CHAPTER- VI

PHYSICOCHEMICAL INVESTIGATION OF DIVERSE INTERACTIONS OF SOME BIOLOGICALLY POTENT MOLECULES PREVALENT IN AQUEOUS IONIC LIQUID SOLUTIONS AT DIFFERENT TEMPERATURES

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.

Keywords: Solute-co-solute interactions, apparent molar volume, viscosity B-coefficient, molar refraction, conductivity study.

V1.1. 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 the ability to dissolve a variety of chemicals, and most importantly, negligible vapour pressure [1,2]. Ionic liquids have been proposed as green and benign replacements for traditional volatile organic solvents, and a rising number of applications in the fields of catalysis, chemical reactions, separations, electrochemistry, Nano-science and biosciences far studied[3,4].

Vitamin C, which is also known as L-ascorbic acid 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. So, it was believed to study the effect of dissolution of L-ascorbic acid on the structure of aqueous ionic liquid medium at different temperatures.

Measurements of density, viscosity and refractive index, 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_2O + IL+ L-ascorbic acid) systems. The nature and degree of molecular interactions in different 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 present study we have endeavoured to make ascertain nature of interaction of solute itself (L-ascorbic acid) and with co-solute 1-butylpyridinium bromide (IL) in w_1=0.001, 0.003 and 0.005 mass fraction of aqueous medium at different temperatures (298.15-313.15)K with 5 interval to explain various noncovalent interactions prevailing in the ternary systems under investigation.

V1.2. Experimental section

V1.2.1 Source and purity of materials

1-butylpyridinium bromide and L-ascorbic acid were purchased from Sigma-Aldrich. The mass fractions purity of both was ≥0.99. The reagents were always placed in the desiccators over P_2O_5 to keep them in dry atmosphere. These chemicals were used as received without further purification. The provenance and purity of the chemical used has been depicted in table1.

V1.2.2 Apparatus and procedure

Solubility of the 1-butylpyridinium bromide and L-ascorbic acid in water (deionised, doubly distilled water) has been checked surely, prior to start of the experimental work and perceived that L-ascorbic acid is soluble in all proportion of aqueous IL solution. The mother solutions of L-ascorbic acid were prepared by mass (Mettler Toledo AG-285 with uncertainty 0.0003g) 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 by using of(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 deionised, 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 detail description has already been described earlier [13].

Refractive index (n_D) was measured with the help of a Digital Refractometer Mettler Toledo instrument. The light source was LED, λ=589.3nm. The refractometer was calibrated twice using distilled water and after every few measurements calibration was checked. [14].The uncertainty of refractive index measurement was ±0.0002 units.

Measurements of conductivity were carried out in a Systronics-308 conductivity meter (accuracy ±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 [15].

V1.3. Result and Discussion

The physical parameters of binary mixtures in different mass fractions (w_1=0.001, 0.003,0.005) of aqueous ionic liquid (IL)solutions at 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-ascorbic acid (AA) as a function of concentration (molality), in different mass fractions of aqueous ionic liquid (IL) mixture at above mentioned temperatures have been listed in **Table 3.**

V1.3.1 Apparent molar volume

Volumetric properties, like, apparent molar volume (φ_V) and limiting apparent molar volume (φ_V^0) contemplate significant tools for 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 solutions densities using the suitable equation [14] and the values are given in **Table 4.**

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

Where M is the molar mass of the L-ascorbic acid, m is the molality of the solution, ρ and $\rho_0$are the density of the solution and aqueous ionic liquid 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 ascorbic acid in same mass fraction of aqueous ionic liquid 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 [16] 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.**

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

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

A scrutiny of **Table 5** shows that φ_V^0 are large and positive for all L-ascorbic acid 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 greater than S_V^*, suggesting that solute-co-solute interactions predominates over itself interaction of solute molecules in all solutions at all studied temperatures. Moreover, S_V^* values are negative at all studied temperatures indicates force of itself interaction of ascorbic acid molecules is very poor.

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

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

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. 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,

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

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-ascorbic acid at (T=293.15K to 313.15) K are reported in **Table 7.**

All the values of φ_E^0 shown in the **Table 7** are positive for L-ascorbic acid in aqueous IL and studied temperature. This fact helps to explain the absence of caging or packing effect for the IL in solution [17].

The long-range structure-making and breaking capacity of the solute in mixed system can be determined by examining the sign of $(\delta \varphi_E^0 / \delta T)_P$ developed by Hepler[18].

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

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 [19]. The perusal of table 6 shows that, $(\delta\varphi_E^0/\delta T)_P$ values of ascorbic acid are all positive under investigation. It shows the more symmetric rearrangement of the interacting molecules (AA and IL) with the formation of H-bonding, van der Waal forces, dipole-dipole interactions etc. This symmetric arrangement is signifying the molecules of ascorbic acid and IL is interacting with structure–making tendency in all of the studied solution systems. The **Table 6** also showing the positively magnitude of $(\delta\varphi_E^0/\delta T)_P$ values in of L-ascorbic acid is depicting this structure–making tendency.

V1.3.2 Viscosity

The experimental viscosity data for studied systems are listed in **Table 3**. The relative viscosity (η_r) has been calculated using extended Jones-Dole equation [20] 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-Ascorbic acid in ternary solutions. Where A is known as Falkenhagen coefficient [21] 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 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 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.

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-ascorbic acid) molecules in solutions has been obtained from viscosity B-coefficient [22]. 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 rise in temperature as well as mass fraction of aqueous IL mixture. These results are in good agreement with those obtained from limiting apparent molar volume φ_V^0 values.

It is observed from **Table 4** that the values of the *B*-coefficient of ascorbic acid increases with temperature, i.e., the *dB/dT* values are positive. From table 8, the small positive *dB/dT* values for the L-ascorbic acid behaves behave almost as structure-maker.

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

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

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-ascorbic acid and IL and it becomes stronger with rise in temperature. As molecules of L-ascorbic acid are engaged with the IL molecules, the interaction among the IL molecules becomes less effective. We have obtained the derived parameters like, limiting apparent molar volume (φ_V^0), 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 increases with increasing mass fraction of IL, which indicates the positive effect of interaction of ascorbic acid with IL

V1.3.3 Refractive Index

The measurement of refractive index is also an appropriate method for inspecting the molecular interaction present in solution. The molar refraction (R_M) can be appraised from the Lorentz-Lorenz relation [23]. The refractive index of a substance is defined as the ratio c_o/c, where c and c_o is the velocity of light in the medium and in vacuum respectively. Stated more simply that the refractive index of 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 [24]. As stated by Deetlefs et al .[25] 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 9** and **Table 10** we found that the refractive index and the molar refraction are higher for the studied ascorbic acid 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.**

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

Accordingly, we found that the higher values of refractive index and R_M^0 which representing the fact that the molecules of ascorbic acid 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.

V1.3.4 Conductivity Study

The conductivity study of the L-ascorbic acid 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 [26]. The specific conductivities (k) of aqueous IL solution has been monitored with increasing the concentration of L-ascorbic acid at five different temperatures and Tabulated in **Table 11**.Consequently, it has been observed that molar conductivity (Λ) values increases with increase in temperatures and gradual addition of L-ascorbic acid to the IL solution causes a continuous decrease in molar conductivity of the solution. The mobility of the ionic species in solution playing the important role, in spite of growing number of ionic species with added L-ascorbic acid solution, as a result the moral conductivity decreases [27, 28]. It may be due to the growing of solute-solvent interaction governed by the dipole-dipole, ion-dipole and hydrophobic – hydrophobic interaction in solution mixtures between the solute and solvent molecules.

V1.4. Conclusion

In the summary of this study, that there is a strong interaction between L-ascorbic and IL and it becomes stronger with 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.

Tables

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}	η /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: $u(\rho)$ =0.002 kg·m^{-3}, $u(\eta)$ =0.02 mP·s, $u(n_D)$ =0.0002and $u(T)$ =0.01K, (0.68 level of confidence)

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: $u(\rho)$ =0.00002 kg·m^{-3}, $u(\eta)$ =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

Table 4. Apparent molar volume (φ_V) and $(\eta_r\text{-}1)/\sqrt{m}$ of L-Ascorbic acid in different mass fraction (w_1) of aqueous IL mixtures at five different temperatures*

[a] molality /mol·kg^{-1}	$\varphi_V \times 10^6$ /m^{3}mol^{-1}	$(\eta_r\text{-}1)/\sqrt{m}$ /kg$^{1/2}$mol$^{-1/2}$	[a] molality /mol·kg^{-1}	$\varphi_V \times 10^6$ /m^{3}mol^{-1}	$(\eta_r\text{-}1)/\sqrt{m}$ /kg$^{1/2}$mol$^{-1/2}$	[a] molality /mol·kg^{-1}	$\varphi_V \times 10^6$ /m^{3}mol^{-1}	$(\eta_r\text{-}1)/\sqrt{m}$ /kg$^{1/2}$mol$^{-1/2}$
\multicolumn{3}{c}{w_1=0.001}			w_1=0.003			w_1=0.005	
\multicolumn{3}{c}{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
\multicolumn{3}{c}{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
\multicolumn{3}{c}{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
\multicolumn{3}{c}{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
\multicolumn{3}{c}{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 $(\eta_r\text{-}1)/\sqrt{m}$ 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

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	$\varphi_V^0 \times 10^6$ /m³ mol⁻¹	$S_V^* \times 10^6$ /m³mol⁻³ᐟ² kg¹ᐟ²	B /kg mol⁻¹	A /kg¹ᐟ² mol⁻¹ᐟ²
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)	$a_0 \times 10^6$ /m³ mol⁻¹	$a_1 \times 10^6$ / m³ mol⁻¹K⁻¹	$a_2 \times 10^6$ / m³ mol⁻¹K⁻²	$(\delta\varphi_E^0/\delta T)_P \times 10^6$ / m³ 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

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 (w_1)	$\varphi_E^0 \times 10^6$/ 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	0.002		

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 (w_1)	*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	$R_M \times 10^6$ / m^3 mol^{-1}	[a] molality /mol·kg^{-1}	n_D	$R_M \times 10^6$ / m^3 mol^{-1}	[a] molality /mol·kg^{-1}	n_D	$R_M \times 10^6$ / 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	

molality^a /mol·kg⁻¹	n_D	$R_M \times 10^6$ / m³ mol⁻¹	molality^a /mol·kg⁻¹	n_D	$R_M \times 10^6$ / m³ mol⁻¹	molality^a /mol·kg⁻¹	n_D	$R_M \times 10^6$ / m³ mol⁻¹
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

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)	$R_M^0 \times 10^6$ / m³ 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

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	Total volume	Conc. L-ascorbic acid solution	Specific Conductivity/ mS cm-1				
/mL	/mL	/mM	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

<u>Schemes</u>

Scheme1. Plausible solute-co solute interaction.