Thermodynamic and Ultrasonic Properties of Ascorbic Acid in Aqueous Protic Ionic Liquid Solutions

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Abstract

In this work, we report the thermodynamic and ultrasonic properties of ascorbic acid (vitamin C) in water and in presence of newly synthesized ammonium based protic ionic liquid (diethylethanolammonium propionate) as a function of concentration and temperature. Apparent molar volume and apparent molar isentropic compression, which characterize the solvation state of ascorbic acid (AA) in presence of protic ionic liquid (PIL) has been determined from precise density and speed of sound measurements at temperatures (293.15 to 328.15) K with 5 K interval. The strength of molecular interactions prevailing in ternary solutions has been discussed on the basis of infinite dilution partial molar volume and partial molar isentropic compression, corresponding volume of transfer and interaction coefficients. Result has been discussed in terms of solute-solute and solute-solvent interactions occurring between ascorbic acid and PIL in ternary solutions (AA + water + PIL).

Introduction

Ionic liquids (ILs) are molten salts with melting point below 100°C. ILs have unique physicochemical properties such as broad liquid temperature range, negligible vapor pressure, wide electrochemical window, high thermal stability, and high specific solvent abilities [1–5]. The thermo-physical properties of ILs can be tuned by appropriate selection of cation and anion, as a result ILs can be made biocompatible and these are found to be very attractive in various analytical applications, particularly, in the fabrication of various modified electrodes which can be used to extract chemicals or compounds (synthetic colors) from food samples. Reports are available [6–12] were ILs have been used for the extraction of Sudan and Para Red dyes from chilli powder employing high performance liquid chromatography (HPLC), thus showing potential application of ILs in food industries [10–11,13–15].

Chailapakul et al. [16] have used IL based carbon electrode for the analysis of sudan I, sudan II, sudan III and sudan IV. Recently, a novel carbon composite electrode of an IL (n-octylpyridinium hexafluorophosphate) and single-walled carbon nanotube (SWCNT) was designed to determine the levels of ascorbic acid from food samples [11]. Ionic liquids have also been proposed as an effective compound to be used in the formation of aqueous biphasic system (ABS)
[17–18]. ABS are considered as an alternative to liquid-liquid extraction techniques, as ABS are being used as powerful technique in bioseparation processes, purification, extraction and enrichment [18–19]. ABS with ILs in combination with salts, amino acids, polyhydroxy compounds (saccharides), and polymers has been reported [18–24]. More recently, it has been reported [25] that the ABS employing ILs with various solutes (saccharides, amino acids, vitamins, etc) requires reliable and systematic thermodynamic data. The acquaintance of thermodynamics of ILs in aqueous solutions with various biomolecules (saccharides, amino acid, etc) is of crucial importance to improve the process design and to understand the molecular interactions between ILs and biomolecules, thus serving with the design of ABS systems.

Furthermore, the increased utilization of ILs for various applications (chemical or separations processes) requires accurate determination of thermodynamic data [25]. The nature and strength of interactions between AA and various co-solutes (electrolytes, non electrolytes, surfactants etc.) have been studied [26–31] by evaluating the thermodynamic properties of ternary systems (AA + water + co-solutes). These thermodynamic properties are useful in characterizing the solvation behaviour of vitamins and to further understand solute-solute and solute-solvent interactions [32–33]. Ascorbic acid (vitamin C) one of the most important vitamin for human health and nutrition, is found in fruits and vegetables [34–39]. It is a sugar acid, having antioxidant properties and can prevent or treat common cold and scurvy. It also acts as a cofactor and thus maintain activity of various enzymes [26–27,32,40–41]. The degradation of AA is very important and is considered to be the major cause of color and quality change during storage or processing of food materials [40, 42].

However, to the best of our knowledge there is no report on thermodynamic and ultrasonic properties of AA in aqueous solutions of ammonium based protic ionic liquid (PIL) as a function of concentration and temperature. So, in order to understand the molecular interactions occurring between AA and PIL, we report herein the volumetric properties of AA in aqueous solutions of newly synthesized protic ionic liquid i.e. diethylethanolammonium propionate ([DEEA][Pro]) at different temperatures (293.15 to 328.15) K. Various parameters such as partial molar volumes and isentropic compression, transfer volumes, interaction coefficients, and thermal expansion coefficients have been evaluated and discussed in terms of solute-solute and solute-cosolute interactions.

Materials and Methods

2.1 Materials

Ascorbic acid (mass fraction purity; 0.99) was purchased from Sisco Research Laboratory Pvt. Ltd. India, N,N-diethylethanol amine (0.99), propanoic acid (0.99) and methanol (0.99) were purchased from Sigma Aldrich. AA was used after drying in a vacuum desiccator (over anhydrous CaCl₂) for 48 h at room temperature and all the other chemicals were used without further purification.

2.2. Synthesis and characterization of ([DEEA][Pro])

PIL, ([DEEA][Pro]) was synthesized by exothermic neutralization of bronsted acid (propanoic acid) by base (N,N- diethylethanol amine). To 10 ml of methanol, N,N- diethylethanol amine (0.1 mol) was added in round bottom flask and this mixture was kept in ice bath for few minutes. Further, propanoic acid (0.11 mol) was added slowly and drop wise (by using dropping funnel) to the above reaction mixture. Addition of acid was completed in 2 hrs at a temperature below 5°C and then reaction mixture was stirred continuously for 24 hrs at room temperature. The excess amount of starting material and solvent were removed by putting the reaction mixture into rotavapor for 4 hrs. The resultant product (PIL) was dried at room temperature under
high vacuum for 36 hrs, in order to remove moisture and excess of amine and further IL was kept in N₂ atmosphere.

Synthesized PIL was characterized by \(^1\)H NMR, \(^{13}\)C NMR (Bruker Avance 400 MHz) and FTIR (JASKO FT/IR-4100) spectroscopic techniques. NMR was recorded in CDCl₃. \(^1\)H NMR of [DEEA][Pro], \(\delta = 4.725\) ppm (broad, 2H, OH and NH\(^+\)), \(\delta = 3.863\) ppm (t, 2H), \(\delta = 3.049\) ppm (q, 3H), \(\delta = 2.972\) ppm (t, 2H), \(\delta = 2.287\) ppm (q, 2H), \(\delta = 1.250\) ppm (t, 6H) and \(\delta = 1.119\) ppm (t, 3H). IR was recorded using KBr disk, the JASKO FT/IR-4100 spectrometer has a maximum resolution of 0.9 cm\(^{-1}\) and signal to noise ratio of 22000:1. The IR broad band appeared in range of 3400–2800 cm\(^{-1}\) correspondsto the characteristic ammonium peak, ν(N-H) and ν(O-H) stretching vibration. The broad band centered around 1600 cm\(^{-1}\) corresponds to the characteristic carbonyl, ν(C = O) stretching and δ(N-H) plane bending, vibrations. The Karl Fischer titrator from Analab (Micro Aqua Cal 100) was used to measure the water content. This instrument operates on conductometric titration principle using dual platinum electrodes that permits detection of water content from less than 10 ppm to 100%. The water content in the synthesized [DEEA][Pro] was \(\approx 7000\) ppm. The amount of water present in PIL has been taken into account for the molality correction of stock solutions (water + PIL).

2.3 Density and speed of sound

The vibrating-tube digital density meter and sound velocity analyzer (Anton Paar, DSA 5000M) was used to measure simultaneously the densities, \(\rho\) and speeds of sound, \(u\) of AA in water and in \(m_B\) (molality of PIL) = (0.10, 0.15, 0.20, and 0.25) mol·kg\(^{-1}\) aqueous solutions of [DEEA][Pro] at temperatures, \(T = (293.15, 298.15, 303.15, 308.15, 313.15, 318.15, 323.15 and 328.15)\) K and at atmospheric pressure. The instrument is equipped with a density cell and a sound velocity cell, which are temperature controlled by a built-in Peltier thermostat (PT-100) with an accuracy of ±0.01 K. It can measure the density in the range of (0 to 3000) kg·m\(^{-3}\) and speed of sound from (1000 to 2000) m·s\(^{-1}\). At regular intervals, instrument was calibrated at atmospheric pressure with dry air and deionized, double distilled, and freshly degassed water according to the procedure mentioned in the instrument manual. The uncertainties in the measurement of density and speed of sound were ±7×10\(^{-3}\) kg·m\(^{-3}\) and ±0.5 m·s\(^{-1}\), respectively. The solutions were made fresh in Millipore quality freshly degassed water on mass basis in air tight glass vials by using Sartorius balance (Model CPA225D) having a precision of ±0.01 mg. The uncertainty in molality was ±1.03×10\(^{-5}\) mol·kg\(^{-1}\).

Results and Discussion

3.1 Apparent molar volume and apparent molar isentropic compression

The understanding of molecular interaction between a solute and solvent (water) and the packing efficiency of solute within the structure of water has been studied in aqueous [43–44] and mixed aqueous solutions [3,45–47]. The packing efficiency of a solute which is governed by solute-solvent interactions can be measured by employing apparent molar volume. Apparent molar volume is smaller for heavily hydrated molecules as compared to those which are weakly hydrated, and this may be due to greater interaction of solute molecules with water [48]. The solvation behaviour of a solute has been studied by two most important parameters i.e. apparent molar volume, \(V_{2,\phi}\) and apparent molar isentropic compression, \(K_{2,\phi}\). In this study, the apparent molar volume, \(V_{2,\phi}\) and apparent molar isentropic compression, \(K_{2,\phi}\) of AA in water and in \(m_B = (0.10, 0.15, 0.20, and 0.25)\) mol·kg\(^{-1}\) aqueous solutions of [DEEA][Pro] at different temperatures (Table 1) were determined from density and speed of sound data
Table 1. The densities, $\rho$, apparent molar volumes, $V_{2,\psi}$, speeds of sound, $u$ and apparent molar isentropic compression, $K_{s,2,\psi}$ of ascorbic acid in water and in aqueous [DEEA][Pro] solutions at temperatures, $T = (293.15$ to $328.15)\, K$ and at ambient pressure.

| $T/K$ | $\delta m_B$ mol kg$^{-1}$ | $\delta m$ mol kg$^{-1}$ | $\rho\,10^{-3}$ kg m$^{-3}$ | $V_{2,\psi}\,10^6$ m$^3$ mol$^{-1}$ | $u$ m s$^{-1}$ | $10^{15}\,K_{s,2,\psi}$ m$^3$ mol$^{-1}$ Pa$^{-1}$ |
|-------|-----------------------------|-----------------------------|-------------------------------|-----------------------------|----------------|-------------------------------|
| 293.15 | 0.0                          | ($\rho_o = 0.998206$)      | ($u_o = 1482.84$)             |                             |                |                               |
|        | 0.06924                     | 1.003091                    | 105.13                        | 1485.32                     | -12.16         |                               |
|        | 0.10269                     | 1.005422                    | 105.16                        | 1486.84                     | -12.12         |                               |
|        | 0.15500                     | 1.009032                    | 105.21                        | 1489.23                     | -12.06         |                               |
|        | 0.19851                     | 1.012001                    | 105.25                        | 1491.23                     | -12.00         |                               |
|        | 0.25161                     | 1.015588                    | 105.28                        | 1493.69                     | -11.95         |                               |
|        | 0.27597                     | 1.017216                    | 105.31                        | 1494.82                     | -11.91         |                               |
|        | 0.33464                     | 1.021103                    | 105.36                        | 1497.56                     | -11.83         |                               |
| 298.15 | ($\rho_o = 0.997049$)       | ($u_o = 1496.85$)           |                               |                             |                |                               |
|        | 0.06924                     | 1.001890                    | 105.81                        | 1499.06                     | -8.59          |                               |
|        | 0.10269                     | 1.004200                    | 105.84                        | 1500.43                     | -8.54          |                               |
|        | 0.15500                     | 1.007777                    | 105.89                        | 1502.58                     | -8.45          |                               |
|        | 0.19851                     | 1.010721                    | 105.92                        | 1504.39                     | -8.43          |                               |
|        | 0.25161                     | 1.014275                    | 105.95                        | 1506.60                     | -8.36          |                               |
|        | 0.27597                     | 1.015888                    | 105.98                        | 1507.61                     | -8.30          |                               |
|        | 0.33464                     | 1.019740                    | 106.03                        | 1510.07                     | -8.21          |                               |
| 303.15 | ($\rho_o = 0.995660$)       | ($u_o = 1509.25$)           |                               |                             |                |                               |
|        | 0.06924                     | 1.000470                    | 106.31                        | 1511.65                     | -5.50          |                               |
|        | 0.10269                     | 1.002766                    | 106.34                        | 1512.88                     | -5.47          |                               |
|        | 0.15500                     | 1.006321                    | 106.38                        | 1514.82                     | -5.43          |                               |
|        | 0.19851                     | 1.009246                    | 106.41                        | 1516.44                     | -5.37          |                               |
|        | 0.25161                     | 1.012775                    | 106.45                        | 1518.43                     | -5.31          |                               |
|        | 0.27597                     | 1.014375                    | 106.49                        | 1519.35                     | -5.27          |                               |
|        | 0.33464                     | 1.018204                    | 106.53                        | 1521.56                     | -5.18          |                               |
| 308.15 | ($\rho_o = 0.994045$)       | ($u_o = 1519.82$)           |                               |                             |                |                               |
|        | 0.06924                     | 0.998811                    | 107.01                        | 1521.41                     | -4.01          |                               |
|        | 0.10269                     | 0.991083                    | 107.07                        | 1522.59                     | -3.95          |                               |
|        | 0.15500                     | 1.004602                    | 107.12                        | 1524.45                     | -3.89          |                               |
|        | 0.19851                     | 1.007488                    | 107.20                        | 1526.02                     | -3.84          |                               |
|        | 0.25161                     | 1.010983                    | 107.23                        | 1527.94                     | -3.80          |                               |
|        | 0.27597                     | 1.012565                    | 107.27                        | 1528.82                     | -3.75          |                               |
|        | 0.33464                     | 1.016344                    | 107.34                        | 1530.96                     | -3.67          |                               |
| 313.15 | ($\rho_o = 0.992228$)       | ($u_o = 1528.89$)           |                               |                             |                |                               |
|        | 0.06924                     | 0.996961                    | 107.57                        | 1531.16                     | 0.01           |                               |
|        | 0.10269                     | 0.999216                    | 107.63                        | 1532.14                     | 0.03           |                               |
|        | 0.15500                     | 1.002713                    | 107.66                        | 1533.67                     | 0.09           |                               |
|        | 0.19851                     | 1.005588                    | 107.70                        | 1534.95                     | 0.15           |                               |
|        | 0.25161                     | 1.009056                    | 107.75                        | 1536.53                     | 0.21           |                               |
|        | 0.27597                     | 1.010625                    | 107.80                        | 1537.27                     | 0.24           |                               |
|        | 0.33464                     | 1.014388                    | 107.84                        | 1539.04                     | 0.29           |                               |
| 318.15 | ($\rho_o = 0.990223$)       | ($u_o = 1536.56$)           |                               |                             |                |                               |
|        | 0.06924                     | 0.994936                    | 107.94                        | 1537.95                     | 1.13           |                               |
|        | 0.10269                     | 0.997180                    | 108.02                        | 1538.87                     | 1.19           |                               |
|        | 0.15500                     | 1.000658                    | 108.07                        | 1540.32                     | 1.24           |                               |
|        | 0.19851                     | 1.003515                    | 108.13                        | 1541.54                     | 1.29           |                               |
|        | 0.25161                     | 1.006965                    | 108.18                        | 1543.03                     | 1.36           |                               |
|        | 0.27597                     | 1.008523                    | 108.24                        | 1543.72                     | 1.42           |                               |

(Continued)
Table 1. (Continued)

| T/K  | \( b^m \) mol kg\(^{-1} \) | \( b^m \) mol kg\(^{-1} \) | \( \rho \) \( 10^{-3} \) kg m\(^{-3} \) | \( V_{298} \) \( 10^6 \) m\(^3\) mol\(^{-1} \) | \( u \) m s\(^{-1} \) | \( 10^{16} \) \( K_{s,2} + \) m\(^3\) mol\(^{-1} \) Pa\(^{-1} \) |
|------|----------------|----------------|----------------|----------------|----------------|----------------|
| 323.15 | 0.33464 | 1.012253 | 108.32 | 1545.39 | 1.51 |
|       | \( (\rho_o = 0.9888030) \) | \( (\rho_o = 1542.73) \) | |
|       | 0.06924 | 0.992708 | 108.54 | 1544.94 | 2.56 |
|       | 0.10269 | 0.994939 | 108.59 | 1545.79 | 2.63 |
|       | 0.15500 | 0.998391 | 108.65 | 1547.14 | 2.67 |
|       | 0.19851 | 1.001229 | 108.70 | 1548.27 | 2.73 |
|       | 0.25161 | 1.004643 | 108.80 | 1549.67 | 2.80 |
|       | 0.27597 | 1.006197 | 108.83 | 1550.32 | 2.82 |
|       | 0.33464 | 1.009899 | 108.91 | 1551.88 | 2.91 |
| 328.15 | 0.06924 | 0.990343 | 109.00 | 1548.43 | 4.07 |
|       | \( (\rho_o = 0.985690) \) | \( (\rho_o = 1547.61) \) | |
|       | 0.10269 | 0.992562 | 109.05 | 1549.21 | 4.09 |
|       | 0.15500 | 0.995996 | 109.11 | 1550.44 | 4.14 |
|       | 0.19851 | 0.998819 | 109.16 | 1551.46 | 4.22 |
|       | 0.25161 | 1.002229 | 109.20 | 1552.73 | 4.26 |
|       | 0.27597 | 1.003773 | 109.24 | 1553.32 | 4.29 |
|       | 0.33464 | 1.007462 | 109.31 | 1554.72 | 4.40 |
| 293.15 | 0.03740 | 1.002499 | 106.86 | 1500.41 | -3.60 |
|       | \( (\rho_o = 0.999919) \) | \( (\rho_o = 1499.13) \) | |
|       | 0.06114 | 1.004132 | 106.78 | 1501.22 | -3.58 |
|       | 0.12575 | 1.008552 | 106.66 | 1503.40 | -3.48 |
|       | 0.14367 | 1.009777 | 106.47 | 1503.99 | -3.44 |
|       | 0.21169 | 1.014398 | 106.20 | 1506.22 | -3.34 |
|       | 0.27537 | 1.018711 | 105.90 | 1508.27 | -3.30 |
|       | 0.32896 | 1.022297 | 105.74 | 1510.00 | -3.24 |
| 298.15 | 0.03740 | 1.001277 | 107.85 | 1513.00 | 1.08 |
|       | \( (\rho_o = 0.998732) \) | \( (\rho_o = 1512.18) \) | |
|       | 0.06114 | 1.002885 | 107.80 | 1513.66 | 1.12 |
|       | 0.12575 | 1.007240 | 107.61 | 1515.44 | 1.17 |
|       | 0.14367 | 1.008456 | 107.45 | 1515.90 | 1.21 |
|       | 0.21169 | 1.013010 | 107.20 | 1517.71 | 1.28 |
|       | 0.27537 | 1.017251 | 106.95 | 1519.35 | 1.36 |
|       | 0.32896 | 1.020816 | 106.69 | 1520.68 | 1.43 |
| 303.15 | 0.03740 | 0.999822 | 108.58 | 1524.37 | 4.49 |
|       | \( (\rho_o = 0.997302) \) | \( (\rho_o = 1523.70) \) | |
|       | 0.06114 | 1.001422 | 108.41 | 1524.89 | 4.62 |
|       | 0.12575 | 1.005741 | 108.22 | 1526.34 | 4.62 |
|       | 0.14367 | 1.006948 | 108.06 | 1526.70 | 4.69 |
|       | 0.21169 | 1.011488 | 107.70 | 1528.12 | 4.74 |
|       | 0.27537 | 1.015719 | 107.38 | 1529.39 | 4.82 |
|       | 0.32896 | 1.019256 | 107.15 | 1530.44 | 4.87 |
| 308.15 | 0.03740 | 0.998153 | 109.31 | 1534.45 | 6.17 |
|       | \( (\rho_o = 0.995657) \) | \( (\rho_o = 1523.36) \) | |
|       | 0.06114 | 0.999738 | 109.12 | 1534.93 | 6.21 |
|       | 0.12575 | 1.004054 | 108.62 | 1536.17 | 6.31 |
|       | 0.14367 | 1.005268 | 108.37 | 1536.48 | 6.31 |
|       | 0.21169 | 1.009779 | 108.07 | 1537.72 | 6.41 |
|       | 0.27537 | 1.014027 | 107.62 | 1538.78 | 6.46 |

(Continued)
| T/K  | \(m_b\) mol kg\(^{-1}\) | \(m\) mol kg\(^{-1}\) | \(\rho \times 10^{-3}\) kg m\(^{-3}\) | \(V_{a,b} \times 10^6\) m\(^3\) mol\(^{-1}\) | \(u\) m s\(^{-1}\) | \(10^{16} K_{a,b} \times 10^{-1}\) m\(^3\) mol\(^{-1}\) Pa\(^{-1}\) |
|------|-----------------|-----------------|------------------|-----------------|-----------------|------------------|
| 313.15 | 0.32896 | 1.017589 | 107.28 | 1539.62 | 6.53 | |
| | \((\rho_o = 0.993814)\) | | | \((\rho_o = 1542.00)\) | | |
| 318.15 | 0.03740 | 0.996285 | 110.07 | 1542.85 | 10.53 | |
| | \((\rho_o = 0.991786)\) | \((\rho_o = 1548.91)\) | | | | |
| 323.15 | 0.06114 | 0.997860 | 109.77 | 1543.15 | 10.60 | |
| | \((\rho_o = 0.9989577)\) | \((\rho_o = 1554.41)\) | | | | |
| 328.15 | 0.12575 | 1.002098 | 109.61 | 1544.16 | 10.74 | |
| | \((\rho_o = 0.999489)\) | \((\rho_o = 1519.38)\) | | | | |
| 293.15 | 0.05512 | 1.004497 | 106.88 | 1508.81 | -2.16 | |
| | \((\rho_o = 1.000704)\) | \((\rho_o = 1506.73)\) | | | | |
| 298.15 | 0.05512 | 1.003234 | 107.80 | 1521.56 | 1.87 | |
| | \((\rho_o = 0.999489)\) | \((\rho_o = 1519.38)\) | | | | |

(Continued)
Table 1. (Continued)

| T/K  | \(\mu_{m}B_{m}\) mol kg\(^{-1}\) | \(\mu m\) mol kg\(^{-1}\) | \(\rho\) \(10^{-3}\) kg m\(^{-3}\) | \(V_{\text{sol}}, 10^{6}\) m\(^{3}\) mol\(^{-1}\) | \(u\) m s\(^{-1}\) | \(10^{16} K_{\text{ex}}\) m\(^{3}\) mol\(^{-1}\) Pa\(^{-1}\) |
|------|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 303.15 | 0.05512 | 1.001743 | 108.64 | 1531.25 | 5.30 |
|       | 0.07286 | 1.002292 | 108.59 | 1531.63 | 5.35 |
|       | 0.11890 | 1.006008 | 108.34 | 1532.60 | 5.36 |
|       | 0.22113 | 1.012733 | 108.18 | 1534.78 | 5.44 |
|       | 0.27993 | 1.016570 | 108.02 | 1535.99 | 5.49 |
|       | 0.40125 | 1.024365 | 107.77 | 1538.48 | 5.60 |
|       | 0.45594 | 1.027839 | 107.65 | 1539.59 | 5.63 |
| 308.15 | 0.05512 | 1.000044 | 109.47 | 1541.42 | 7.13 |
|       | 0.07286 | 1.001223 | 109.33 | 1541.76 | 7.10 |
|       | 0.11890 | 1.004252 | 109.24 | 1542.64 | 7.18 |
|       | 0.22113 | 1.010912 | 109.00 | 1544.58 | 7.23 |
|       | 0.27993 | 1.014702 | 108.85 | 1545.66 | 7.29 |
|       | 0.40125 | 1.022405 | 108.61 | 1547.88 | 7.39 |
|       | 0.45594 | 1.025833 | 108.50 | 1548.87 | 7.42 |
| 313.15 | 0.05512 | 0.998152 | 110.22 | 1544.30 | 11.42 |
|       | 0.07286 | 0.999318 | 110.10 | 1544.51 | 11.46 |
|       | 0.11890 | 1.002324 | 109.95 | 1545.07 | 11.47 |
|       | 0.22113 | 1.008913 | 109.74 | 1546.29 | 11.56 |
|       | 0.27993 | 1.012683 | 109.53 | 1546.93 | 11.62 |
|       | 0.40125 | 1.020327 | 109.26 | 1548.29 | 11.70 |
|       | 0.45594 | 1.023730 | 109.14 | 1548.86 | 11.76 |
| 318.15 | 0.05512 | 0.996079 | 110.96 | 1547.55 | 13.53 |
|       | 0.07286 | 0.997233 | 110.85 | 1547.71 | 13.55 |
|       | 0.11890 | 1.000207 | 110.71 | 1548.13 | 13.58 |
|       | 0.22113 | 1.006709 | 110.60 | 1549.07 | 13.69 |
|       | 0.27993 | 1.010407 | 110.49 | 1549.59 | 13.74 |
|       | 0.40125 | 1.017946 | 110.23 | 1550.60 | 13.85 |
|       | 0.45594 | 1.021312 | 110.09 | 1551.02 | 13.90 |
| 323.15 | 0.05512 | 0.993841 | 111.59 | 1559.57 | 13.53 |
|       | 0.07286 | 0.994987 | 111.47 | 1560.40 | 13.55 |
|       | 0.11890 | 0.997932 | 111.38 | 1560.71 | 13.58 |
|       | 0.22113 | 1.004384 | 111.24 | 1561.39 | 13.69 |
|       | 0.27993 | 1.008079 | 111.03 | 1561.73 | 13.74 |
|       | 0.40125 | 1.015571 | 110.76 | 1562.44 | 13.85 |
|       | 0.45594 | 1.018910 | 110.63 | 1562.72 | 13.90 |
| 328.15 | 0.05512 | 0.991440 | 112.29 | 1563.68 | 17.26 |
|       | 0.07286 | 0.992572 | 112.21 | 1563.91 | 17.34 |
|       | 0.11890 | 0.995490 | 112.11 | 1564.07 | 17.35 |
|       | 0.22113 | 1.001870 | 112.02 | 1564.43 | 17.43 |
|       | 0.27993 | 1.005509 | 111.88 | 1564.60 | 17.48 |
|       | 0.40125 | 1.012869 | 111.73 | 1564.98 | 17.58 |
| T/K  | $b_m$ mol kg$^{-1}$ | $\bar{m}$ mol kg$^{-1}$ | $\rho$ 10$^{-3}$ kg m$^{-3}$ | $V_{298.15}$ 10$^{-6}$ m$^3$ mol$^{-1}$ | $u$ m s$^{-1}$ | 10$^{16}$ $K_{a,2}$ + m$^{-3}$ mol$^{-1}$ Pa$^{-1}$ |
|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 293.15 | 0.20 | 0.05334 | 1.005107 | 107.79 | 1516.85 | -1.75 |
|       |      | 0.10306 | 1.008484 | 107.42 | 1518.46 | -1.71 |
|       |      | 0.11587 | 1.009365 | 107.23 | 1518.85 | -1.70 |
|       |      | 0.16129 | 1.012422 | 107.10 | 1520.30 | -1.62 |
|       |      | 0.28817 | 1.020918 | 106.57 | 1524.25 | -1.52 |
|       |      | 0.31479 | 1.022701 | 106.42 | 1525.03 | -1.47 |
|       |      | 0.50949 | 1.035583 | 105.55 | 1530.65 | -1.26 |
| 298.15 |      | 0.05334 | 1.003835 | 108.53 | 1528.04 | 2.20 |
|       |      | 0.10306 | 1.007160 | 108.33 | 1529.38 | 2.27 |
|       |      | 0.11587 | 1.008023 | 108.20 | 1529.70 | 2.32 |
|       |      | 0.16129 | 1.011035 | 108.09 | 1530.91 | 2.36 |
|       |      | 0.28817 | 1.019377 | 107.69 | 1534.20 | 2.47 |
|       |      | 0.31479 | 1.021157 | 107.46 | 1534.80 | 2.51 |
|       |      | 0.50949 | 1.037366 | 106.76 | 1539.48 | 2.68 |
| 303.15 |      | 0.05334 | 1.002327 | 109.39 | 1537.85 | 5.87 |
|       |      | 0.10306 | 1.005613 | 109.18 | 1538.93 | 5.88 |
|       |      | 0.11587 | 1.006449 | 109.03 | 1539.18 | 5.91 |
|       |      | 0.16129 | 1.009459 | 108.84 | 1540.12 | 5.98 |
|       |      | 0.28817 | 1.019377 | 108.49 | 1542.72 | 6.10 |
|       |      | 0.31479 | 1.021157 | 108.31 | 1543.19 | 6.14 |
|       |      | 0.50949 | 1.031941 | 107.54 | 1546.74 | 6.32 |
| 308.15 |      | 0.05334 | 1.000586 | 110.15 | 1548.20 | 7.74 |
|       |      | 0.10306 | 1.003800 | 109.87 | 1549.21 | 7.76 |
|       |      | 0.11587 | 1.004637 | 109.73 | 1549.44 | 7.81 |
|       |      | 0.16129 | 1.007606 | 109.55 | 1550.26 | 7.83 |
|       |      | 0.28817 | 1.015778 | 109.08 | 1552.51 | 7.96 |
|       |      | 0.31479 | 1.017529 | 108.89 | 1552.88 | 8.00 |
|       |      | 0.50949 | 1.030001 | 107.96 | 1555.78 | 8.17 |
| 313.15 |      | 0.05334 | 0.998704 | 110.69 | 1554.82 | 11.93 |
|       |      | 0.10306 | 1.001917 | 110.60 | 1555.43 | 11.98 |
|       |      | 0.11587 | 1.002748 | 110.46 | 1555.57 | 12.02 |
|       |      | 0.16129 | 1.005659 | 110.04 | 1556.11 | 12.06 |
|       |      | 0.28817 | 1.013661 | 109.48 | 1557.60 | 12.20 |
|       |      | 0.31479 | 1.015365 | 109.21 | 1557.83 | 12.24 |
|       |      | 0.50949 | 1.027427 | 108.26 | 1559.75 | 12.45 |
| 318.15 |      | 0.05334 | 0.996620 | 111.64 | 1560.03 | 13.78 |
|       |      | 0.10306 | 0.999815 | 111.37 | 1560.50 | 13.76 |
|       |      | 0.11587 | 1.000644 | 111.23 | 1560.59 | 13.83 |
|       |      | 0.16129 | 1.003549 | 111.03 | 1560.98 | 13.86 |
|       |      | 0.28817 | 1.011567 | 110.62 | 1562.00 | 13.99 |
|       |      | 0.31479 | 1.013285 | 110.37 | 1562.10 | 14.05 |

(Continued)
Table 1. (Continued)

| T/K  | $b^o m$ | $b m$ | $\rho \times 10^{-3}$ | $V_{298} \times 10^6$ | $u$ | $10^{16} K_{s,2} \times 10^4$ |
|------|---------|-------|-----------------------|-----------------------|-----|-----------------------------|
|      | mol kg$^{-1}$ | mol kg$^{-1}$ | kg m$^{-3}$ | m$^3$ mol$^{-1}$ | m s$^{-1}$ | m$^3$ mol$^{-1}$ Pa$^{-1}$ |
| 323.15 | 0.50949 | 1.025399 | 109.68 | 1563.29 | 14.22 |
|       | (\(\rho_o = 0.990963\)) | (\(u_o = 1564.84\)) | | | |
| 328.15 | 0.05334 | 0.994369 | 112.33 | 1565.43 | 15.43 |
|       | 0.10306 | 0.997519 | 112.21 | 1565.79 | 15.48 |
|       | 0.11587 | 0.998337 | 112.10 | 1565.87 | 15.47 |
|       | 0.16129 | 1.001187 | 112.03 | 1566.19 | 15.52 |
|       | 0.28817 | 1.009067 | 111.72 | 1567.01 | 15.63 |
|       | 0.31479 | 1.010735 | 111.55 | 1567.11 | 15.67 |
| 293.15 | 0.50949 | 1.022542 | 111.08 | 1568.14 | 15.84 |
|       | (\(\rho_o = 0.988575\)) | (\(u_o = 1568.48\)) | | | |
| 298.15 | 0.05459 | 1.006053 | 112.86 | 1569.01 | 17.90 |
|       | 0.08555 | 1.008156 | 112.35 | 1569.18 | 17.88 |
|       | 0.12314 | 1.010692 | 112.73 | 1569.35 | 17.97 |
|       | 0.14154 | 1.011952 | 112.54 | 1569.72 | 18.09 |
|       | 0.23030 | 1.017941 | 112.43 | 1569.76 | 18.12 |
|       | 0.24087 | 1.018665 | 112.06 | 1570.18 | 18.28 |
| 303.15 | (\(\rho_o = 1.002344\)) | (\(u_o = 1522.61\)) | | | |
| 308.15 | 0.05459 | 1.004751 | 110.20 | 1536.29 | 3.56 |
|       | 0.08555 | 1.006821 | 108.60 | 1537.06 | 3.60 |
|       | 0.12314 | 1.009322 | 108.33 | 1537.98 | 3.68 |
|       | 0.14154 | 1.010554 | 108.19 | 1538.41 | 3.71 |
|       | 0.19493 | 1.014097 | 107.77 | 1539.67 | 3.77 |
|       | 0.23030 | 1.017941 | 106.54 | 1540.47 | 3.83 |
|       | 0.24087 | 1.018665 | 106.27 | 1540.68 | 3.85 |
|       | (\(\rho_o = 0.999601\)) | (\(u_o = 1544.44\)) | | | |
| 313.15 | 0.05459 | 1.003222 | 109.42 | 1546.25 | 3.34 |
|       | 0.08555 | 1.005269 | 109.27 | 1546.84 | 3.37 |
|       | 0.12314 | 1.007744 | 109.13 | 1547.54 | 3.43 |
|       | 0.14154 | 1.009652 | 108.99 | 1547.86 | 3.47 |
|       | 0.19493 | 1.012472 | 108.72 | 1548.79 | 3.55 |
|       | 0.23030 | 1.014796 | 108.52 | 1549.37 | 3.61 |
|       | 0.24087 | 1.015513 | 108.36 | 1549.50 | 3.64 |
|       | (\(\rho_o = 0.997905\)) | (\(u_o = 1553.07\)) | | | |
| 323.15 | 0.05459 | 1.001488 | 110.20 | 1554.83 | 9.47 |
|       | 0.08555 | 1.003517 | 110.01 | 1555.31 | 9.56 |
|       | 0.12314 | 1.005968 | 109.86 | 1555.89 | 9.61 |
|       | 0.14154 | 1.007172 | 109.73 | 1556.15 | 9.66 |
|       | 0.19493 | 1.010661 | 109.39 | 1556.88 | 9.75 |
|       | 0.23030 | 1.012959 | 109.21 | 1557.35 | 9.81 |

(Continued)
| $T / K$ | $^{a} m_{B}$ mol kg$^{-1}$ | $^{b} m$ mol kg$^{-1}$ | $p \times 10^{-3}$ kg m$^{-3}$ | $V_{2,\phi}$ 10$^{6}$ m$^{3}$ mol$^{-1}$ | $u$ m s$^{-1}$ | $10^{15} K_{s,2,\phi}$ m$^{3}$ mol$^{-1}$ Pa$^{-1}$ |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 313.15  | 0.24087         | 1.013651        | 109.13          | 1557.46         | 9.87            |
|         | ($^{a} \rho_{o} = 0.996018$) | ($^{a} u_{o} = 1560.26$) |                  |                  |                 |
| 318.15  | 0.05459         | 0.999566        | 111.79          | 1566.87         | 15.38           |
|         | ($^{a} \rho_{o} = 0.9971716$) | ($^{a} u_{o} = 1570.28$) |                  |                  |                 |
|         | 0.08555         | 0.999442        | 111.61          | 1567.05         | 15.51           |
|         | 0.12314         | 1.001839        | 111.53          | 1567.20         | 15.38           |
|         | 0.14154         | 1.003008        | 111.41          | 1567.38         | 15.59           |
|         | 0.19493         | 1.006393        | 111.20          | 1567.64         | 15.71           |
|         | 0.23030         | 1.008621        | 111.08          | 1567.82         | 15.74           |
|         | 0.24087         | 1.011611        | 111.00          | 1567.84         | 15.78           |
|         | ($^{a} \rho_{o} = 0.989322$) | ($^{a} u_{o} = 1573.88$) |                  |                  |                 |
|         | 0.05459         | 0.997456        | 112.37          | 1570.39         | 17.18           |
|         | 0.08555         | 0.9991774       | 112.11          | 1570.49         | 17.20           |
|         | 0.12314         | 0.999571        | 111.86          | 1570.58         | 17.28           |
|         | 0.14154         | 1.000745        | 111.72          | 1570.62         | 17.29           |
|         | 0.19493         | 1.004134        | 111.43          | 1570.70         | 17.39           |
|         | 0.23030         | 1.006372        | 111.25          | 1570.75         | 17.41           |
|         | 0.24087         | 1.009296        | 111.15          | 1570.74         | 17.42           |
|         | ($^{a} \rho_{o} = 0.991716$) | ($^{a} u_{o} = 1573.88$) |                  |                  |                 |

$^{a} m_{B}$ is the molality of [DEEA][Pro] in water.

$^{b} m$ is the molality of ascorbic acid in water or water + [DEEA][Pro] solutions.

$^{c} \rho_{o}$ is the density of [DEEA][Pro] in water.

$^{d} u_{o}$ is the speed of sound of [DEEA][Pro] in water.

The standard uncertainties are $u (T) = 0.01$ K, $u (m) = 1.03 \times 10^{-5}$ mol kg$^{-1}$, $u (p) = 7.0 \times 10^{-3}$ kg m$^{-3}$, $u (u) = 0.5$ m s$^{-1}$, $u (P) = 0.05$ kPa. The combined uncertainties, $U$ are $U (V_{2,\phi}) = (0.20$ to 0.04)$ \times 10^{6}$ m$^{3}$ mol$^{-1}$ and $U (K_{s,2,\phi}) = (0.60$ to 0.12)$ \times 10^{-15}$ m$^{3}$ mol$^{-1}$ Pa$^{-1}$ for low and high concentration range of ascorbic acid, respectively (level of confidence, $k = 0.95$). The experiment was conducted under atmospheric pressure.

doi:10.1371/journal.pone.0126091.t001
(Table 1) by using the following Eqs (1) and (2):

\[
V_{2,\rho} = \frac{[M]}{\rho} - \frac{[(\rho - \rho_o)/(m \cdot \rho \cdot \rho_o)]}{\frac{1}{2} \left( \frac{\kappa_s}{\rho_o} \right)} \tag{1}
\]

\[
K_{s,2,\phi} = \frac{[\kappa_{s,M}/\rho]}{\frac{1}{2} \left( \frac{\kappa_s}{\rho_o} \right)} - \frac{[(\kappa_s^o \cdot \rho - \kappa_s \cdot \rho_o)/(m \cdot \rho \cdot \rho_o)]}{\frac{1}{2} \left( \frac{\kappa_s}{\rho_o} \right)} \tag{2}
\]

where \( M \) and \( m \) are respectively, the molar mass and molality of AA; \( \rho \) and \( \rho_o \) are the densities of solution and solvent (water or water + [DEEA][Pro]), \( \kappa_s \) and \( \kappa_s^o \) are the isentropic compressibilities of solution and solvent, respectively.

The experimentally measured densities and speeds of sound of the solutions were used to evaluate the isentropic compressibility, \( \kappa_s \), as \( u_s = \frac{\kappa_s}{\rho_o} \cdot \rho^2 \). The combined uncertainties in \( V_{2,\phi} \) values resulting from experimentally measured quantities \([u(m) = 1.03 \cdot 10^{-5} \text{ mol} \cdot \text{kg}^{-1}, \ u(\rho) = 7.0 \cdot 10^{-3} \text{kg} \cdot \text{m}^{-3}, \ u(T) = 0.01 \text{ K}] \) ranges from \( 0.2 \times 10^{-6} \text{ mol}^{-1} \cdot \text{at} \) \( \leq 0.05 \text{ mol} \cdot \text{kg}^{-1} \) and high concentration range of AA, respectively and combined uncertainties in \( K_{s,2,\phi} \) values ranges from \( 0.6 \times 10^{-15} \text{ mol}^{-1} \cdot \text{Pa}^{-1} \) at low and high concentration range of AA, respectively (level of confidence, \( k = 0.95 \)).

The \( V_{2,\phi} \) and \( K_{s,2,\phi} \) values (Table 1) of AA in water increase with increase in concentration of AA and temperature, whereas in aqueous [DEEA][Pro] solutions \( V_{2,\phi} \) values decrease with increase in concentration of AA. The variation of \( V_{2,\phi} \) versus molality of AA in water at different temperature is shown in Fig 1. In this plot, \( V_{2,\phi} \) value increase as color of the figure change from dark blue region to dark orange region. The \( K_{s,2,\phi} \) value of AA in water and in aqueous solutions of [DEEA][Pro] are negative as well positive (at high temperature and cosolute concentration). For ionic compounds in water, highly negative \( K_{s,2,\phi} \) values have been observed, whereas for hydrophobic solute \( K_{s,2,\phi} \) values are positive and for uncharged hydrophilic solutes, \( K_{s,2,\phi} \) values are...
intermediate (small and negative). Negative $K_{s2,φ}$ values suggest that AA gets hydrated due to electrostricted water molecules in the vicinity of hydrophilic groups of AA. At high temperature and cosolute ([DEEA][Pro]) concentration, $K_{s2,φ}$ values increase and become positive, which indicate the removal of electrostricted water around the solute (AA) molecules. Due to the presence of both hydrophilic and hydrophobic groups in AA, the $K_{s2,φ}$ values obtained reflects the competition between various types of interactions between AA and solvent [32].

3.2 Infinite dilution partial molar volume and partial molar isentropic compression

Infinite dilution partial molar volume ($V_{2,φ} = V_{2,φ}^o$) and partial molar isentropic compression ($K_{s2,φ} = K_{s2,φ}^o$) has been evaluated by least-square fitting to the corresponding data as Eqs (3) and (4):

\[ V_{2,φ} = V_{2,φ}^o + S_v m \]  
\[ K_{s2,φ} = K_{s2,φ}^o + S_k m \]

where $S_v$ and $S_k$ are respective experimental slopes. Apparent molar volume, $V_{2,φ}$ of AA in water has been reported by various workers [33, 49–52] and in few reports, $V_{2,φ}$ values were determined without considering the ionization of AA. Ayranci et al. [33] studied the volumetric properties of AA in 0.01 M HCl solutions, by suppressing the ionization of AA. A modified Debye-Huckel equation was proposed by Hakin, Mudrack, & Beswick [49] to consider the partial dissociation of AA in water, since at high concentration of weak acid, degree of hydrolysis is small, later some workers reported the volumetric properties of AA in water [50–52] and are given in Tables 2 and 3, respectively. The $V_{2,φ}^o$ values of AA increase with concentration of [DEEA][Pro] and temperature, which indicate an increase in interactions between ions of [DEEA][Pro] (–NH$_3^+$, C$_2$H$_5$COO$^-$) and AA, which may be due to the dominance of hydrophilic-ionic interactions. Both negative and positive $K_{s2,φ}^o$ values were observed for AA in water and also in presence of [DEEA][Pro], which increase with concentration of PIL and temperature, thus indicating reduction in the electrostriction.

The influence of PIL on solvation behaviour of AA can be studied on the basis of partial molar volumes of transfer, ($ΔV_{2,φ}^o$ and $ΔK_{s2,φ}^o$), which is considered to be free from solute-solute interactions, and were calculated using Eq (5):

\[ ΔX_{2,φ}^o = X_{2,φ}^o \text{ (in aqueous [DEEA][Pro] solutions)} - X_{2,φ}^o \text{ (in water)} \]

where $ΔX_{2,φ}^o = (ΔV_{2,φ}^o$ or $ΔK_{s2,φ}^o$), the plot of $ΔV_{2,φ}^o$ versus $m_B$ has been illustrated in Fig 2a and $ΔK_{s2,φ}^o$ versus $m_B$ in Fig 2b. The transfer parameters ($ΔV_{2,φ}^o$ and $ΔK_{s2,φ}^o$) are positive and increase with concentration of newly synthesized PIL (synthesis is shown in Fig 3) and temperature. The $ΔV_{2,φ}^o$ values increase with cosolute (PIL) concentration, however a slight decrease in $ΔV_{2,φ}^o$ values from $m_B ≈ (0.10$ to $0.15$) mol·kg$^{-1}$ have been observed, whereas $ΔK_{s2,φ}^o$ values increase continuously with PIL concentration at all temperature. This behaviour in $ΔV_{2,φ}^o$ values for AA is different (only between $[0.10$ to $0.15$] mol·kg$^{-1}$) as compared to $ΔK_{s2,φ}^o$ values. The observed difference may be due to the fact that apparent molar isentropic compression is more sensitive parameter as compared to apparent molar volume [44] in measuring the structural changes occurring in solutions.
### Table 2. Infinite dilution partial molar volumes, $V_2$ of ascorbic acid in water and in aqueous solutions of [DEEA][Pro] at $T = (293.15$ to $328.15) \text{ K}$.

| $m_b$/mol kg$^{-1}$ | $T$ (K) | $V_2 \times 10^{6}$/m$^3$ mol$^{-1}$ |
|----------------------|--------|----------------------------------|
|                      | 293.15 | 298.15                           |
| 0.00                 | 105.07 | ±0.01                           |
|                      | (1.23) | (1.38)                          |
| 0.10                 | 107.03 | ±0.03                           |
|                      | (3.95) | (-3.92)                          |
| 0.15                 | 107.36 | ±0.06                           |
|                      | (3.53) | (-2.46)                          |
| 0.20                 | 108.39 | ±0.08                           |
|                      | (4.66) | (-3.81)                          |
| 0.25                 | 108.90 | ±0.04                           |
|                      | (6.09) | (-5.01)                          |

$a_{mb}$, molality of [DEEA][Pro] in water.
$b$, standard deviation.
$c$, $S_v$/m$^3$ kg$^{-1}$ mol$^{-2}$.
$d$, Ref [32].
$e$, Ref [33].
$f$, Ref [49].
$g$, Ref [50].
$h$, Ref [52].
$i$, Ref [29].

### Table 3. Infinite dilution partial molar isentropic compression, $K_{s,2}$ of ascorbic acid in water and in aqueous solutions of [DEEA][Pro] at $T = (293.15$ to $328.15) \text{ K}$.

| $m_b$/mol kg$^{-1}$ | $T$ (K) | $K_{s,2} \times 10^{-15}$ / m$^3$ mol$^{-1}$ Pa$^{-1}$ |
|----------------------|--------|-----------------------------------------|
|                      | 293.15 | 298.15                                  |
| 0.00                 | -12.25 | ±0.01 $^{b3}$                           |
|                      | (1.23) | (1.38)                                  |
| 0.10                 | -3.64  | ±0.02 $^{b}$                           |
|                      | (1.27) | (1.19)                                  |
| 0.15                 | -2.20  | ±0.01 $^{b3}$                           |
|                      | (0.83) | (0.91)                                  |
| 0.20                 | -1.81  | ±0.01 $^{b3}$                           |
|                      | (1.08) | (1.01)                                  |
| 0.25                 | -0.46  | ±0.01 $^{b3}$                           |
|                      | (1.80) | (1.54)                                  |

$a_{mb}$, molality of [DEEA][Pro] in water.
$b$, standard deviation.
$c$, $S_v$/m$^3$ kg$^{-1}$ mol$^{-2}$ Pa$^{-1}$.
$d$, Ref [32].
$e$, Ref [52].
$f$, Ref [29].

doi:10.1371/journal.pone.0126091.0002
Ascorbic acid has a five membered ring containing two carbonyl groups and exists as a conjugate ene-diol (having two unstable keto form and one stable ene-diol form) as shown in Fig 4. The enol form is stable and is delocalized, as shown in Fig 4. The two possible forms of AA in solutions are: 1,2 diketone (X) and 1,3-diketone (Y) as shown in Fig 4, and these forms rapidly interconvert (Fig 4). AA contains two acidic protons, namely, H_{\alpha} and H_{\beta} (I of Fig 4), on dissociation of any of these protons, ascorbate ion is formed. The stability of respective ascorbate ion formed determines the acidity of proton (H_{\alpha} or H_{\beta}). As shown in Fig 4, structure A has one more equally contributing resonating structure B [53], therefore the stability of conjugate base on removal of H_{\beta} is more (shown in I of Fig 4) compared to conjugate base generated on removal of H_{\alpha} (shown in II of Fig 4). The carboxylate anion of [DEEA][Pro] will probably interact more strongly with H_{\beta} (most acidic hydrogen), which may be responsible for positive transfer volumes (\Delta V^\circ or \Delta K^\circ_{s,2}), further, it has been observed that these interactions dominate over the whole concentration range of PIL. Aryanci et al. [33] studied the solvation behaviour of AA in aqueous sodium chloride solutions (in 0.01 M HCl) and they observed no regular trend in \Delta V^\circ values for AA, and suggested that the irregular trend in \Delta V^\circ values indicate the presence of complex interactions between solute and cosolute in aqueous NaCl solutions (containing background 0.01 M HCl). However, in the present study, regular trend observed in \Delta V^\circ and \Delta K^\circ_{s,2} values suggest that with increase in PIL concentration and temperature, the hydrophilic-ionic types of interactions become more favorable.

The \Delta V^\circ and \Delta K^\circ_{s,2} values can be interpreted in terms of structural interaction model [54] and group additivity model [55]. According to these models [54–55], the type of interactions between AA and [DEEA][Pro] in ternary solutions can be classified as: a) Hydrophobic—cation interactions between hydrophobic parts of AA and —NH_{3}^+ of PIL; b) Hydrophilic—cation interactions between (—OH, —C = O, and —O—) groups of AA and —NH_{3}^+; c) Hydrophobic—anion interactions between hydrophobic parts of AA and C_{2}H_{5}COO^{-}; d) Hydrophilic—hydrophobic interactions between the hydrophilic groups of AA and hydrophobic parts of [DEEA][Pro]. According to the structural interaction model [54], types (a, c and d) interactions are repulsive as the groups involved are incompatible or inability of the groups to orient water.

Fig 3. Synthesis of diethylethanolammonium propanoate [DEEA][Pro].

doi:10.1371/journal.pone.0126091.g003
contribute negative volume. Interactions of type b contribute positive to transfer volume due to the overlap of hydration co-sphere of ions of [DEEA][Pro] and hydrophilic groups (—OH, —C = O, and —O—) of AA, which leads to a decrease in structure-breaking tendency of ion and thus reduction of electrostriction. Transfer volumes (ΔtV² and ΔtK°s,2) increase with cosolute concentration and temperature, which indicate dominance of hydrophilic-ionic interactions (type b) over hydrophobic type of interactions. The positive ΔtV² values of AA in presence of NaCl [33] and in PEG3350[29] have also been reported, which also suggests the dominance of hydrophilic type of interactions.

The thermal expansion coefficients (∂V²/∂T)p and its second derivatives (∂²V²/∂T²)p have been calculated by using the following Eq (6):

\[
V² = v_o + v_1 T + v_2 T^2
\]

(6)

where \(v_o\), \(v_1\) and \(v_2\) are constants. The derivative of \(V²\) with respect to temperature at constant pressure i.e. (∂V²/∂T)p for AA in water and in presence of [DEEA][Pro] is given in Table 4. Hepler [56] used a mathematical equation, to deduce information regarding structure-making or-breaking ability of an ion in solution. According to Hepler’s [56] criteria: \(\left(\frac{∂^2 V²}{∂T^2}\right)_P\) = − \(T \left(\frac{∂ V²}{∂T}\right)_P\), negative (∂²V²/∂T²)p values obtained for AA in water and in aqueous PIL solutions suggest that AA behave as structure breaker (chaotropes). Banipal et al.[32] and Dhonge et al. [40] have also reported that AA behaves as structure breaker in water.

3.3 Interaction coefficients

Pair (Y_AB) and triplet (Y_ABB) volumetric and compression interaction coefficients have been calculated from corresponding volume of transfer (ΔtV² or ΔtK°s,2) based on McMillan-Mayer
theory [57] of solutions  

\[
\Delta Y_2 = 2Y_{AB}m_B + 3Y_{ABB}m_B^2
\]

where A denotes AA and B denotes PIL ([DEEA][Pro]). Constants \(Y_{AB}\) (\(V_{AB}\) or \(K_{AB}\)) and \(Y_{ABB}\) (\(V_{ABB}\) or \(K_{ABB}\)) are pair and triplet volumetric or compression interaction coefficients, respectively. Pair interaction coefficients, \(Y_{AB}\) contribute positively and triplet coefficients, \(Y_{ABB}\) can contribute negatively (Tables 5 and 6). Pair volumetric interaction coefficients, \(Y_{AB}\) are found to be positive and triplet interaction coefficients, \(Y_{ABB}\) are negative, at all temperatures. Overall, triplet volumetric interaction coefficients, \(Y_{ABB}\) are small, which indicate that the interactions between AA and PIL are mainly pair wise. Positive values of both \(V_{AB}\) and \(K_{AB}\) parameters suggest that interactions occur due to the overlap of hydration co-spheres of AA and ions of PIL.

### Conclusions

The volumetric and compression transfer volumes (\(\Delta V_2^o\) and \(\Delta K_{2s3}\)) for AA in presence of diethylethanolammonium propionate ([DEEA][Pro]) were found to be positive, which increase with increase in concentration of [DEEA][Pro] and temperature. The positive \(\Delta V_2^o\) and \(\Delta K_{2s3}\) values suggest the dominance of hydrophilic-ionic type of interactions between the ions.

### Table 4. Partial molar expansion coefficients, \((\partial V_2^i T)/P\) and \((\partial^2 V_2^i T^2)/P\) of ascorbic acid in water and in aqueous [DEEA][Pro] solutions at temperatures, \(T = (293.15\) to \(328.15\) K).

| \(m_B\) / mol·kg\(^{-1}\) | \(\partial V_2^i T/P\times10^6\) | \(\partial^2 V_2^i T^2/P\times10^6\) |
|--------------------------|-------------------------------|-------------------------------|
|                          | \(m^3\cdot mol^{-1}\cdot K^{-1}\) | \(m^3\cdot mol^{-1}\cdot K^{-2}\) |
| \(T/K\)                  |                               |                               |
| 293.15                   | 0.129                         | 0.112                         |
| 298.15                   | 0.155                         | 0.123                         |
| 303.15                   | 0.145                         | 0.118                         |
| 308.15                   | 0.135                         | 0.112                         |
| 313.15                   | 0.124                         | 0.105                         |
| 318.15                   | 0.114                         | 0.095                         |
| 323.15                   | 0.104                         | 0.089                         |
| 328.15                   | 0.094                         | 0.080                         |

*SD—standard deviation.

doi:10.1371/journal.pone.0126091.t004

### Table 5. The pair, \(V_{AB}\) and triplet, \(V_{ABB}\) interaction coefficients for ascorbic acid in aqueous [DEEA][Pro] solutions at \(T = (293.15\) to \(328.15\)K).

| \(V_{AB}\times10^6\) m\(^3\) mol\(^{-2}\) kg | \(V_{ABB}\times10^6\) m\(^3\) mol\(^{-2}\) m\(^{-3}\) kg\(^2\) | \(V_{AB}\times10^6\) m\(^3\) mol\(^{-2}\) kg | \(V_{ABB}\times10^6\) m\(^3\) mol\(^{-2}\) m\(^{-3}\) kg\(^2\) |
|---------------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|
| \(T = 293.15 \) K                       | \(T = 298.15 \) K                       | \(T = 303.15 \) K                       | \(T = 308.15 \) K                       |
| 10.18                                      | -11.42                                    | 11.84                                      | -15.16                                    |
| \(T = 303.15 \) K                       | \(T = 308.15 \) K                       | \(T = 313.15 \) K                       | \(T = 318.15 \) K                       |
| 13.37                                      | -17.32                                    | 13.89                                      | -18.25                                    |
| \(T = 313.15 \) K                       | \(T = 318.15 \) K                       | \(T = 323.15 \) K                       | \(T = 328.15 \) K                       |
| 15.04                                      | -20.42                                    | 16.39                                      | -22.04                                    |
| \(T = 323.15 \) K                       | \(T = 328.15 \) K                       | \(T = 323.15 \) K                       | \(T = 328.15 \) K                       |
| 17.02                                      | -23.22                                    | 17.65                                      | -24.01                                    |

doi:10.1371/journal.pone.0126091.t005
of PIL and hydrophiles of AA (−OH, −C = O, −O−), due to the overlap of hydration co-
sphere of PIL and AA.

The negative values of second derivative i.e. $\left( \frac{\partial^2 V^o}{\partial T^2} \right)_P$ obtained for AA in water and also in aqueous solutions of [DEEA][Pro] suggest that AA behave as structure breaker. The values of pair interaction coefficients ($V_{AB}$ and $K_{AB}$) were found to be positive, which further support the view that interactions occur due to the overlap of hydration co-sphere of AA and ions of PIL. The transfer parameters and interaction coefficients suggest that AA interacts strongly with [DEEA][Pro] in aqueous solution.

### Author Contributions

Conceived and designed the experiments: VS RG. Performed the experiments: VS GS. Analyzed the data: VS GS RG. Contributed reagents/materials/analysis tools: RG. Wrote the paper: VS GS RG. Performed calculations: VS RG. Created figures: VS GS.

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