in different mass fraction of aqueous IL (w_1) at different temperature

Aqueous IL mixture ($w1$)	$\varphi_E^0 \times 10^6/$m^3 mol^{-1} K^{-1}				
T/K	293.15	298.15	303.15	308.15	313.15
0.001	1.15497	0.97397	0.79297	0.61197	0.43097
0.003	1.24284	1.01084	0.77884	0.54684	0.31484
0.005	1.36212	1.08612	0.81012	0.53412	0.25812
Average standard deviation	0.003	0.003	w0.002		

Table 8: Values of dB/dT, A_1, A_2 coefficients for the L-Ascorbic acid in different mass fraction of aqueous IL acid (w_1) at studied temperatures*

Aqueous IL mixture ($w1$)	dB/dT	A_1	A_2
0.001	0.043	-6.943	0.023
0.002	0.028	-7.869	0.024
0.003	0.039	-8.573	0.039
Average standard deviation	0.001	0.003	0.002

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

Table 9: Refractive index (n_D) and molar refraction (R_M) of L-ascorbic acid in different mass fraction of aqueous solutions at different temperatures and at pressure 1.013 bar*

[a]molality/ mol·kg^{-1}	n_D	$R_M\times10^6$/ m^3 mol^{-1}	[a]molality/ mol·kg^{-1}	n_D	$R_M\times10^6$/ m^3 mol^{-1}	[a]molality/ mol·kg^{-1}	n_D	$R_M\times10^6$/ m^3 mol^{-1}
	w1=0.001			**w1=0.003**			**w1=0.005**	
	T=293.15K			T=293.15K			T=293.15K	
0.010	1.3326	36.2241	0.010	1.3328	36.2398	0.010	1.3331	36.2597
0.025	1.3327	36.1977	0.025	1.3329	36.2135	0.025	1.333	36.2212
0.040	1.3329	36.1820	0.040	1.333	36.1864	0.040	1.3331	36.1938
0.055	1.3331	36.1634	0.055	1.3332	36.1682	0.055	1.3333	36.1752
0.070	1.3333	36.1442	0.070	1.3334	36.1493	0.070	1.3336	36.1679
0.085	1.3336	36.1384	0.085	1.3337	36.1421	0.085	1.3338	36.1509
	T=298.15K			T=298.15K			T=298.15K	
0.010	1.3325	36.2530	0.010	1.3327	36.2633	0.010	1.3329	36.2784
0.025	1.3327	36.2405	0.025	1.3328	36.2460	0.025	1.333	36.2600
0.040	1.3329	36.2236	0.040	1.333	36.2302	0.040	1.3332	36.2471
0.055	1.3331	36.2064	0.055	1.3332	36.2120	0.055	1.3333	36.2186
0.070	1.3333	36.1875	0.070	1.3334	36.1934	0.070	1.3335	36.1978
0.085	1.3335	36.1707	0.085	1.3336	36.1741	0.085	1.3337	36.1745
	T=303.15K			T=303.15K			T=303.15K	
0.010	1.3324	36.2936	0.010	1.3326	36.3109	0.010	1.3328	36.3271
0.025	1.3325	36.2719	0.025	1.3327	36.2902	0.025	1.3329	36.3075
0.040	1.3327	36.2550	0.040	1.3329	36.2711	0.040	1.3331	36.2898
0.055	1.3330	36.2480	0.055	1.333	36.2440	0.055	1.3332	36.2605
0.070	1.3332	36.2297	0.070	1.3334	36.2415	0.070	1.3334	36.2422
0.085	1.3334	36.2136	0.085	1.3336	36.2203	0.085	1.3337	36.2265
	T=308.15K			T=308.15K			T=308.15K	
0.010	1.3322	36.3307	0.010	1.3324	36.3410	0.010	1.3326	36.3576
0.025	1.3323	36.3111	0.025	1.3325	36.3254	0.025	1.3327	36.3449
0.040	1.3326	36.3047	0.040	1.3327	36.3099	0.040	1.3329	36.3272
0.055	1.3328	36.2860	0.055	1.333	36.3028	0.055	1.3331	36.3087
0.070	1.333	36.2683	0.070	1.3332	36.2823	0.070	1.3333	36.2849
0.085	1.3333	36.2620	0.085	1.3334	36.2639	0.085	1.3335	36.2647
	T=313.15K			T=313.15K			T=313.15K	
0.010	1.3320	36.3755	0.010	1.3321	36.3789	0.010	1.3322	36.3881
0.025	1.3321	36.3569	0.025	1.3322	36.3654	0.025	1.3323	36.3742
0.040	1.3324	36.3509	0.040	1.3325	36.3561	0.040	1.3325	36.3546
0.055	1.3326	36.3332	0.055	1.3327	36.3402	0.055	1.3328	36.3461
0.070	1.3329	36.3253	0.070	1.333	36.3301	0.070	1.3331	36.3353
0.085	1.3332	36.3190	0.085	1.3333	36.3198	0.085	1.3334	36.3242

*Standard uncertainties u are: u (n_D)=0.02 and u (T)=0.01K (0.68 level of confidence), [a]Molality has been expressed per kilogram of (IL+water) solvent mixture

It is observed from Table 4 that the values of the *B*-coefficient of AA increase with temperature, that is, the *dB/dT* values are positive. From Table 8, the small positive *dB/dT* values for the L-AA behave almost as structure-maker.

Furthermore, it is attractive to observe that there is a linear correlation between viscosity *B*-coefficients of the studied L-AA with the limiting apparent molar volumes (φ_V^0) in different mass fraction of aqueous IL solutions. From the above fact, it means

$$B = A_1 + A_2\, \varphi_V^0 \qquad (7)$$

The coefficients A_1 and A_2 are listed in Table 8. As both viscosities, *B*-coefficient and limiting apparent molar volumes define the solute-solvent interaction in solution. The linear variation of viscosity *B*-coefficient and limiting apparent molar volume (φ_V^0) reflects the positive slope (or A_2).

It is evident from this study that there is a strong interaction between L-AA and IL and it becomes stronger with a rise in temperature. As

molecules of L-AA are engaged with the IL molecules, the interaction among the IL molecules becomes less effective. We have obtained the derived parameters such as limiting apparent molar volume (φ_V^0) and viscosity B-coefficient by interpolation and presented in Table 5. The positive and significant magnitude of φ_V^0 and B-coefficient from Table 5 clearly indicates that the limiting apparent molar volume (φ_V^0), viscosity B-coefficient is increasing with increasing mass fraction of IL, which indicates the positive effect of the interaction of AA with IL.

3.3. Refractive Index

The measurement of refractive index is also anappropriate method for inspecting the molecular interaction present in solution. The molar refraction (R_M) can be appraised from the Lorentz-Lorenz relation [22]. The refractive index of a substance is defined as the ratio c_o/c, where c and c_o are the velocity of light in the medium and in a vacuum, respectively. Stated more simply that the refractive index of

Table 10: Limiting molar refraction (R_M^0) of L-ascorbic acid in different temperatures and in different mass fraction of aqueous IL solutions at pressure 1.013 bar*

Aq. IL mixtures (w1)	$R_M^0 \times 10^6/m^3\ mol^{-1}$				
	293.15K	298.15K	303.15K	308.15K	313.15K
0.001	36.27	36.30	36.33	36.37	36.40
0.003	36.29	36.31	36.36	36.38	36.41
0.005	36.31	36.34	36.38	36.41	36.42

a compound describes its capability to refract light as it passes from one medium to another, and thus, the higher the refractive index of a compound, the more the light is refracted [23]. As stated by Deetlefs *et al*. [24], 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 Tables 9 and 10, we found that the refractive index and the molar refraction are higher for the studied AA and in all the mass fraction of aqueous IL, indicating to the fact that the molecules are more tightly packed in the solution.

The limiting molar refraction (R_M^0) estimated from the following equation (14) and presented in Table 10.

$$R_M = R_M^0 + R_S \sqrt{m} \qquad (8)$$

Accordingly, we found that the higher values of refractive index and R_M^0 which representing the fact that the molecules of AA and are more tightly packed and greater solute-solvent interaction with IL molecules than solute-solvent interaction. This is also in good agreement with the results obtained from apparent molar volume and viscosity B-coefficients discussed above.

3.4. Conductivity Study

The conductivity study of the L-AA for the interaction (solute-co-solute) in the aqueous solution of IL has been done at five different temperatures. Transport phenomena, molecular, and ionic interaction in the ternary system gives some valuable information [25]. The specific conductivities (k) of aqueous IL solution have been monitored with increasing the concentration of L-AA at five different temperatures and tabulated in Table 11. Consequently, it has been observed that molar

Table 11: Specific conductivity (k) of L-ascorbic acid in different temperatures and in different mass fraction of aqueous IL solutions at pressure 1.013 bar*

Added L-Ascorbic acid/mL	Total volume/mL	Conc. L-ascorbic acid solution/mM	Specific Conductivity/mS cm^{-1}				
			293.15K	298.15K	303.15K	308.15K	313.15K
0	10	0.001	0.11	0.14	0.15	0.22	0.23
1	11	0.003	0.37	0.41	0.42	0.44	0.39
2	12	0.003	0.47	0.44	0.47	0.48	0.50
3	13	0.004	0.53	0.48	0.50	0.49	0.57
4	14	0.004	0.57	0.49	0.61	0.51	0.63
5	15	0.005	0.61	0.51	0.66	0.55	0.67
6	16	0.005	0.64	0.53	0.67	0.60	0.69
7	17	0.005	0.67	0.54	0.71	0.65	0.73
8	18	0.006	0.69	0.59	0.74	0.69	0.74
9	19	0.006	0.70	0.62	0.76	0.74	0.76
10	20	0.006	0.72	0.63	0.78	0.76	0.78
11	21	0.007	0.73	0.64	0.79	0.77	0.79
12	22	0.007	0.74	0.66	0.80	0.78	0.79
13	23	0.007	0.76	0.68	0.82	0.79	0.80
14	24	0.007	0.77	0.69	0.82	0.79	0.82
15	25	0.007	0.78	0.70	0.83	0.80	0.83
16	26	0.007	0.78	0.72	0.85	0.81	0.85
17	27	0.007	0.79	0.73	0.85	0.85	0.86
18	28	0.008	0.80	0.74	0.85	0.86	0.87
19	29	0.008	0.81	0.75	0.86	0.87	0.88
20	30	0.008	0.81	0.78	0.87	0.88	0.90

conductivity (Λ) values increases with an increase in temperatures and gradual addition of L-AA to the IL solution causes a continuous decrease in molar conductivity of the solution. The mobility of the ionic species in solution playing an important role in spite of a growing number of ionic species with added L-AA solution; as a result, the moral conductivity decreases [26,27]. It may be due to the growth of solute-solvent interaction governed by the dipole-dipole, ion-dipole, and hydrophobic – hydrophobic interaction in solution mixtures between the solute and solvent molecules.

4. CONCLUSION

In the summary of this study, there is a strong interaction between L-ascorbic and IL and it becomes stronger with a rise in temperature. As molecules of L-ascorbic and IL have engaged each other, solute-co-solute interaction is much greater than the solute-solute and solvent-solvent interactions in the ternary system.

5. ACKNOWLEDGMENT

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